



XXII MENDELEEV CONGRESS
ON GENERAL AND APPLIED CHEMISTRY

BOOK OF ABSTRACTS

IN 7 VOLUMES

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**XXII MENDELEEV CONGRESS
ON GENERAL AND APPLIED CHEMISTRY**

*Dedicated to the 190th anniversary
of D.I. Mendeleev and the 300th anniversary
of the Russian Academy of Sciences*

BOOK OF ABSTRACTS

Volume 1

Book of abstracts in 7 volumes

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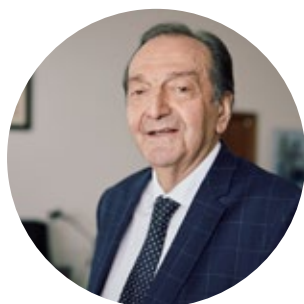
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The background is a dark, almost black, space filled with vibrant, glowing particles and textured, organic shapes. These shapes are primarily in shades of magenta, cyan, and blue, with some areas appearing more solid and others more like a cloud of fine dust or small spheres. The overall effect is one of dynamic energy and complex, interconnected forms, reminiscent of a microscopic view of a biological process or a digital data visualization.

PLENARY LECTURES

CRITICAL TECHNOLOGIES FOR THE DEVELOPMENT OF THE MINERAL RESOURCES BASE OF THE RUSSIAN FEDERATION: FROM FORECASTING AND ORE MINING TO METAL EXTRACTION AND THE HIGH-TECH PRODUCTS

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The solution to the most actual present-day state task - achieving the technological sovereignty of Russia and localization of all related technological chains - cannot be achieved without a strong reliance on domestic mineral resources. To do this, it is necessary to restore and develop the mining industries. Currently, Russian industry is still strongly dependent on import of strategic metals, and for some positions this dependence reaches 100%. Despite this, many domestic deposits of strategic mineral resources are not developed due to their low profitability and lack of industrial demand for metals.

For the period until 2035, the proven geological reserves meet the needs of the high-tech industry with strategic metals of only 17 types (copper, nickel, tin, wolfram, molybdenum, tantalum, niobium, cobalt, scandium, germanium, platinoids, etc.). The achieved levels of production of lead, antimony, gold, silver, zinc are provided by reserves of developed deposits for a period of less than 15 years. Most of the strategic metals necessary to support high-tech, knowledge-intensive industries are scarce even at current levels of consumption.

Our country can completely replace the import of strategic mineral raw materials through the development of its own resources. This requires work at all stages of the search and exploration of new deposits, including the poorly studied Arctic territories of Siberia and the Far East, the development of new breakthrough technologies for mining, ore-dressing, extraction and refinery of mineral raw materials, and the creation of a competitive production of ultra-pure rare metals.

The presentation discusses in detail the current state of Russia's mineral resource base, problematic issues of achieving import independence in providing Russian industry with strategic metals. The activities of the Russian Academy of Sciences in developing the mineral resource base are considered, and solutions proposed by the Russian Academy of Sciences for some of the identified problems are given. The issues of mining and extraction of lithium and rare earth elements will be discussed in detail.

ARTIFICIAL INTELLIGENCE IN CHEMISTRY

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Integration of artificial intelligence (AI) algorithms into chemical research has become increasingly important due to the rapid growth in experimental data volumes, the complexity of correlating phenomena at molecular and nanoscale levels, and the increasing need for a qualitative leap in the development of new generation of chemical technologies [1]. This presentation focuses on the application of AI in the field of chemistry, specifically in the design of new chemical processes. Cutting-edge trends in the development of AI applications for the creation of next-generation synthetic methods are explored [2,3], the analysis of experimental data [4], and the understanding of the mechanisms of formation and operation of chemical micro-reactors [5]. Particular emphasis is placed on the use of AI to develop universal photocatalysts [6], highlighting how these technologies enable unprecedented precision and efficiency in chemical science.

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FROM THE REFINERY TO THE RESERVOIR: APPLICATION TO IN-SITU UPGRADING OF HEAVY CRUDE OILS

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Various processes currently used in petroleum refineries were identified to be similar to those employed for in-situ upgrading of heavy crude oil in reservoirs. In-situ hydrogen production uses similar concept than vacuum residue gasification, in-situ solvent addition is comparable to the widely used solvent deasphalting, in-situ hydrogen addition mimics the hydrogen addition technology particularly slurry-phase hydrocracking, and catalytic aquathermolysis is based on aquaconversion process. Although similar in nature, the petroleum refinery processes make use of properly designed reactor, while in-situ upgrading technologies use the reservoir as a natural reactor. Monitoring and controlling of reaction conditions, particularly temperature and pressure, result to be crucial for in-situ upgrading of heavy crude oils. In-situ hydrogen production emerges as a viable alternative to produce aqua hydrogen to complement the production of green hydrogen, both aiming at satisfying the future energy requirements. Catalytic aquathermolysis does not require huge additional equipment in fields already using cyclic steam stimulation, in fact the required equipment is minimal. While in-situ hydrogen addition indeed needs costly surface infrastructures. It is concluded that among all technologies catalytic aquathermolysis is an attractive approach to reduce the heavy crude oil viscosity at values required for transportation, so that the recovery factor can be increased.



ORGANIC SYNTHESIS

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The role of organic synthesis as the basis of organic chemistry in modern science and industry will be considered in the lecture. New advances in organic synthesis in the 21st century will be discussed.

This work was supported by the grant of the Ministry for Education and Science of the Russian Federation (agreement of 24.04.2024 no. 075-15-2024-547).

SUPPORTED BIFUNCTIONAL AND BIMETALLIC CATALYSTS – WHAT IS MORE IMPORTANT IS THE CHOICE OF PREPARATION METHODS OR ACTIVATION CONDITIONS?

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One of the ways to increase the efficiency of supported monometallic catalysts (improvement of activity, selectivity and stability) used in a huge number of industrial chemical processes is to introduce a second component (modifier), which provides bifunctionality.

In the traditional sense, bifunctional catalysts are catalysts that contain two types of active centers, which differ in their functions. Bifunctional catalysts are used when the reaction occurs in two elementary stages, and these stages are catalyzed at active sites of different types. For example, bifunctional supported Pt/Al₂O₃ catalysts with dehydrogenating (Pt) and acidic (Al₂O₃) properties are effective for the hydrocarbon reforming process.

At the same time, bifunctionality can also manifest itself in bimetallic catalysts, provided that each type of metal performs a different function in the reaction mechanism. At the same time, in bimetallic catalysts, synergistic effects may occur, in which the activation of molecules participating in the catalytic process occurs over different metals.

Another important case in the development of bimetallic catalysts is the introduction of an inactive second metal, which allows either modifying the electronic properties of the active metal (ligand effect) or changing the geometry of active center consisting of the active metal (ensemble effect), up to single site catalysts. I believe that in this case we also can talk about the bifunctionality of the catalyst, but the function of the second metal is not to participate in the catalytic process, but to create active center of the required geometry.

Some examples of the researches from the experience of Boreskov Institute of Catalysis, which illustrate the effectiveness of the aforementioned approaches to improvement the properties of bifunctional and bimetallic catalysts, will be presented in my report. One of the conclusions of the presented studies is the statement that it is important not only to develop adequate methods for the synthesis of these catalysts, but also to select activation conditions that lead to the creation of the desired structure of active centers. This once again emphasizes the importance to perform catalytic studies using in situ and operando modes and methods. The commissioning of a 4+ generation synchrotron radiation source at the SKIF Center, which is currently being created in the science city of Koltsovo, Novosibirsk region, will greatly increase the possibilities of such research.

QUANTUM PHYSICS: 100 YEARS OF OPEN QUESTIONS

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Quantum mechanics, formally initiated a century ago with the works of Heisenberg and Schrödinger, has developed and spread enormously. The strength of the theory can be measured by its predictive power and its many applications in physics, chemistry and beyond. Yet it is an incomplete theory, for it describes phenomena but, by ignoring their causes, deprives us of capturing their essence.

This essential shortcoming has metaphysical consequences—for our understanding of the world and our conception of reality—and serious scientific implications. Incompleteness leads to gaps that are filled with *ad hoc* postulates and *ad libitum* interpretations, sometimes even contrary to science. The quantum paradoxes are a manifestation of this unsatisfactory situation.

The open questions I will discuss are related to the incompleteness of the theory. Some of the most important are directly relevant to chemistry, such as: the source of atomic stability, the nature of the wave function, the Pauli exclusion principle and quantum entanglement. So as not to leave the reader in the dark, I will talk about how this veil of mystery can be lifted by completing the theory with a physical element that has been left out of the current formalism.

CREATION OF NEW MATERIALS USING EXPLOSION ENERGY

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For many centuries, mankind has used the energy of the explosion for the purposes of destruction, primarily in military operations and mining. It was only since the end of the 19th century that the vector of application of explosion energy was redirected from the goals of destruction to the tasks of creation, and today there are many technological applications for using explosion energy to create and process materials.

The report provides an overview of examples of practical applications of explosion energy for peaceful purposes, in particular for the creation of new materials, to give materials new operational properties. Various schemes of explosive loading are given. Some issues of explosion physics and the theory of high-speed collision of bodies are considered.¹

One of the first and successful experiments on the creative use of explosion energy in the 20th century was an attempt to use it to harden metals. It turned out that powerful shock waves affect the density of defects. In this case, the hardening turns out to be much greater than under normal deformation conditions.

The most effective use of explosion energy is manifested in the production of new metal, cermet, metal polymer, etc. composites by explosion welding of layered or explosive compression of powder materials². The connection between dissimilar components occurs due to the occurrence of intense shear deformation, leading to the formation of physical contact and activation of contact surfaces. As a result of a two-stage topochemical reaction, setting (welding) occurs in the solid phase with the formation of a strong joint. Composite materials obtained using explosion energy have found wide application in such high-tech branches of technology as rocket and space, nuclear energy, petrochemical engineering, and many others.

The report also discusses some other examples of the use of explosion energy for the synthesis of new materials, as well as a fundamental change in their structure and properties.

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CHEMICAL AND REFINING IN INDUSTRY: NEW CHALLENGES AND OPPORTUNITIES

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Refining of carbon based feedstock to produce base chemicals products is currently faced with a number of new requirements: high efficiency and environmental friendliness of chemical processes, the need for changing raw materials (including use of biofeedstocks, methane, carbon dioxide, plastic and organic wastes) and expanding the use of new energy sources, primarily renewable electricity and solar energy.

The main directions of research and development aimed at creating new technologies taking into account these changes will be presented in the report. It is expected to consider the processes of heavy oil residues and crude oil refining to obtain petrochemical products (“oil to chemistry”), new “green” low-carbon technologies in petrochemistry; new approaches to the chemical processing of polymer waste and bio-raw materials and the conversion of methane into large-scale petrochemical products that have emerged in the last decade; processes for producing low-carbon hydrogen and its use in chemistry. Special attention will be paid to the carbon dioxide capture processes and its catalytic transformations into valuable basic products of industrial organic synthesis.

New opportunities will be discussed that are opening up in the development of new approaches to the chemical refining of raw materials with the expansion of the use of electricity for large- and medium-tonnage industrial chemistry (both direct using electrochemical methods and indirect - using various types of electric heating and plasma chemistry) and solar energy (for thermocatalytic and thermophotocatalytic processes).

DIGITAL ANALOGS OF INDUSTRIAL TECHNOLOGIES FOR THERMOMECHANICAL PROCESSING (TMP) OF STEEL

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Digital analogs of TMO technologies are designed for high-performance large-scale computer experimentation underlying the development and adjustment of modern TMO technologies, such as hot rolling, heat treatment, cold rolling with additional heat treatment and other processes. Digital analog of TMO is a complex of computer programs, including finite element program, which realizes calculations of temperature fields and stress-strain state, as well as an integral mathematical model of structure formation processes, which allow to perform calculations of changes in the structure of metal in the course of the entire processing process, as well as models of the relationship between the determining parameters of the final structure with the properties of steel¹.

The digital analog should take into account the peculiarities of technology, characteristics of industrial equipment, as well as describe the processes of structure formation during heating, deformation of austenite, release of excess phases during deformation, as well as the features of phase transformations during controlled cooling, taking into account the state of austenite and release of excess phases during subsequent cooling. Since the structure determines almost all properties of metals and alloys, the digital analogs of TMO developed in SPbPU allow to predict the properties of steels when changing the processing parameters and chemical composition of the metal, to develop new technologies, materials with a predetermined set of properties and technologies of their processing. Digital analogs have been implemented at Severstal's hot and cold rolling mills and heat treatment sections. They enable the company to respond quickly to changes in the metal market and optimize the costs of production and development of new products.

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SUBPHTHALOCYANINES: SINGULAR AROMATIC NON-PLANAR AND CHIRAL MOLECULES

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Due to their exceptional structural and photophysical properties, such as pronounced absorption and/or emission in the UV-vis and near-infrared (NIR) spectrum, superior charge transport characteristics, and a broad chemical adaptability, **Subphthalocyanines (SubPcs)** (Figure 1a) occupy a distinguished position among the most widely explored and versatile porphyrinoids [1]. These aromatic macrocycles, characterized by their distinctive non-planar structure, exhibit significant potential across various cutting-edge applications. These applications include the creation of polar superstructures, the development of thermotropic and lyotropic liquid crystals, the utilization as non-fullerene acceptors, and as materials for singlet fission.

Herein, we unveil pivotal aspects within SubPc chemistry that are ushering in a new era in the conception, synthesis, and utilization of these macrocycles [2]. We will elucidate how SubPcs can be harnessed in molecular photovoltaics, serving as materials for singlet fission, and explore their enantiopure versions in chiral technologies (Figure 1b-d) [3]. Additionally, we will present the synthesis and characterization of SubPc columnar materials and the on-surface synthesis approaches to construct 2D-Chiral Polymers.

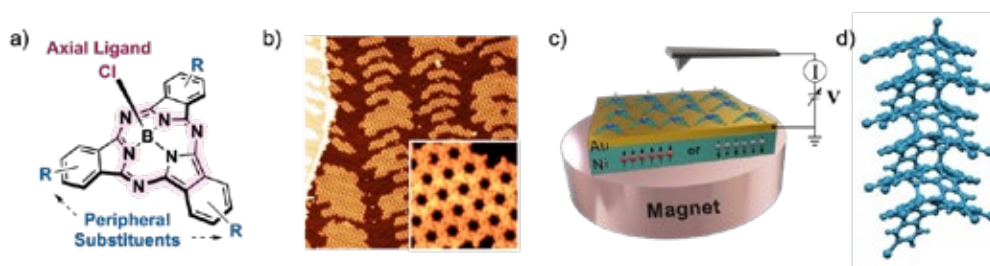


Figure 1. a) The molecular structure of SubPcs.

b) An example of a self-organized network composed of SubPcs absorbed on Au (111).

c) A SubPc-based spintronic device.

d) A columnar array based on SubPcs interacting in a head-to-tail fashion at solid state.

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The predecessors of the Mendeleev Congresses were the Congresses of Russian Naturalists (since 1967), which since 1871 have become Congresses of Russian Naturalists and Physicians. The first Mendeleev Congress was organized in December 1907; In the period up to 2023, 21 congresses were held. The topics of the congresses varied: the first two congresses were devoted to chemistry and physics (the theme of the first was even broader); The Third Congress of 1922 was aimed at applied chemistry; The IX Congress of 1965 was devoted to the chemicalization of agriculture, the use of chemistry in the production of food and medicinal substances; In addition to chemistry, the subjects of the congresses beginning in 1969 included the material science. The names of the congresses did not remain unchanged either: the word “physics” was present in the title of the second congress. Although most of the congresses were on “general and applied chemistry”, the word “pure” is used in the title of three congresses, and “theoretical” in the title of one; one congress was called the “A.M. Butlerov”.

The organizer of the first two congresses was the Russian Physico-Chemical Society, and the Supreme Council of the National Economy (VSNKh) participated in the organization of the Third Congress in 1922. The participation of various state bodies increased from congress to congress. The Academy of Sciences began to partially participate in the organization of congresses, starting in 1932 (congress in Kharkov), its role gradually increased, although the organizer after 1934 was the D.I. Mendeleev All-Union Chemical Society named after (VHO). The Academy of Sciences has played a key role in the preparation and holding of the last ten congresses. Usually, the intervals between congresses ranged from 2 to 6 years, but 11 years passed between the Second and Third Congresses (1911-1922), and 25 years between the Seventh and Eighth Congresses (1934-1959). Eight congresses were held in St. Petersburg (Petrograd, Leningrad) – 1907, 1911, 1922, 1934, 1969, 1984, 1998, 2019, four in Moscow – 1925, 1934, 1959, 2007, two in Kazan – 1928, 2003, one each in Kharkov – 1932, Kiev – 1965, Alma-Ata – 1975, Baku – 1981, Tashkent – 1989, Minsk – 1993 Volgograd – 2011, Yekaterinburg – 2016.

Acquaintance with the history of congresses showed that it might be necessary to have a statute on congresses, which would provide, in particular, for the creation of a standing committee of congresses from officers (not specific persons), and also fix the name of congresses (see above on general, pure, theoretical chemistry).

An abstract visualization of a molecular structure, possibly a protein or a complex polymer, rendered in a vibrant, multi-colored palette. The structure is composed of numerous small, spherical beads in shades of blue, green, yellow, and orange, which are interconnected by a network of thin, translucent, and slightly wavy lines. The overall shape is irregular and complex, with many protrusions and recesses, giving it a three-dimensional, almost crystalline appearance. The background is a solid, deep black, which makes the colorful structure stand out prominently. The lighting appears to come from the upper left, casting soft shadows and highlighting the edges of the structure.

SECTION 1

FUNDAMENTAL BASES OF CHEMICAL SCIENCE

NOVEL ELECTRODE MATERIALS FOR METAL-ION BATTERIES

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Lithium-ion batteries, originally developed for portable devices, are already widely used as stationary energy storage devices, in electric vehicles, etc. Rapid progress in the mass use of metal-ion batteries is intensifying the search for new electrode materials for Na- and K-ion batteries as a possible alternative to the already developed lithium-ion technology. Similar to lithium-ion intercalation systems, Na/K-based mixed oxides and polyanionic compounds are being intensively studied as potential cathodes with the aim of achieving high specific energy and cycling stability. Layered oxides are characterized by higher volumetric energy densities, however, polyanionic materials generally exhibit higher specific power, better cyclic and thermal stability due to covalently bonded structural frameworks. Polyanionic compounds are also characterized by a wide variety of crystal structures, which significantly expands the playground of the search for new materials with electrochemical characteristics attractive for practical applications. Additional benefits are expected from the synergistic effect of combining different anions (such as $(\text{PO}_4)^{3-}$ and F^-) in the crystal structure.

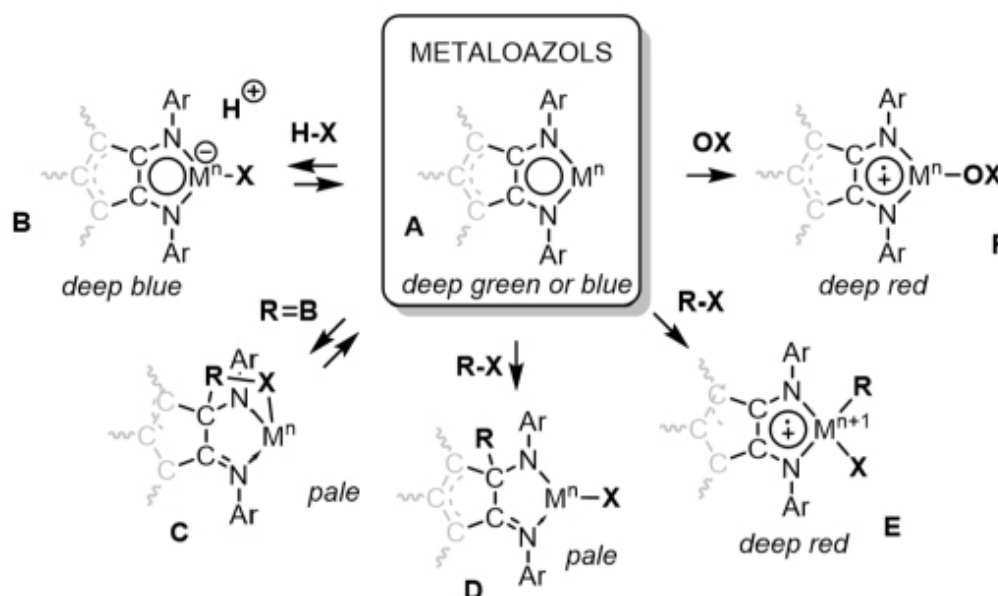
An overview of the research on novel phosphates and fluoride-phosphates as prospective electrode materials for the Na/K-ion batteries will be presented with a special emphasis on the interrelation between composition, synthesis conditions, crystal structure and electrochemical properties of the materials intended for practical applications.

METALLOIMIDAZOLS – NEW CLASS OF ORGANIC HETEROCYCLES

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A two-electron reduction of diazadienes, $\text{ArN}=\text{C}(\text{R})-\text{C}(\text{R})=\text{NAr}$, by metals affords five-membered metal-nitrogen heterocycles – metalloimidazolls (MIAs). Conjugation of p_z orbitals of all five atoms in the cycles in these compounds provides for the formation of a π system. The properties of MIAs differ significantly of those of acyclic metal bisamides, $(\text{R}_2\text{N})_2\text{M}$, as well as of metal-free azols. In contrast to the formers, all the MIAs (structural types **A**, **B**, **E** and **F**) are intensively colored; their solutions absorb in different regions of a visible spectrum. Some of them, as for instance **E** and **F**, reveal also absorption in the IR region. 2+4 (Cyclo)addition reactions destroy the conjugation within the cycles and, as the consequence, affords pale products **C** and **D**.



Involvement of the metal orbitals in the formation of the frontier molecular orbitals in MIDs causes an increase of their energy and, as a consequence, to a lowering of the ionization potential. Therefore all the MIDs represent highly reactive species that are reactive even towards unreactive molecules such as CO_2 .

The study has been supported by the Russian Science Foundation, project 24-13-00369.

COLLOIDAL QUANTUM DOTS – A NEW CLASS OF PHOSPHORS

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In 2023, Munji Bavendi, Louis Bruce and Alexey Ekimov were awarded the Nobel Prize in Chemistry for the discovery and synthesis of quantum dots. As stated in the press release of the Nobel Committee, "one of the exciting and unusual properties of quantum dots is that they create light of different colors depending on the particle size, while maintaining the atomic structure unchanged".

Quantum dots (QD) are semiconductor nanocrystals, the properties of which can be adjusted depending on their based on the quantum size effect discovered by Bruce and Ekimov, and Bavendi developed a chemical synthesis process that allows to obtain nanoparticles of the same size and quality. All this marked the beginning of the creation of a fundamentally new class of phosphors, the luminescent properties of which are determined by the average size of nanoparticles of a crystalline semiconductor, variable within 2-10 nm, while the width of the luminescence spectrum of a single nanoparticle at room temperature is only 20-30 nm, and the position of the nanoparticle spectrum can vary within the order of 100 nm relative to the band gap of a massive semiconductor.

Thus, a rather limited set of luminescent quantum dots based on semiconductors such as AIIBVI, AIIIBV or AIVBVI easily cover the spectral range from 350 to 3500 nm only by varying their size. Unlike organic molecular phosphors, QD has significantly greater thermal stability, photostability and, in addition, has a number of functional advantages, thanks to which they are already being used in photodetectors, light-emitting diodes, displays, solar panels, optical amplifiers, lasers, in chemo- and biosensors, in biomedical diagnostics. A more distant prospect of using QD is related to molecular electronics and quantum computing. In addition to the quantum-dimensional effect, a number of new physical phenomena were discovered in QD, such as multi-exciton generation, the effect of fluorescence blinking, inhomogeneous spectral broadening, etc.

In this overview report examines in detail the fundamental principles of the luminescent properties of QD, discusses the problems and prospects of their application.

The work was carried out with the financial support of the Russian National Fund, project 21-73-20245.

MATERIALS FOR CHEMICAL CURRENT SOURCES

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In recent years, the main trends in the energy sector have become energy conservation and the transition to environmentally friendly, renewable energy sources. However, the possibilities for using solar, wind and water energy are characterized by significant variability, primarily due to daily and seasonal fluctuations. To ensure a constant energy supply, energy storage devices are also needed, the main of which are metal-ion batteries and the hydrogen cycle. In Russia, as in a number of other technologically developed countries, a program for the development of hydrogen energy has been adopted and the construction of several large factories for the production of lithium-ion batteries has begun. This report reviews current trends and advances in materials for advanced chemical power sources.

The desire for stable operation of lithium-ion batteries has led to the replacement of lithium anodes with carbon ones, which prevent the formation of dendrites. However, this significantly limits the energy intensity of the batteries, and a return to lithium electrodes is being considered as an opportunity to increase it. A necessary condition for ensuring their safety is the use of solid electrolytes (inorganic polymer or composite). The development of such electrolytes, along with new cathode materials, is becoming a key challenge for the creation of a new generation of lithium batteries.

The main objectives of modern hydrogen energy are the environmentally friendly production of relatively cheap hydrogen, its transportation to the point of consumption and the creation of stably operating fuel cells, characterized by tolerance to low humidity and carbon monoxide impurities. Catalysts and membrane materials must play a key role in solving these problems. Similar problems must be solved when developing other promising current sources, which have received significant attention in recent years - flow batteries and reverse electrodialysis units. Materials for them are also being developed by Russian scientists.

The work was carried out with the financial support of the RSF, project 21-73-20229.

NITRIXIDE AND TRITYL RADICALS AND BIRADICALS AS POLARIZING AGENTS FOR DYNAMIC NUCLEAR POLARIZATION

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Solid-state nuclear magnetic resonance (NMR) spectroscopy with magic angle spinning (MAS - magic angle spinning) is a powerful method for obtaining information on the structure of biopolymers (proteins and nucleic acids, as well as their complexes). Dynamic nuclear polarization (DNP) is a hyperpolarization method that is widely used for increasing the sensitivity of nuclear magnetic resonance (NMR) experiments. DNP is based on polarization transfer from the polarized unpaired electron spins of polarizing agents by resonant microwave magnetic radiation to the nuclear spins (^1H or ^{13}C) of the molecules under study, which allows increasing the signal-to-noise ratio in the NMR spectra of the molecules studied by one to two orders of magnitude.

In this presentation the approaches to the synthesis and application of novel nitroxyl-nitroxyl^{1,2,3,4}, trityl-nitroxyl^{1,4,5} and trityl-trityl^{3,4,5} biradicals synthesized in NIOCH SB RAS will be overviewed. Another very interesting approach is based of application of trityls as polarizing agent in viscous liquids ⁷⁻⁹. It was shown that a ^1H DNP enhancement of over 50 can be obtained in viscous liquids at a magnetic field of 9.4 T and a temperature of 315 K. This was accomplished by using narrow-line polarizing agents in glycerol, both the water-soluble triarylmethyl radicals, and a microwave/RF double-resonance probehead⁹. DNP mechanism in electron spin cluster formed by covalently coupled tetra-trityl radical was recently understood¹⁰ and will be discussed.

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NEW PERSPECTIVES OF EPR SPECTROSCOPY IN STUDY AND DESIGN OF FUNCTIONAL NANOSTRUCTURES

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Electron paramagnetic resonance (EPR) spectroscopy is a highly informative method in modern chemistry that allows one to study and optimize the magnetic, structural and functional properties of nanostructures and nanomaterials. In our recent series of works, we developed a number of new approaches to the study of micro/nanoporous media,¹ including metal-organic frameworks (MOFs),^{2,3} porous organosilica,^{4,5} ionic liquid glasses and composites based on them.⁶ In particular, the method of encapsulated spin probes in MOFs opens up many opportunities for studying and optimizing these materials in such tasks as selective sorption, separation of mixtures of isomers, design of pressure sensors and catalytic systems. The functional properties of porous organosilica materials with grafted stable radicals can be studied using EPR and optimized both for quantum computing⁴ and for environmental applications in the selective sorption of nitrogen oxide from air.⁵ The combined application of pulse and continuous wave EPR techniques allows one to obtain unique information on the structuring of ionic liquids on a nanometer scale.⁶

This report focuses on key results obtained over the past few years and discusses the prospects for the EPR spectroscopy in the research and design of new functional nanostructures.

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LUMINESCENT LN-MOF FOR DETECTION OF BIOLOGICALLY ACTIVE SUBSTANCES AND ENVIRONMENTAL POLLUTANTS

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With further industrialization, pollution with heavy metals and organic toxicants poses a threat to the environment and human physical health. Therefore, there is an urgent need to develop sensor materials that can rapidly detect very low amounts of organic and inorganic pollutants. In our work, we obtained a series of monometallic and bimetallic Ln-MOFs with efficient and tunable photoluminescence based on 5,5'-(pyridine-2,6-diylbis(oxy))diisophthalic and 4-(3,5-dicarboxyphenoxy)isophthalic acids [1-4]. These compounds exhibit excellent stability in water over a wide pH range, high thermal stability, and high photoluminescence quantum yields. In addition, they demonstrated excellent sensor properties due to their luminescence quenching effect with exceptionally low detection limits for Fe³⁺, the antibiotic ofloxacin and the phytotoxin gossypol. Notably, Tb-MOF is the first high-performance sensor that can detect trace amounts of gossypol in water and can also visualize and quantify gossypol in edible cottonseed oil, proving its great potential for practical applications.

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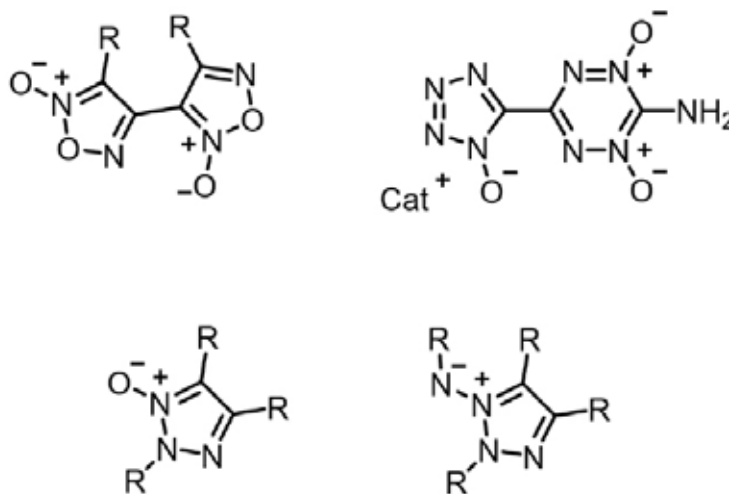
ADVANCES IN THE SYNTHESIS OF POLYNITROGEN HETEROCYCLES

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The current stage of development of science and technology necessitates a constant search for new organic materials with improved applied properties. From the point of view of the molecular structure of such organic materials, one of the most promising classes of compounds are conjugated polyheteroatom heterocyclic systems. As a rule, such structures have a number of advantages, including high thermal stability and balanced physicochemical and photophysical properties. Such a vast potential of organic molecular systems built on the basis of nitrogen heterocycles explains their multipurpose use in various advanced applications. Therefore, the development of new approaches to the target design of polynitrogen heterocyclic systems remains highly relevant.

Herein, we present the latest achievements of our scientific group in the development of new methods for the synthesis of polynitrogen heterocyclic structures for various purposes. Over the past 5 years, we created promising synthetic strategies for an assembly of a wide variety of heterocyclic systems, including 1,2,5-oxadiazoles and their N-oxides (furazans and furoxans), 1,2,3-triazole-1-oxides and mesoionic 1,2,3-triazol-1-imines, as well as stable heterocyclic radicals (Blatter radicals and verdazyl radicals).



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DESIGN OF BIOCOMPATIBLE LUMINESCENT SYSTEMS BASED ON TRANSITION METAL COMPLEXES WITH P,N-LIGANDS

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The interest in artificial luminescent compounds stems from the widespread use of various emitting devices in people's daily lives. Transition metal complexes are most suitable for luminescent sensors due to relatively high PLOY values, long lifetime and sensitivity of their phosphorescence to changes in the coordination sphere. Among ligands used effectively for such complexes, phosphinopyridines and other phosphines with chromophore functional groups play a special role. In our laboratory, heterocyclic phosphines with exocyclic chromophore groups are used to create luminescent transition metal coordination compounds. A wide range of mono-, bi-, tetra- and hexanuclear gold (I) and copper (I) complexes have been prepared on the basis of such ligands. Phosphorescence has been observed for these compounds in a wide range of wavelengths, including infrared band¹ and a rare two-band white emission.^{2,3} The possibility of using both the complexes themselves and biocompatible materials created through their immobilisation on a polyelectrolyte matrix as sensors for pH, temperature⁴, presence of organic solvents⁵, as well as for illumination of cell organelles in confocal microscopy and generation of reactive oxygen species in cancer cells has been demonstrated.^{6,7} This makes the presented complexes perspective building blocks for the design of luminescent materials for biomedical application.

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TETRYLENES BASED ON COORDINATING LIGANDS: SYNTHESIS, ELECTRONIC STRUCTURE AND REACTIVITY

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Since the mid-1970s, when M. Lappert's pioneering work led to the discovery of sufficiently stable organic derivatives (or based on organic substituents) of group 14 elements in oxidation state +2, known as tetrylenes, these compounds have been actively studied. The stabilization of the low-valent center can be achieved through both electronic factors, such as the donation of an unshared electron pair from a substituent atom to an empty orbital (thermodynamic stabilization), and steric factors, such as bulky substituents (kinetic stabilization). Currently, researchers are investigating the use of tetrylenes as catalysts in various processes, such as polymerization, cyanosilylation, and hydroboration. They are also exploring the possibility of producing more complex organometallic derivatives from these compounds.

Research aimed at finding correlations between the structure of tetrylene and its chemical properties is essential. The report will present the author's work in collaboration with colleagues¹ and other data from the literature on the study of the electronic structure of stable tetrylene compounds and their reactivity in oxidative addition reactions. In particular, the study of stannylene, germylene, and plumbylene compounds based on bidentate, tridentate, and tetradentate ligands that form one or two covalent bonds with an atom from the 14th group will be discussed. The rates of these reactions depend primarily on the electronic properties of the central atom and its steric accessibility.²

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BIOCOMPATIBLE MATERIALS BASED ON CALCIUM PHOSPHATES FOR REGENERATIVE MEDICINE AND TISSUE ENGINEERING

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A comprehensive cycle of studies was carried out to develop the fundamental principles of the technology for developing biomaterials based on calcium phosphates for the replacement and regeneration of human tissues and organs. A wide range of medical materials has been developed, differing in chemical and phase composition, structure, mechanical, and biological properties, and intended application.

The research developed principles for forming the architecture, microstructure, and nanostructure of porous ceramic and composite materials, which are crucial for ensuring both high mechanical properties and clinical effectiveness in surgical interventions. Fundamental principles for enhancing the strength of porous bioceramics have been developed and studied, particularly through the method of infiltration of biocompatible polymers into ceramic scaffolds. This approach led to the creation of biocompatible, resorbable hybrid composites based on biopolymers and calcium phosphates that exhibit high mechanical properties.

The fundamental problems were investigated concerning the formation of the structure and properties of ceramics based on calcium phosphates at physiological temperatures. The research focused on using the principle of reaction hardening within binder systems to fabricate bulk product.

Biocompatible materials based on calcium-magnesium phosphates doped with rare earth elements, designed for treatment and non-invasive diagnostics, have been developed.

Innovative methods for the certification of the biomaterials using microtomography and computer modeling have been developed, enabling the prediction of their structural properties.

The technologies for formation of inorganic materials adapted to the additive manufacturing have been developed, particularly in the context of three-dimensional (3D) printing. This includes the development of gene-activated personalized tissue-engineered scaffolds. Clinical trials and the introduction into clinical practice of the world's first gene-activated material for the treatment of patients with bone injuries have been carried out.

The synthesis of bone tissue samples using three-dimensional (3D) fabrication on the orbital International Space Station (ISS) was performed for the first time in the world. This pioneering work has demonstrated that under weightlessness conditions, it is possible to study complex biological processes and create tissue-engineered scaffolds with high regenerative potential.

The work was supported by the Russian Science Foundation Grant No. 23-63-10056.

CHLORINE DIOXIDE - A NEW SELECTIVE OXIDIZING AGENT FOR ORGANIC SYNTHESIS

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One of the most popular methods for the functionalization of different classes of compounds is the oxidation process. The use of chlorine dioxide (ClO_2) as an oxidizing agent produced on an industrial scale for pulp bleaching and water disinfection is of interest from a fundamental and practical point of view. Having such structural features as the presence of an unpaired electron and two reaction centers (chlorine and oxygen), it has properties different from other oxidants. Being highly soluble in both water and organic solvents, ClO_2 allows reactions to be carried out in various media.

We have studied the reactions of mono- and polyfunctional terpene thiols, disulfides or thioacetates of pinane, carane, mentane and bornane structures with ClO_2 . The influence of the substrate structure and synthesis conditions on the direction, chemo- and stereoselectivity of reactions is shown. The features of alkylphenol oxidation have been revealed using various reaction conditions, including catalytic systems. When alkylphenols interact with ClO_2 , quinones and oxidative chlorination products are formed. The yield of quinones depends on the position of the substituents in the aromatic ring of the studied phenols.

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PHYSICAL - CHEMICAL PROPERTIES OF MATTER UNDER EXTREME CONDITIONS

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According to modern conceptions¹, more than 90% of the observed matter in the Universe is under conditions of extremely high pressures and temperatures. The questions of the behavior of the structure of matter under extreme conditions, the expected new chemical effects, methods for obtaining extreme states in the laboratory and the study of physical and chemical properties of substances are considered in the review².

The report discusses the state of the problem of experimental and theoretical study of the fundamental physical and chemical properties of substances under extreme conditions, the description of physical and chemical transformations, the phase boundaries of melting and evaporation, the effects of restructuring of the electronic structure, ionization, metallization and dielectrization.

The results of calculations of the properties of metals and structural materials are presenting with the use of wide-range models of physical - chemical properties in comparison with the available theoretical and experimental data under extreme conditions. Discussing are problems of the numerical simulation of physical-chemical processes of various nature under conditions of high energy density, implementation of models of substance properties in numerical codes, the quality of descriptions and the reliability of the modeling results. Examples of 3-and 2-dimensional numerical modeling of high-energy-density processes are given, the importance of reliable description of physical and chemical properties of matter in a wide area of the phase diagram is indicated.

The problems of development, functioning and presentation of experimental data and approximations of thermodynamic properties of substances in the form of an online data bank are discussing.

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The work was carried out within the framework of the project "Supercomputer numerical simulation of high-speed impacts on artificial space objects and the Earth", Agreement No. 21-72-20023 (Project No. 21-72-20023).

APPROACHES FOR INVESTIGATION OF LIGAND-RECEPTOR INTERACTION: ROLE OF THE LIGAND DISPLAY

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Efficient methods are still required to assess the fine ligand specificity of cellular receptors. One of the most challenging tasks in this field is the development of precise methods for characterization of the recognition of carbohydrate ligands by carbohydrate-recognizing protein receptors that is important for the selection of most efficient ligands to design glycovaccines and glycodiagnostic systems for prevention and detection of infections.

A number of publications report contradictory results about the specificity of known antibodies and lectins. In some cases they report totally or partially mismatched conclusions, but mainly – overestimated specificities. In this lecture several recent examples of such cases will be discussed, with the emphasis on the importance of using synthetic oligosaccharides of strictly known structure as reference antigens (for selected publications see references 1-7). The significance of loading density, equimolarity and efficient spatial presentation of the assayed glycoligands, as well as their multimericity will also be discussed on the examples of the investigation of the recognition of fungal and bacterial antigenic polysaccharides by Abs and lectin receptors.

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PREDICTING AND RATIONALIZING NEW COMPOUNDS AND PHENOMENA

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The breakthrough of crystal structure prediction has resulted in breakthroughs in related problems of compound prediction and prediction of stable molecules/clusters. I will discuss several chemically significant cases:

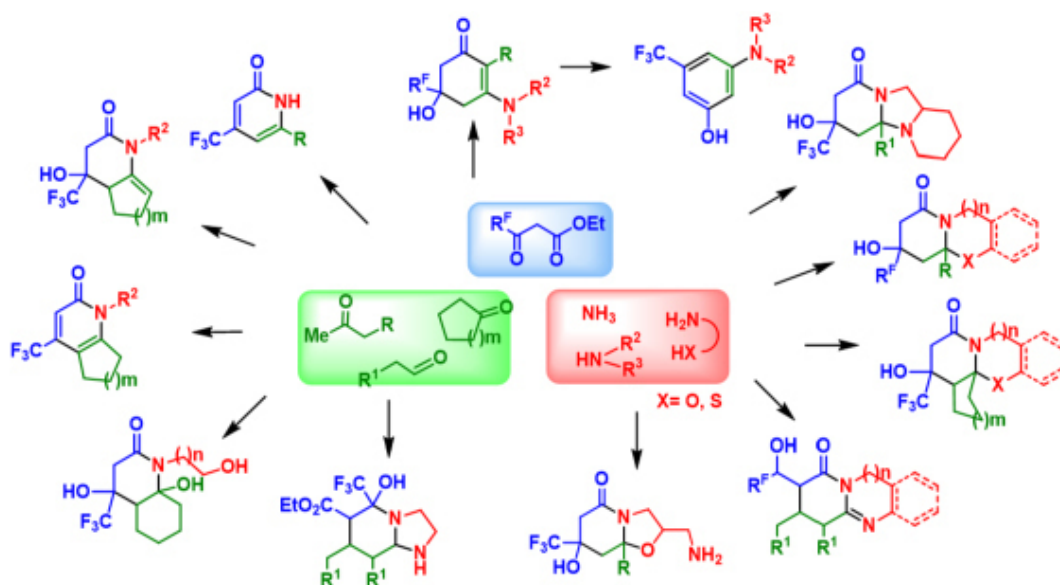
1. Discovery of anomalous compounds under pressure, such as Na_3Cl , NaCl_7 and highest-temperature superconductors known to date – H_3S , YH_6 , CaH_6 , ThH_{10} , LaH_{10} .
2. Discovery of counterintuitive phenomena at high pressure – formation of transparent insulating phase of sodium and chemical reactivity of helium.
3. Rationalization of these and other phenomena based on newly developed scales of electronegativity and chemical hardness.
4. Prediction of stable molecules – the formalism and its applications. In particular, I shall discuss the results on molecules and crystalline allotropes of sulfur, phosphorus and boron. Chemical diversity of hydrocarbons will be explained, as well as unusual molecules in the C-H-N-O system.

MULTICOMPONENT REACTIONS OF POLYFLUORALKYL 3-OXO ESTERS WITH α -METHYLENE CARBONYL COMPOUNDS AND AMINES AS A NEW TOOL FOR ORGANIC SYNTHESIS

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A new universal multicomponent approach to biologically promising fluorine-containing hetero- and carbocyclic structures is comprehensively discussed in the report. This way is based on an autocatalyzed one-pot domino reaction of polyfluoroalkyl-3-oxo esters with α -methylene carbonyl compounds and amines.¹⁻⁴



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The work was carried out with the financial support of the Russian Science Foundation (project 24-13-00427) and within the framework of a state assignment (No. 124020500044-4).

ORGANIC SYNTHESIS IN LIQUIFIED GASES: ACHIEVEMENTS AND CHALLENGES

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The global environment pollution with industrial and social wastes is becoming more serious problem over the past decades. The chemical industry contributes significantly into this negative tendency. A perspective way to reduce harmful impact of chemical industry on the environment may be re-placement of organic solvents in liquid-phase chemical processes for sustainable, readily recyclable and requiring no utilization liquefied or super-critical gases, such as carbon dioxide or a lower freon, particularly 1,1,2-tetrafluoroethane.

In the contribution, we discuss recent applications of these media in fine organic synthesis, including enantioselective processes¹, to afford compounds of high molecular complexity, in multicomponent, cascade and domino reactions^{2,3}, in the UV-light-induced direct CH-functionalization of alkanes⁴ and photocatalytic oxidation of alcohols⁵, and for safe and waste-free nitration of various organic compounds⁶. Advantages and so far unsolved problems, associated with these processes, are considered. In all cases, non-renewable petroleum originated organic solvents are eliminated from the reaction mass. Organic reactions in liquefied gases may be promising prototypes of future green technologies for preparation of important medications, natural compounds analogues, energetic materials and other useful chemical products.

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TOWARDS BIOELECTROCHEMICAL DEVICES RESEARCH AND DEVELOPMENT

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Enzymes and living cells are widely used in various bioelectrochemical devices research and development. These devices are alternative of traditional electrolysis cells, fuel cells, electrosynthesis cells, sensors etc. based on inorganic or organic catalysts. Nevertheless, only few types of biodevices such as biosensors for detection of various physiologically important analytes (for personal control of diseases, e.g. diabetes), for control of biotechnology processes are commercially produced.

The key restrictions for research and development of such bioelectrochemical devices are the problems for increase of sensitivity or activity and stability, the expansion of durability and transfer of technology to minimally invasive or invasiveless types.

In research practice the non-trivial tasks of mediator or electrocatalysts using, analytical medium composition developed [1,2]. The using of living biocatalysts, their profiling, development of stable bioelectrochemical platforms for analysis of various substances [3, 4] discussed. In addition, the problems of correct electrochemical measurements with bioelectrodes and electrode/support choice will be discussed.

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HEXANUCLEAR METALLOCLUSTER COMPLEXES – AN ORIGINAL CLASS OF RED LUMINOPHORS

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Octahedral cluster complexes described by the general formulas $[\{\text{Mo}_6\text{X}_8\}\text{L}_6]^n$ and $[\{\text{Re}_6\text{Q}_8\}\text{L}_6]^m$ ($\text{X} = \text{Cl}, \text{Br}$ or I ; $\text{Q} = \text{S}$ or Se ; L = apical inorganic or organic ligands) harmoniously combine promising chemical and physical properties for various applications.^{1–3} In particular, such complexes exhibit high chemical and photostability of the $\{\text{Mo}_6\text{X}_8\}^{4+}$ and $\{\text{Re}_6\text{Q}_8\}^{2+}$ cluster cores, which are responsible for the triplet excited state luminescence. Compounds based on these clusters are characterized by broad luminescence spectra extending in the red/near-infrared region (from ~550 to over 950 nm), impressive for inorganic materials quantum yields of emission and are effective photosensitizers of singlet oxygen generation. Various research groups have confirmed the biocompatibility and low toxicity of various octahedral metal-cluster complexes. Together, these properties make octahedral cluster complexes of molybdenum and rhenium attractive targets for the development of luminescent materials and for biomedical applications, for example, as photosensitizers for photodynamic therapy and luminescent markers for biovisualization.

Some details on the synthesis, structure and properties of various luminescent octahedral cluster complexes of molybdenum and rhenium and materials based on them will be presented in a conference presentation.

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MECHANISM OF THE REVERSIBLE REACTION OF [2+2]-PHOTOCYCLOADDITION: FORWARD CONCERTED REACTION ACCORDING TO THE WOODWARD-HOFFMANN RULES AND REVERSE STEPWISE CYCLE-OPENING REACTION ACCORDING TO THE PREDISSOCIATION MECHANISM

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The [2+2] photocycloaddition (PCA) reaction of ethylene, leading to the formation of cyclobutane, is one of the fundamental reactions widely used in organic chemistry. According to the symmetry of molecular orbitals, the ground state of the two ethylene molecules involved in the PCA reaction correlates with the excited state of cyclobutane, and vice versa. Therefore, it is believed that both the forward and reverse reactions obey the Woodward–Hoffmann rules for concerted pericyclic reactions, i.e. are forbidden in the ground state (thermally), but allowed in the excited state (photochemically).

However, for substituted ethylenes, in which the double bond is included in the common π -conjugation chain, this scheme is valid only for the forward reaction. In this case, the long-wavelength absorption band (LWAB) is determined by the entire conjugated π -system, and the “ethylene” $\pi\pi^*$ -excited state, necessary for the PCA reaction, is populated upon irradiation with relatively soft light in the LWAB region.

The reverse reaction of retro-PCA requires excitation of cyclobutane into a $\sigma\sigma^*$ -excited state, which can only be populated by irradiation with hard UV light. The LWAB of substituted cyclobutane is determined by the absorption of substituents. In this case, upon irradiation with light in the LWAB region, the binding $\pi\pi^*$ -excited state, in which the excitation energy is localized on the substituent, is first populated. Next, energy must be transferred to the cyclobutane core and localized on the σ -bond of cyclobutane, which leads to bond rupture and ring opening. The transition from a binding to a dissociative term corresponds to the predissociation mechanism.

It is obvious that the predissociation mechanism is common to most practically important cyclobutanes, in which, upon irradiation with light, the π -system of the substituent, rather than the σ -system of the cyclobutane ring, is excited.

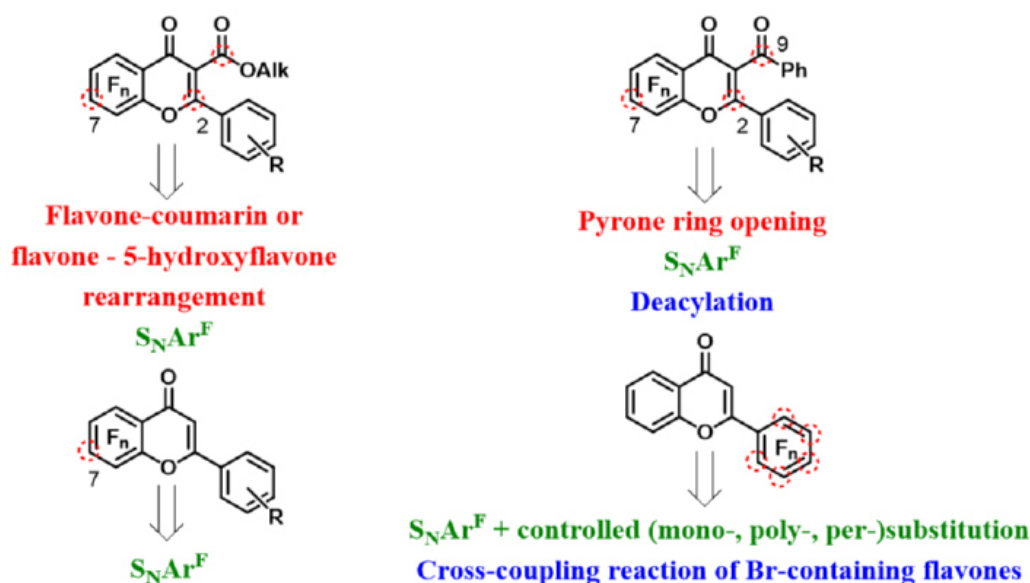
The work was performed in accordance with the state task No. 124013000686-3 with the financial support of the Russian Science Foundation, project 22-23-00482.

APPROACHES TO SYNTHESIS AND MODIFICATION OF POLYFLUOROFLAVONES

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The methods for the synthesis and transformation of structurally diverse polyfluoroflavones are discussed in the report. The polyfunctional nature of 3-carbonylpolyfluoroflavones in the reactions with amines is found, since they can react at the electrophilic centers C2, C7 and C9. In this case, transformations at the C2 center occur with the opening of the heteroring, giving aminoenketones or new benzopyrones depending on the carbonyl function. 3-Unsubstituted flavones are characterized by S_NAr^F reactions at the polyfluoroaromatic fragment with the possibility of controlled fluorine atoms substitution.^{1,2} The possibility of functionalization in cross-coupling reactions has been shown for bromine-containing fluoroflavones.³



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1,3-DEHYDROADAMANTANE AND ITS DERIVATIVES: A UNIVERSAL SYNTHETIC PLATFORM FOR OBTAINING FUNCTIONAL COMPOUNDS WITH FRAMEWORK STRUCTURE

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A promising strategy in the synthesis of functional compounds of the frame structure is the use of 1,3-dehydroadamantane (tetracyclo[3.3.1.1.1.3,7.0.1,3]-decane; 1,3-DHA, bridge [3.3.1]propellant) and its derivatives, which in chemical transformations are capable of restoring the adamantane structure.

Information is provided on the methods of synthesis of 1,3-DHA and its homologues, some spectral characteristics, and probable intermediates generated from 1,3-DHA.

A classification of reactions involving 1,3-DHA is proposed. These are reactions that occur with the rupture or preservation of the propellant bond. Propellant bond rupture reactions lead to the restoration of the adamantane framework and are key in the synthesis of various mono- and disubstituted adamantane derivatives, including hard-to-reach compounds. Reactions with the preservation of the propellant bond are associated with the participation of functional groups in the tertiary carbon atoms C5 and C7. The range of such transformations of 1,3-DHA is small.

Reactions of 1,3-DHA with a number of different organic compounds containing functional groups are considered. A comparative assessment of the reactivity of 1,3-DHA with respect to CH-, NH-, OH- and SH-acids, as well as arenes, heterocyclic compounds, and hydantoines was carried out. The probable mechanisms of reactions involving 1,3-DHA are discussed, depending on the nature of the substrate.

Special attention is paid to the reactions of 1,3-DHA with various weak and strong C-H acids, which make it easy to form C-CAd bonds to obtain hard-to-reach adamantane derivatives. For substrates with an activated methylene group, substitution of the C-H bond by a 1-adamantyl substituent in reactions with 1,3-DHA leads to chirality.

Some examples of trimolecular reactions of 1,3-DHA with substrates occurring with the introduction of solvent molecules (diethyl ether, THF, dioxane) are given

New chemo- and regioselective methods of single-stage introduction of the 1-adamantyl group into molecules of various substrates have been developed. The advantages of using 1,3-DHA in reactions are noted – low-stage, atomic precision and "green chemistry".

The results of the use of compounds obtained by reactions involving 1,3-DHA in various fields are presented: medical chemistry, polymer materials and others.

The work was carried out with the financial support of the Russian Science Foundation (grant No. 21-73-20123).

ALKYLATION OF PHENOLS AND ANILINE BY TERPENOIDS – A METHOD FOR OBTAINING NEW SUBSTANCES

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In organic chemistry, alkylation reactions are a common way to produce new substances. A convenient method of direct introduction of an alkyl group into an aromatic ring is the Friedel-Crafts reaction (Friedel-Crafts alkylation). Alkylating agents are usually olefins, alcohols, alkyl sulfates or alkyl halides, and typical catalysts are Brønsted acids (HF , H_2SO_4 or H_3PO_4), Lewis acids (AlCl_3 , $(\text{PhO})_3\text{Al}$, BF_3 , ZnCl_2 , TiCl_4), effective and environmentally friendly heterogeneous catalysts (zeolites, sulfocationites) can also be used¹.

Alkylation is often accompanied by rearrangements, the direction of which is determined by the nature of the catalyst. The variation of reaction conditions (catalyst, temperature, pressure, ratio of reagents) makes it possible to obtain a variety of products. The study of the Friedel-Crafts alkylation patterns opens up prospects for controlling the direction of the reaction.

Alkylation of phenols and aniline with terpenoids was used by us to synthesize analogues of natural terphenols² and terphenylanilines³. The tendency of terpenes to skeletal rearrangements under acidic conditions leads to undesirable reactions with the formation of a large number of by-products. This circumstance requires taking into account many factors related to the nature of the catalyst, its acid-base properties, as well as certain reaction parameters. Nevertheless, the synthesis of analogues of natural compounds with identified physiological activity and substances with a new structure is an important fundamental and applied task of organic chemistry.

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The study was financially supported by the Ministry of Science and Higher Education of the Russian Federation (state assignment No. 122040600073-3) and the grant from the Russian Science Foundation (project No. 21-73-20091, <https://rscf.ru/en/project/21-73-20091/>).

SURFACTANT ASSOCIATES AS A TEMPLATE: NEW OPPORTUNITIES FOR SYNTHESIS AND FUNCTIONALISATION OF NANOPARTICLES

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Surfactant micelles and vesicles are among the most interesting objects of colloidal chemistry. They are actively used to localize and accelerate various reactions, to deliver genetic material and drugs, and to solve other scientific and practical problems.

Using mesoporous silica nanoparticles (MSNs) and gold nanorods (GNRs) as examples, the report analyses the opportunities and prospects of using surfactant associates as a template for the synthesis of nanoparticles with predetermined morphology and properties.

The main attention is paid to finding ways to control the structure and functionality of surfactant associates (e.g. by introducing hydrophobic components into the solution) as well as determining the influence of such a hybrid template characteristics and the conditions of nanoparticle synthesis on their morphology and properties.

The report consists of two parts. The first part presents original data demonstrating the possibility of creating MSNs on micelles and vesicles consisting of several biologically active compounds. This sol–gel synthesis method provides the formation of MSNs with an extremely high content of target templating compounds. The rate of their subsequent release into the environment can be controlled by changing the medium pH.

The second part of the report discusses the features of the formation of GNRs in micellar solutions of cetyltrimethylammonium bromide in the presence of hydrophobic polyphenols that can solubilize in surfactant micelles and change their shape. According to the data obtained, the introduction of such additives into the reaction system allows to significantly reduce the concentration of templating surfactant without losing the quality of the GNRs. It is very important from a practical point of view. In some cases, the hydrophobic additive can also act as a reducing agent for metal ions.

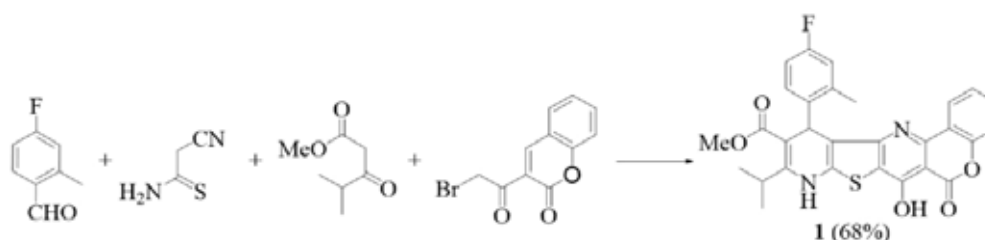
MULTICOMPONENT TANDEM IN THE SYNTHESIS OF FIVE- AND SIX-MEMBERED HETEROCYCLES

Dyachenko I.V.

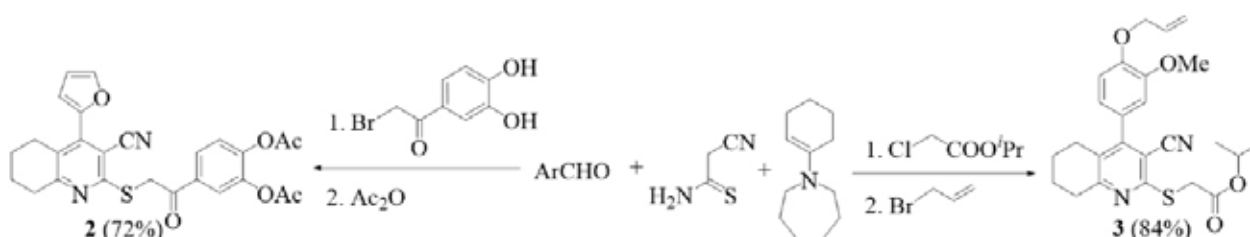
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In the course of our research, effective multicomponent tandems **I-III** were developed, proceeding under mild conditions with the sequential addition of starting reagents, which make it possible to synthesize new derivatives of thiophene, thiazole, selenazole, pyran, pyridine and quinoline **1-5** in a short period of time.

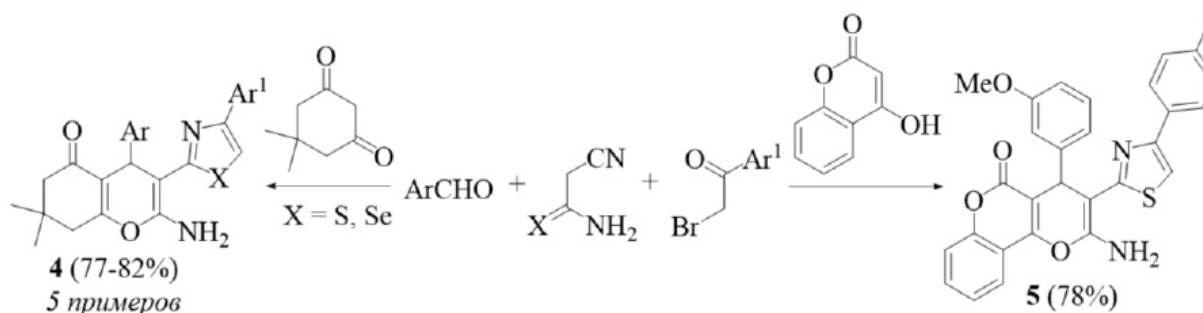
Tandem **I**: Knoevenagel condensation – Michael reaction – intramolecular cyclization – alkylation – cascade cyclization.¹



Tandem **II**: Knoevenagel condensation – Stork reaction – intramolecular transamination – alkylation – acylation.²



Tandem **III**: Knoevenagel condensation – Hantzsch reaction – Michael reaction – intramolecular cyclization.^{3,4}



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COORDINATION CHEMISTRY OF GOLD(III): PECULIARITIES OF COMPLEX FORMATION IN AQUEOUS SOLUTION, COMPLEX STRUCTURE AND INTERACTION WITH PROTEINS AND DNA

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Gold(III) complexes that are isoelectronic and isostructural to cisplatin have been considered promising cytotoxic agents for a quarter of a century¹⁻². Free cations cannot be used for medical purposes directly because they are prone to hydrolyzing in water and reducing to Au⁰. Therefore, the stabilizing of gold(III) ions via binding them into stable complexes is necessary. Early stage studies³ suggested that the interaction between DNA and gold(III) complex provides a base for the action of the latter. Then, one more mechanism beyond the cytotoxic effect was proposed: thioredoxin reductase inhibiting⁴. Thus, a synthesis of gold(III) complexes, the prodrugs¹, that are supposed to deliver Au³⁺ ions in the cells, as well as the study of the interaction between gold(III) ions with proteins (including serum albumins, the transport proteins of blood serum) and DNA, are of great interest.

The approach prevalent in literature, which considers the metal complex-biomolecule interaction a single reaction, which occurs in stoichiometric ratio of n:1 (1:1, most often)⁵, seems ambiguous. One should describe such interactions using a set of competing reactions of complexation between Au³⁺ ion and low-molecular weight ligands, proteins and/or DNA taking into account the hydrolysis process as well. The present lecture generalize the literature and our own data on stability and structure of coordination compounds of gold(III) with the ligands of the different nature.

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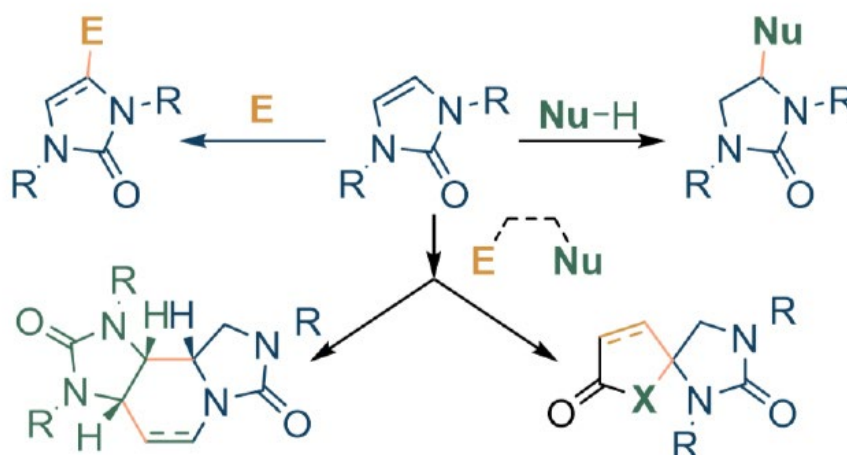
CHEMISTRY OF IMIDAZOLINE-2-ONES – ACHIEVMENTS, CHALLENGES AND PROSPECTS.

**Gazizov A.S.,^a Kuznetsova E.A.,^{a,b} Kamaletdinov A.Z.,^b Chugunova E.A.,^a
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The imidazolin-2-one scaffold is widespread in natural products and is a key motif of many biologically relevant compounds. Despite of this, the reactions of imidazolin-2-ones are only scarcely known and their reactivity towards various electrophilic and nucleophilic reagents remains rather underexplored. Herein, we summarize the results of our research in this area and demonstrate the versatility of imidazolinones as precursors to the various polycyclic structures, including phosphorylated heterocycles.¹⁻⁴ Existing limitations of the known transformations, ways to overcome them, and promising areas of future research are also discussed.



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AROMATIC NITROSOOXIDES: PHYSICO-CHEMICAL PROPERTIES AND REACTIVITY

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The report presents the results of the author's research¹ on the structure, electronic properties, reactivity, kinetics of formation and transformations of nitroso oxides, labile peroxide species of the general formula $RNOO$, which are intermediates of photochemical and thermal reactions of azides RN_3 in the presence of molecular oxygen. Information concerning both the simplest nitrosooxide $HNOO$ (peroxynitrene) and its aromatic analogues $ArNOO$ has been systematized. The mechanism of the unusual intramolecular *ortho*-cyclization of $ArNOO$ and the pathways for the transformation of the nitrile oxide intermediate² into various heterocyclic structures depending on the structure of the starting aryl azide have been studied in detail:

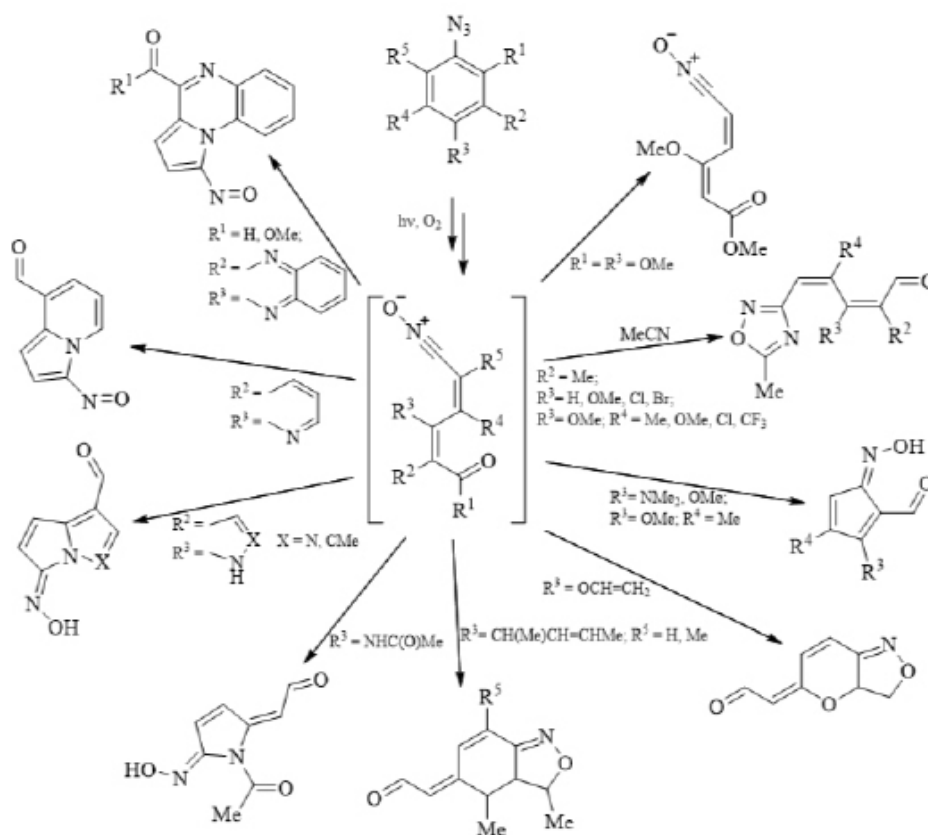


Figure 1. Products of $ArNOO$ transformation occurring through the *ortho*-cyclization stage. If the substituent is not specified, then $R^1 \dots R^5 = H$.

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INFLUENCE OF INTERMOLECULAR INTERACTIONS ON THE MAGNETIC EFFECT IN COORDINATION COMPOUNDS OF COBALT(II) WITH 1,6-DIAMINOHEXANE

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Interest in materials based on coordination compounds for which bistability of physical properties is realized is determined by fundamental and practical points of view, since these unique properties can be used in the development of intelligent materials for data storage, processing and transmission, in sensors, electronic components, etc. Particular attention is drawn to systems in which magnetic effects related to spin state changes (spin crossover phenomenon, spin transition induced by charge transfer, superexchange), the presence of residual magnetization, magnetization hysteresis, and slow magnetic relaxation are realized. Such magnetic effects in crystals of coordination compounds are due to a wide range of causes, including the electronic structure of the metal center, the coordination environment of the metal atom and the nature of the ligands, packing effects, and intra- and intermolecular interactions. For example, the tuning of the spin state of the metal center can be determined by the crystallization of the metal complex involving halogen bonds, inter-ligand π -stacking interactions, and the presence of hydrogen bonds between ligands. In some cases, these spin transitions are accompanied by structural phase transitions, which, as a rule, are reversible and accompanied by a thermal hysteresis loop and may be accompanied by changes in the geometry of the coordination environment of the metal center, including the breakage of metal-ligand bonds and the strength of exchange interactions between paramagnetic centers.

This work will present results on the study of coordination compounds of cobalt(II) with 1,6-diaminohexane, and determine the role of crystal packing effects and structural phase transitions on the metal ion orbital angular momentum and/or magnetic ordering.

The work was financially supported by the Ministry of Education and Science of Russia within the framework of the state assignment of IGIC RAS.

OXIDATIVE TRANSFORMATIONS OF POLYSUBSTITUTED FURANS – A NEW STRATEGY FOR THE SYNTHESIS OF STRUCTURE DIVERSIFIED GABA ANALOGUES

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The report examines the methodology for the synthesis of GABA and racetams analogues, including those with limited conformational mobility based on the use of substituted oxygen-containing functional derivatives of furan as key structural blocks.

The proposed methodology is based on two approaches: alkylation of furan compounds available from renewable raw materials, or formation of a furan system based on natural terpenoids, oxidative cleavage of polysubstituted furans to ketoacids or polycarbonyl compounds with the conversion of the latter into modified butyrolactams and GABA analogues.

DEEP EUTECTIC SOLVENTS AS CARBON DIOXIDE ABSORBENTS

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The emission of greenhouse gases, such as CO₂, into the atmosphere, causes significant environmental problems. The traditional methods of CO₂ capture with amine-based solutions is expensive. Alternative CO₂ absorbents have not proven to be technologically and economically efficient. In this regard, researchers have begun to focus on deep eutectic solvents (DES) as an alternative. They are characterized by environmental friendliness, the ability to vary properties, relative cheapness, and the ability to dissolve CO₂. The report provides basic information about DES, including their classification, and physicochemical characteristics. The issue of the “Carbon Footprint” and possible ways to manage carbon emissions are briefly considered. The forecast of the use of DES as carbon dioxide absorbents, conducted on the basis of a machine learning algorithms, is given¹. The authors present their own as well as literature data on the absorption of CO₂ by various DES. The possibilities of both physical absorption in the general case of DES and chemical absorption of CO₂ with the formation of carbamates in the case of amino-containing DES are considered. To clarify the mechanism of the CO₂ absorption process, IR, Raman and NMR (¹H, ¹³C) spectroscopy of samples containing no amine and amino-containing DES before and after CO₂ absorption was carried out. DES based on choline chloride and urea in a ratio of 1:2 was also studied (the subject of many studies, which is called “reline”) by methods of quantum chemistry and molecular dynamics. The structures have been obtained for various complexes consisting of choline cations, chloride anions, urea molecules and CO₂ molecules with these particles.

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DESIGN OF METAL-ORGANIC PARAMAGNETS BASED ON METALLOCOMPLEXES, FULLERENES, HEXAAZATRIPHENYLENES AND SPIROPYRANS

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Assemblies containing paramagnetic transition metals and organic molecules can show magnetic transitions, charge transfer between metals and ligands, reversible transfer to a high-spin state and single ion magnetism. Fullerene C_{60} can coordinate paramagnetic $Fe(CO)_2$ which bind fullerenes forming metal-bridged anionic dimers in $\{Cryptand(K^+)\}_2\{[Fe(CO)_2]-\mu_2-\eta^2, \eta^2-\eta^2, \eta^2-(C_{60})_2\}^-$. Spin density is mainly localized on Fe ($S = 1/2$) and dimers transfer to a triplet state above 50 K.¹ Contrary, isomeric dimer with a Fe-Fe bond is diamagnetic. The reduction of nickel(II) porphyrin and hemihexaphyrazine is metal-centred yielding paramagnetic Ni(I) ($S = 1/2$) in $\{Cryptand(Cs^+)\}_2\{Ni^{II}(TPP^2-)\}^-$ and $\{Cryptand(Cs^+)\}_2\{Ni^{II}_2Ni^{II}O(Hhp^5-)\}^{2-}$. A reversible increase of magnetic moment is observed due to metal-to-ligand CT or transition of a macrocycle to a triplet state. Assemblies with metalloporphyrins can also transfer to a high-spin state when they are coordinated to thioindigo radical anion in $\{(MnTPP)_2(thioindigo^{\bullet-})\}$ or paramagnetic bridge in $\{Cryptand(Na^+)\}_2\{(MnTPP)_2(Mn^{II}(triazole)_2Pc)\}$. In the first case coupling is defined by an angle between porphyrin and thioindigo planes.² Hexaazatriphenylenes coordinating Co^{II} ($S = 3/2$) or Fe^{II} ($S = 2$) can possess various spin states and coordinate different number of metal atoms. Giant metal-ligand coupling was found for binuclear radical anions that show high-spin system behavior even at 300 K. Depending on the M-M coupling assemblies can show parallel or antiparallel alignment of spins and transition between these states is also possible. Magnetic assemblies with photochromic spiropyran molecules were also obtained. They show transition to high-spin ($S = 5$) state in $\{Mn^{II}(hfac)_2 \cdot (\mu_2-TMI-NPS)\}_2$ or single ion magnet behavior for $\{Co^{II}(hfac)_2 \cdot MNPS\}^3$.

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The work was supported by the Russian Science Foundation (grant № 24-13-00060).

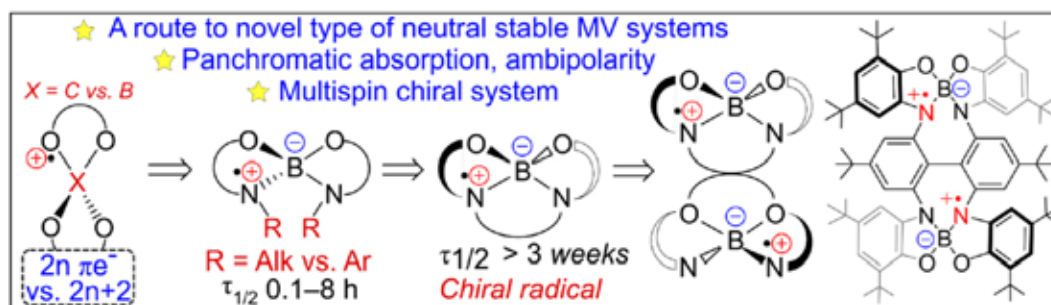
RIGID SPIROAMINYL RADICALS: A NOVEL TYPE OF STABLE MONO- AND POLYRADICAL SYSTEMS

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The most breakthrough properties needed to create a new generation of materials for optoelectronics, biomedicine, energy conversion systems, etc. are often inherent to molecules containing atoms in unusual valence states, e.g., organic compounds with an open electronic shell. In this case, stability of the targeted compound sufficient for its efficient functioning is an important precondition.

Step-by-step methodology for the fundamentally sound design and synthesis of mixed-valence aminyl radicals of novel structural type will be discussed in the presentation. The radicals contain several aminophenol fragments, spiro-conjugated via a tetrahedral boron center and additionally fastened with the biphenyl bridge. The bridge is an important stabilizing element, an independent tool for tuning of the electronic properties as well as a convenient unit opening the way to mixed-valence polyradicals. Each step of “structural evolution” yielding the targeted compounds includes synthesis, electrochemical and DFT testing of stability of the radical and its oxidized/reduced states. The nature of the heteroatoms (N, O), the type and electronic properties of the substituents at the N atoms (Alk or Ar), the number of atoms and π -electrons in the spiro-conjugated fragments are varied, to reveal the guidelines for the optimal design.



Intramolecular interaction between the N atoms in the different valence states is of special interest, as well as the interaction of two radical centers in the biradical. This largely determines the properties of novel radicals that have no analogs. This will also be discussed in the presentation.

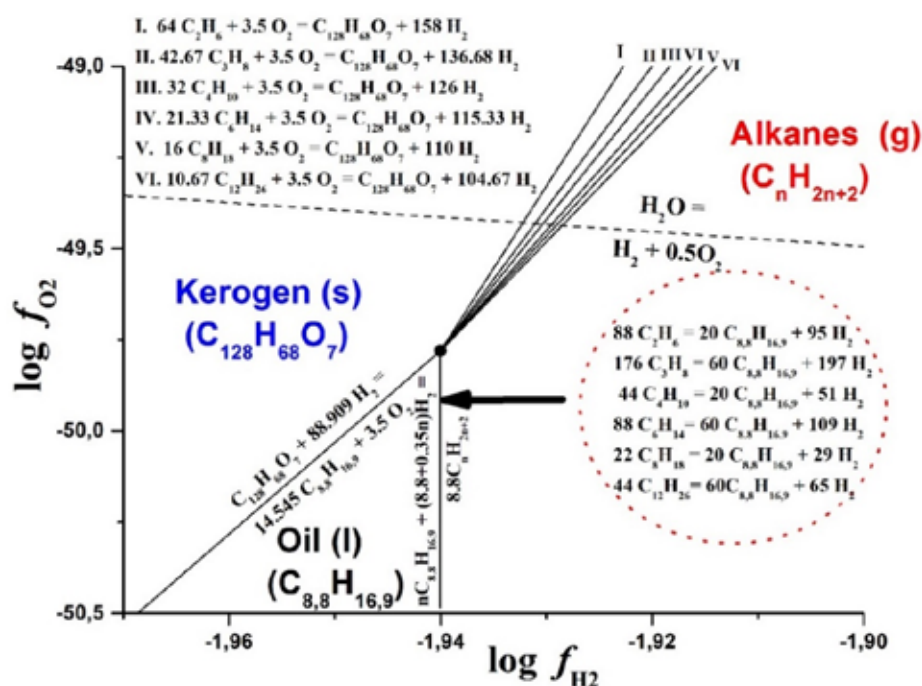
This work was supported by Russian Science Foundation (Project number 22-13-00093).

MODERN DEVELOPMENT OF D.I. MENDELEEV'S CONCEPT: ORIGIN OF DEEP HYDROCARBONS AND THEIR ACCUMULATIONS IN THE EARTH'S CRUST

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In recent decades, new convincing evidence has been obtained to confirm the truth of D.I. Mendeleev's concept of the inorganic deep origin of oil and gas deposits. These include experimental work on synthesis of hydrocarbons in different ranges of simulated depths of the Earth's crust and mantle, geological observations of oil replenishment in active and depleted wells by upward migration of deep hydrocarbon fluids and thermodynamic justifications.



The phase diagram of fugivities (f) of gaseous O_2 and H_2 presents a thermodynamic model of a typical equilibrium oil and gas deposit at a depth of ~ 4.3 km at a temperature of 150°C and pressure of 830 bar in the form of phase interrelations of deep gaseous hydrocarbons (alkanes, $\text{C}_n\text{H}_{2n+2}$), liquid oil (average composition $\text{C}_{8.8}\text{H}_{16.9}$) and solid phase of "mature" kerogen ($\text{C}_{128}\text{H}_{68}\text{O}_7$), as an illustration of the process of oil and black (oil) shales kerogen formation during upward migration of hydrocarbons and under changing redox conditions in the forming deposit.

The work was performed within the framework of the state assignment (Registration number 1022040700256-5-1.4.3 (FFSG-2024-0004))

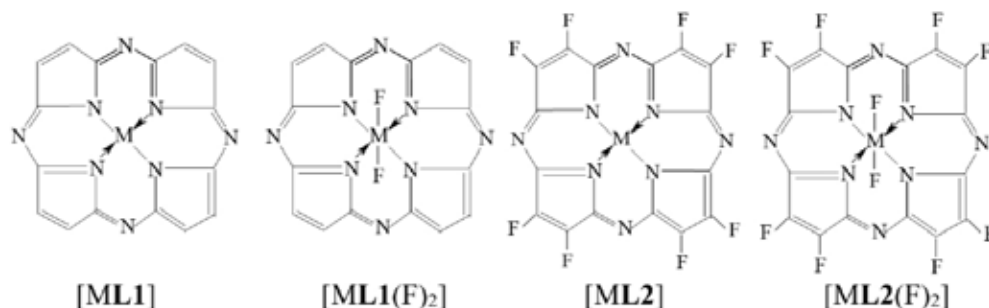
HOMO- AND HETEROLIGAND COMPLEXES OF 3d ELEMENTS WITH PORPHYRAZINE/ PERFLUOROPORPHYRAZINE AND FLUORINE LIGANDS ACCORDING TO DATA OF THE DFT METHOD: INFLUENCE OF AXIAL AND PERIPHERAL FLUORINE ATOMS

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Using the DFT method with the B3PW91, M06 and OPBE functionals and the TZVP basis set, we calculated the parameters of molecular and electronic structures, as well as the thermodynamic characteristics of four types of macrotetracyclic chelates of 3d elements – homoligand M(II) with porphyrizine [ML1] and perfluoroporphyrizine [ML2], and heteroligand M(IV) [ML1(F)₂] or [ML2(F)₂] with two axially oriented fluorine ligands (M= Ti-Cu).



Particular attention was paid to the fact that for complexes [ML1] and [ML1(F)₂] the values of ΔH^0 and ΔG^0 are positive, whereas for complexes [ML2] и [ML2(F)₂] they are negative, and in the series [ML1] – [ML1(F)₂] – [ML2] – [ML1(F)₂] there is an increase in the thermodynamic stability of the complexes, which is undoubtedly due primarily to the presence of peripheral fluorine atoms in the structure of perfluoroporphyrizine L2. Good agreement was noted between similar structural and thermodynamic parameters calculated by various DFT methods, both qualitatively and quantitatively.

MOLECULAR DESIGN AND FORMATION OF LUMINESCENT MECHANO- AND CHEMOSENSORY PROPERTIES OF BORON AND LANTHANIDE COMPLEXES

Mirochnik A.G., Kalinovskaya I.V., Fedorenko E.V., Emelina T.B., Bukvetskii B.V., Petrochenkova N.V., Lyubykh N.A., Khrebtov A.A., Zhikhareva P.A., Sedakova T.V., Shishov A.S., Tretyakova G.O.

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The report provides information on new lanthanide triboluminophores and “turn-on” luminescent chemosensors based on boron and lanthanide compounds, the luminescence of which is “turned on” by mechanical action (triboluminophores, mechanofluorochromes), or substrate binding (analyte) due to intra- and intermolecular energy transfer processes (optical chemosensors). Data on the relationship between the geometric and electronic structure of boron and lanthanide complexes and their chemosensory, triboluminescent and mechanofluorochromic properties are presented. Boron difluoride curcuminoids have been synthesized, and a comparative study of the electronic structure, luminescent, and semiconductor properties of compounds and their potential for use in cell biovisualization has been carried out¹. The obtained molecular systems based on beta-diketonates of boron difluoride with intense exciplex luminescence are promising for the creation of OLED displays and light-transforming materials². A model and a possible mechanism for the formation of triboluminescent properties in lanthanide complexes are proposed³. The obtained optical chemosensory compositions based on europium and boron complexes are promising for environmental monitoring and medicine. The prospect of searching for new functional smart materials for the needs of optical sensors, optoelectronics, ecology, and biovisualization has been determined.

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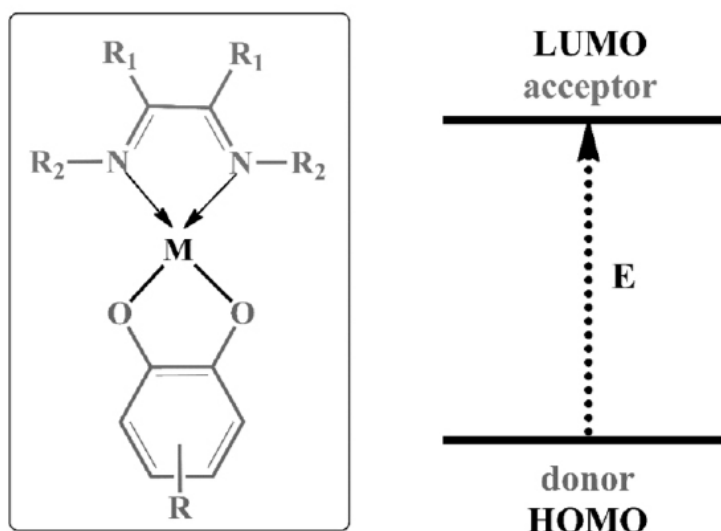
Financial support of this work by the Russian Science Foundation, project 23-23-00461.

LIGAND-TO-LIGAND' CHARGE TRANSFER IN CATECHOL-DIIMINE METAL COMPLEXES

**Piskunov A.V., Maleeva A.V., Trofimova O.Yu., Pashanova K.I.,
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In recent years, various high-tech fields of science and technology have widely used (D- π -A) type chromophores based on organic electron donors and acceptors covalently linked by π bridges. They have been applied to the fabrication of light-emitting diodes, nonlinear optical materials, organic photovoltaic cells, and so on. An alternative to these dyes can be coordination compounds in which the donor and acceptor organic fragments interact through the cation of the complexing agent (D-M-A).



The report deals with the aspects of molecular design of coordination compounds containing catecholate ligands as donors and diimine ligands as acceptors. This allows to obtain chromophoric compounds with ligand-ligand' charge transfer. It discusses issues of charge transfer energy tunability by forming specific coordination polyhedra, variation of electronic properties of organic ligands, and nature of complexing agents using examples of some transition and non-transition metals.

The work has been financially supported by the Russian Science Foundation under the grant number 22-13-00351.

SENSOR PROPERTIES OF LUMINESCENT COORDINATION POLYMERS WITH LIGANDS – DERIVATIVES OF 2,1,3 BENZOCHALCOGENADIAZOLES

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Luminescent metal-organic frameworks (MOFs) are interesting for their sensor properties, i.e., the response of photophysical characteristics to the presence of certain analytes. This report discusses the synthesis, structure, luminescent and sensor properties of MOFs based on ligands with fluoro-phore fragments of 2,1,3-benzochalcogenadiazoles (Figure 1). The possibility of determination of amines and ammonia in water with limits of detection (LOD) 2-18 ppb¹, the phytotoxicant gossypol in cottonseed oil with LOD 0.65 μM², as well as aluminum³ and gallium⁴ ions in water with LOD 0.12 μM and 1.1 μM, respectively, has been demonstrated.

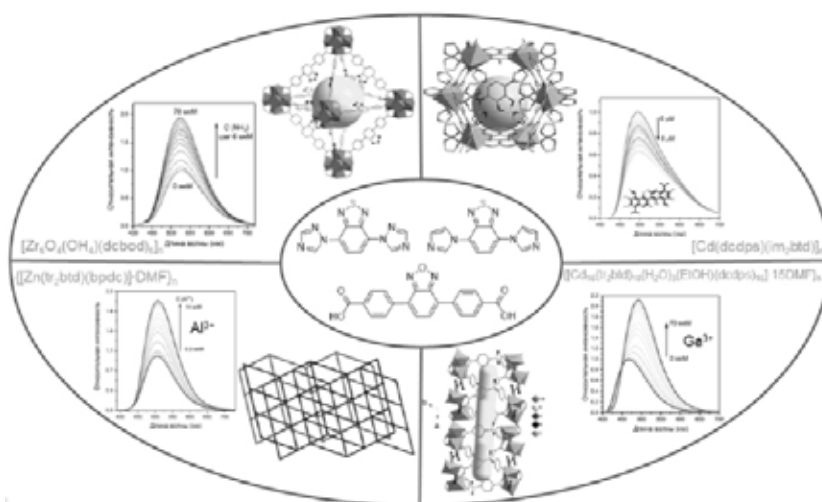


Figure 1. Sensor properties of MOFs with 2,1,3-benzochalcogenadiazole fragments

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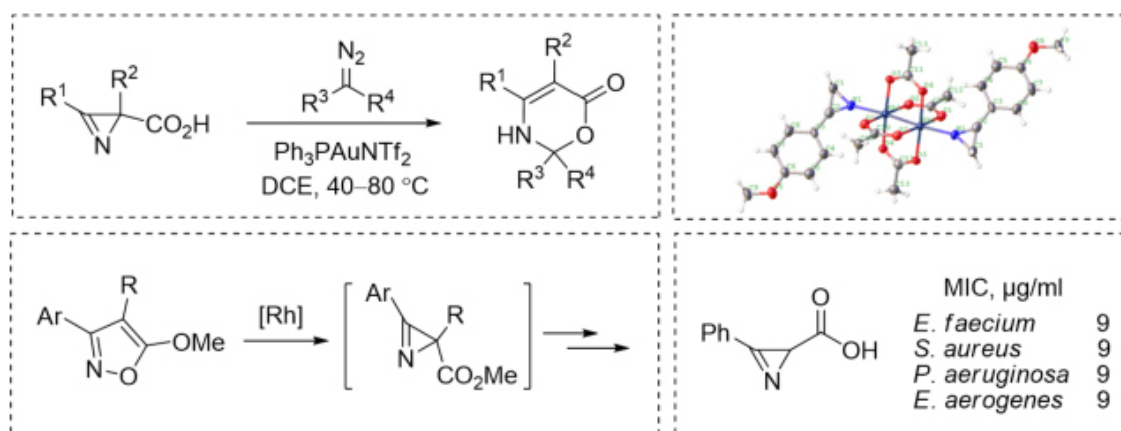
The work was supported by RSF, project № 23-43-00017.

2H-AZIRINES: SYNTHETIC BLOCKS, LIGANDS, INTERMEDIATES AND BIOACTIVE SUBSTANCES

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2H-Azirines are three-membered heterocycles containing a carbon-nitrogen double bond^{1,2}. Despite the high ring strain, many such compounds can be synthesized and are quite stable compounds. The report will present some results achieved in the chemistry of azirines in our laboratory in recent years. In particular, azirines were used as synthetic blocks³ and ligands⁴, were intermediates in the reactions of isoxazoles⁵ and showed promising antibacterial activity.⁶



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ASSEMBLY OF NANO AND MICROSTRUCTURES IN CASE OF COLLAPSE OF SYNTACTIC FOAM MICROSPHERES UNDER EXTREME CONDITIONS

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The unique properties of nanofibers make them in demand for using in computer facilities, photonics, power delivery and the energy conversion and storage devices, and biomedical technologies. Therefore, it is of interest to search for the new ways to synthesize them ¹⁻³. This work presents the studies of changes in chemical and phase composition, formation of micro- and nanostructured objects in syntactic foam consisting of tungsten-modified glass spheres and polymer binder based on phenylsilsesquioxane and dimethylsiloxane block copolymer caused by the action of a single relativistic electron beam with average energy of 180–260 keV and peak current power of 4.5–6.8 GW, which were investigated using scanning electron microscopy, energy dispersive and X-ray phase analysis. It was demonstrated that under extreme conditions (temperature above 1600 K, pressures in the range of 3–8 GPa and electric field strength over 108 V/m) near the surface of the microspheres tungsten and tungstic acid hydrate react with products of polysiloxane decomposition and conditions for the nanofibers formation (including a diameter of up to 38 nm) are created. It is shown that the appearance of micro and nanostructures in extreme conditions of collapsing microsphere is the result of non-stationary multi-parameter process, which differs from classical methods for producing nanofibers implemented under conditions of vapor deposition.

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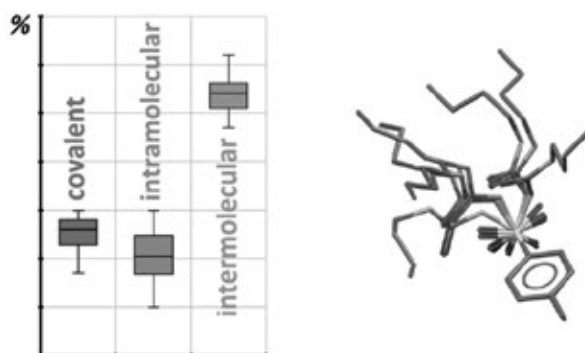
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QUANTITATIVE DESCRIPTION OF ATOMIC INTERACTIONS IN CRYSTAL STRUCTURES ON THE EXAMPLE OF BENZENESULFONAMIDE DERIVATIVES

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For a complete and comprehensive description of chemical compounds and processes occurring with their participation, it is necessary, among other things, to be able to describe all atomic interactions in their crystal structures, including chemical bonds and noncovalent interactions. One of the most capable methods for strict quantitative description of atomic interactions is the method of molecular Voronoi–Dirichlet polyhedra (MVDP).^{1,2} On the basis of unambiguous multi-dimensional geometric parameters this method allows for an accurate quantitative analysis of all types of interactions in any crystal structures.



Here we have demonstrated the abilities of the MVDP method on the example of a series of six highly polymorphic compounds, all of which exhibit pronounced biological activity: sulfapyridine, sulfamerazine, sulfamethoxazole, sulfathiazole, chlorpropamide and tolbutamide. Outcomes of such an analysis of full landscapes of atomic interactions in crystal structures including correlations with available experimental data are discussed.

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RARE-EARTH HALIDE COMPLEXES OF ACETYLUREA: UNUSUAL VARIETY OF STRUCTURES

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Regularities in compositions, structures and properties of rare-earth compounds attract attention since they should allow understanding roles of various factors on some parameters in a row of relative elements.

Rare-earth elements often form isostructural compounds for the whole row or two series of isostructural compounds for light and heavy lanthanides.

Complexes of rare-earth earth chlorides of acetylurea (AcUr) show two series, $[\text{Ln}(\text{AcUr})_2(\text{H}_2\text{O})_5]\text{Cl}_3$ (Ln = Pr, Nd, Sm) and $[\text{Ln}(\text{AcUr})_2(\text{H}_2\text{O})_4]\text{Cl}_3 \cdot \text{H}_2\text{O}$ (Ln = Ho, Er, Lu, Y) [1, 2]. We have found that praseodymium and samarium compounds change structures on cooling; although they are isostructural at room temperature, their low-temperature structures differ.

Acetylurea complexes with rare-earth bromides show surprising structural variability. We have isolated and structurally characterized complexes $[\text{Y}(\text{AcUr})_2(\text{H}_2\text{O})_{4.61}][\text{Y}(\text{AcUr})_2(\text{H}_2\text{O})_4]\text{Br}_6 \cdot 2\text{H}_2\text{O}$, $[\text{Ln}(\text{AcUr})_2(\text{H}_2\text{O})_5]\text{Br}_3$ (Ln = La, Ce, Pr, Nd, Sm), $[\text{Ln}(\text{AcUr})_2(\text{H}_2\text{O})_5]\text{Br}_3 \cdot \text{H}_2\text{O}$ (Ln = Eu, Gd, Tb), $[\text{Ln}(\text{AcUr})_2(\text{H}_2\text{O})_{4.5}][\text{Ln}(\text{AcUr})_2(\text{H}_2\text{O})_4]\text{Br}_{6.2} \cdot \text{H}_2\text{O}$ (Ln = Dy, Ho), $[\text{Er}(\text{AcUr})_2(\text{H}_2\text{O})_4]\text{Br}_3$, $[\text{Ln}(\text{AcUr})_2(\text{H}_2\text{O})_4]\text{Br}_3 \cdot \text{H}_2\text{O}$ (Ln = Tm, Yb), and $[\text{Lu}(\text{AcUr})(\text{H}_2\text{O})_6]\text{Br}_3$. Complexes $[\text{Ln}(\text{AcUr})_2(\text{H}_2\text{O})_5]\text{Br}_3$ (Ln = La–Sm) are isostructural at room temperature, but at 100 K they form three types of different structures.

Slight decrease of the Ln atomic radius when going from Ln to Lu results in the smooth reduction of their coordination number from 9 to 8. Dysprosium and holmium compounds contain two types of complex cations $[\text{Ln}(\text{AcUr})_2(\text{H}_2\text{O})_4]^{3+}$ (coordination number 8) and $[\text{Ln}(\text{AcUr})_2(\text{H}_2\text{O})_5]^{3+}$ (coordination number 9) in the 3 : 1 ratio; the Y complex has the similar structure. In some cases, decrease of the size of the complex cation is compensated by additional outer-sphere water molecule. As a results, six different types of complexes form in the lanthanide row.

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NANOHETEROGENEOUS STRUCTURE OF LIQUIDS AND METHODS OF ITS CHARACTERIZATION

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Many ionic liquids, as well as solvent mixtures, have a special kind of mesoscale self-organization, called nanoheterogeneity. In nanoheterogeneous systems, segregation of two domains occurs, consisting respectively of polar and nonpolar fragments of molecules or ions¹. These domains individually have a sponge-like structure and together form an interpenetrating bicontinuous network. The information about the liquid structure obtained using experimental methods can be effectively supplemented and interpreted based on atomistic simulation data using molecular dynamics methods. However, visual analysis of trajectories usually does not allow identifying the presence of a nanoheterogeneous structure even at a qualitative level.

We compared existing and proposed novel computational approaches to identify domains and characterize domain sizes. Protic ionic liquids are convenient objects for studying nanoheterogeneity, since their polar domains are additionally stabilized by hydrogen bonds between cations and anions. We examined several alkylammonium salts with different propensities for domain segregation.

The results show that, in addition to the well-known behavior of the structure factor and the radial distribution function, it is possible to recognize and characterize the size of domains from the peaks of the Ripley functions, peaks and large-period oscillations of finite-volume radial distribution function, as well as peaks of the local atom density variance. These peaks disappear with increasing temperature due to the domain disruption. In addition, the probability of formation of molecular-sized cavities is much higher in nonpolar domains, which causes better solubility of apolar solutes in domain-forming ILs. It is shown that in all cases the domains form continuous percolation clusters. The proposed approaches can be applied to various self-organized fluid systems.

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COBALT(II) COORDINATION COMPOUNDS WITH FIELD INDUCED SLOW RELAXATION OF MAGNETIZATION

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High spin Co(II) mononuclear coordination compounds with polydentate organic ligands are attracting special interest of the coordination chemistry community among 3d-metal complexes for design of the single ion magnets (SIM) - the subclass of the single molecule magnets family (SMMs) - in which storage of the magnetization is restricted to single paramagnetic metal center. Rich Co(II) coordination chemistry provide the flexibility to influence on the local electronic spin-states and magnetic anisotropy of metal ion by proper molecular design of the ligand surroundings determining the desired ligand field strength and symmetry. For rationalizing of the experimental magnetic properties and formulation of magnetostructural correlations of great importance is availability of precise high-level quantum chemical approaches (CASSCF+NEVPT2/def2-TZVP) to modelling of the spin-orbit coupling and magnetic anisotropy parameters (quasi-degenerate perturbation theory - QDPT).

In the report magnetostructural correlations of magnetic anisotropy for hexa-¹ and heptacoordinated² Co(II) mononuclear compounds will be discussed. Based on the established correlations several families of SIMs based on flexible platforms, allowing fine-tuning of the magnetic anisotropy and SIM properties, will be discussed³⁻⁶.

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THE STRUCTURE OF MOLECULES OF LANTHANIDES CARBOXYLATE COMPLEXES IN SOLID SOLUTIONS AND CO-CRYSTALS

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The synthesis of the heteroanionic benzoate(bnz)-pentafluorobenzoate(pfb) complex with 1,10-phenanthroline (phen) $[\text{Eu}_2(\text{phen})_2(\text{pfb})_4(\text{bnz})_2]$ was carried out in MeCN. According to X-ray diffraction data, the synthesis with different initial ratios of reagents resulted in obtaining a series of compounds with non-integer occupancy of four out of six positions of carboxylate anions, thus creating solid solutions of $[\text{Eu}_2(\text{phen})_2(\text{pfb})_{4-x}(\text{bnz})_{2+x}]$.

Stacking interactions between phen and the C_6F_5 fragment occur in the equatorial position of the molecules. The formation of such compositions allows to combine in a crystal the molecules $[\text{Eu}_2(\text{phen})_2(\text{pfb})_4(\text{bnz})_2]$ and $[\text{Eu}_2(\text{phen})_2(\text{pfb})_2(\text{bnz})_4]$, which do not crystallize as individual compounds in MeCN. Recrystallization of solid solutions in chloroform or aromatic hydrocarbons leads to the formation of another isomer of the complex $[\text{Eu}_2(\text{phen})_2(\text{pfb})_4(\text{bnz})_2]$. Solv. In this isomer, phen is the axial ligand, and the stacking interactions between phenyl and pentafluorophenyl substituents of the carboxylate anions are observed in the equatorial position. Recrystallization of stoichiometric products in MeCN revealed the reversibility of the isomerization reaction.

Using bathophenanthroline (bphen) instead of 1,10-phenanthroline resulted in a co-crystal, in which molecules $[\text{Eu}_2(\text{bphen})_2(\text{pfb})_4(\text{bnz})_2]$ and $[\text{Eu}_2(\text{bphen})_2(\text{pfb})_2(\text{bnz})_4]$ combined in ratio 1:1. The composition is similar to the molecules forming the solid solution, but is in the form of isomers with axial N-donor ligands. The compounds $[\text{Eu}_2(\text{phen})_2(\text{pfb})_4(1\text{-naph})_2]$ and $[\text{Eu}_2(\text{phen})_2(\text{pfb})_2(1\text{-naph})_4]$ were obtained in the 1-naphthoate(1-naph)-pentafluorobenzoate system. This compounds are structural analogues of molecules with bphen, as well as $[\text{Eu}_4(\text{phen})_4(\text{pfb})_{11}(1\text{-naph})]_n \cdot n[\text{Eu}_2(\text{phen})_2(\text{pfb})_4(1\text{-naph})_2]$ is a co-crystal of a heteroanionic coordination polymer and a heteroanionic bimetallic complex.

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SYNTHESIS OF ARTIFICIAL AuSb_2 AUROSTIBIT AND ITS PHYSICO-CHEMICAL STUDY

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AuS_2 predominates in antimony ores, which seriously complicates the process of gold extraction, since Au and Sb are genetically related. The minerals of gold alloys with Sb- AuSb_2 , the technological properties of which have not been practically studied, are of great importance for the Olympiadinsky deposit. The further development and study of flotation reagents for the flotation of precious metals and minerals is demonstrated. A forecast of collector activity (POAS) has been developed based on the expression:

$E_v = E$ of the complex- (E of the cluster + E of the collector), E_v (POAS). The smaller the value of the POAC, the more preferable the interaction of the created flotation collector with the mineral cluster.

The synthesis of artificial aurostibit was performed by sintering. The resulting alloy corresponds to AuSb_2 . The ratio was chosen based on the calculation to obtain stoichiometry.

Modern physico-chemical methods were used for the study. We have received original information. The electrokinetic potential of the alloy from pH and flotation reagents was measured using a Zeta-Check device. The pH zeta potential shifts to the negative side and the dependence is represented by a straight line.

Measurement of the time of adhesion of an air bubble to the surface of an unpolished strip. At a concentration of butyl xanthogenate from 15 mg/dm³ to 60 mg/m³, the adhesion time to the alloy corresponded to 500/50 ms.

The adhesion time of the bubble to synthetic aurostibnite pretreated with $\text{Pb}(\text{NO}_3)_2$ was 50 ms. The measurement of the wetting edge angle showed a wetting edge angle of 86.88 degrees.

Flotation experiments were conducted in a Hollimond tube. It has been found that diethyldithiocarbamates are more effective than butyl xanthogenate.

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ORGANIC SPIN SWITCHES: COMPUTATIONAL MODELING

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An active study of the compounds with externally controlled magnetic properties is conditioned by the possibility of their using for the development of the elemental base of the next generations of electronic devices. Traditionally, metal complexes containing paramagnetic ions of d- or f-elements are considered in this capacity. Despite a number of advantages of organic magnets, which include low density, plasticity and rich modification possibilities, examples of successful control of spin states of such compounds are rare.¹

In this study, by means of systematic quantum chemical calculations of organic bi- and polyradical compounds, approaches to the design of organic spin switches are proposed. Modeling of the isomerization processes of organic molecules with two polycyclic radical groups made it possible to identify the compounds demonstrating transition from a triplet state to a singlet state due to two-electron multicenter interactions.² By varying the type and position of radical groups in photoactive organic molecules, systems have been revealed whose isomerization is accompanied by transitions between benzoid and quinoid forms and also spin-state-switching.³ The predicted sharp changes in magnetic properties of the studied organic molecules as a result of temperature variation or light irradiation make them a potential basis for logical switches and memory components of computing systems.

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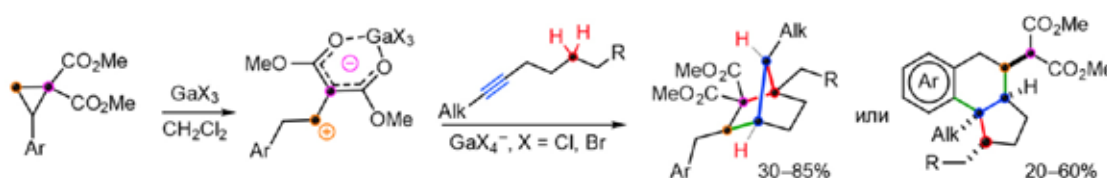
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NEW CARBOCATION CYCLIZATION REACTIONS BASED ON THE FUNCTIONALIZATION OF ALIPHATIC CH_2 GROUPS

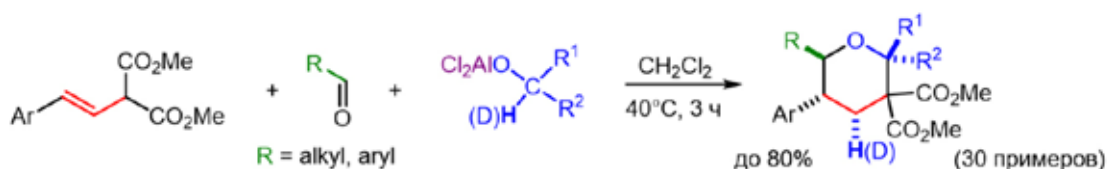
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Direct C–H activation (functionalization) of inert $\text{C}(\text{sp}^3)\text{--H}$ bonds in the hydrocarbon chain is an attractive goal. In this study, we developed an unprecedented mono- and dual-functionalization of non-activated CH_2 groups in the hydrocarbon chain. One of these processes is a complex cascade of reactions of alkyl acetylenes with activated cyclopropanes or alkenes, controlled by the combined action of $\text{Ga}(\text{III})$ salts and GaHal_4^- anions and leading to the formation of a polysubstituted norbornane framework or cyclopenta[a]tetraline derivatives. The peculiarity of the developed processes is the high resulting molecular complexity, which combines the simultaneous polyfunctionalization of simple C–H substrates in one step with the formation of several new rings and stereocenters¹.



Another process related to the C–H activation of the alkyl fragment is the new reaction of β -styrylmalonates with aldehydes in the presence of alkoxyaluminum dichloride, $\text{RCH}_2\text{OAlCl}_2$, prepared by the oxidation of EtAlCl_2 in the presence of air or by mixing equimolar amounts of AlCl_3 with a primary or secondary alcohol. As a result, a three-component synthesis of substituted dimethyldihydro-2H-pyran-3,3(4H)-dicarboxylates with yields of up to 80% was developed and the use of the $\text{CH--O}\cdots\text{Al}$ fragment in cycloaddition reactions was demonstrated for the first time².



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EXPERIMENTAL THERMOCHEMICAL STUDY OF PEROVSKITE-TYPE CsPbX_3 (X – Cl, Br, I) HALIDES AND THERMODYNAMIC MODELLING OF BINARY PHASE DIAGRAMS INVOLVING THESE COMPOUNDS

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Perovskite-type halides have received great attention in recent years due to high conversion efficiency obtained in solar cells based on such materials. However, despite very promising achievements their fundamental chemistry and physics is far from being completely understood. This is particularly true for thermodynamic properties of perovskite-type ABX_3 halides (A = CH_3NH_3 , formamidinium, Cs, Rb, etc; B = Sn, Pb; X = Cl, Br, I). Therefore, experimental study of the formation thermodynamics of the ABX_3 halides is strongly required. Therefore, the main aim of this work was to study the thermodynamics of formation of perovskite-type halides CsPbX_3 (X – Cl, Br, I) and their solid solutions and thermodynamic modelling of binary phase diagrams: CsX-PbX_2 and $\text{CsPbX}_3\text{-CsPbX}'_3$ (X, X' – Cl, Br, I).

The standard formation enthalpies of CsPbX_3 (X – Cl, Br, I) halides and solid solutions at 298,15 K were measured by solution calorimetry. Enthalpy increments and constant pressure heat capacity were measured in the temperature range 298-800 K using drop-calorimetry. Standard entropies at 298.15 K were either calculated from the results of the EMF-measurements or estimated from the S°_i vs. $\log(M_i)$ linear dependencies, where M_i is a molar mass of a perovskite halide. Standard Gibbs free energies of CsPbX_3 (X – Cl, Br, I) halides were evaluated using the as-determined formation enthalpies and entropies. Mixing enthalpies, entropies and Gibbs free energies of $\text{CsPbX}_3\text{-CsPbX}'_3$ (X, X' – Cl, Br, I) solid solutions were calculated as well. The trends in the variation of the thermodynamic functions with chemical composition and crystal structure of perovskite-type halides were analyzed and compared with available results of DFT calculations.

Also, binary phase diagrams CsX-PbX_2 and $\text{CsPbX}_3\text{-CsPbX}'_3$ (X, X' – Cl, Br, I) were built using differential scanning calorimetry measurements. The resulting diagrams were compared with those available in literature. Their thermodynamic assessment was successfully carried out.

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WATER AND CATION MOBILITY IN SULFONIC CATION EXCHANGERS STUDIED BY NMR

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In order to understand the mechanism of ionic transport in ion exchange systems the interconnection of ionogenic channels structure, ionic hydration and water molecules and cation mobilities in spatial scales from tenth nanometer to micron should be investigated. NMR is giving this possibility. The comparison of local ionic mobility with macroscopic self-diffusion let us to construct the morphology of transport channels. Cation hydration numbers are calculated from ^1H water hydrogen atoms chemical shift temperature dependences. The number of contact (or separated) ionic pairs of sulfonate group-cation can be measured from ^7Li , ^{23}Na and ^{133}Cs NMR spectra analysis. Local mobility of water molecules and lithium, sodium and cesium cations as well as its self-diffusion coefficients may be estimated from ^1H , ^7Li , ^{23}Na and ^{133}Cs spin relaxation and pulsed field NMR data. These set of measurements were carried out for Nafion membranes and membranes MSC based on polyethylene and grafted sulfonated polystyrene. It was concluded that macroscopic transfer is controlled by ion motion near sulfonate groups. Lithium cation translation displacement is taken place by a rearrangement of hydrated water molecules hydrogen bond that explains a symbiosis of water and lithium cation self-diffusion behavior. It may be assumed that in opposite to Li^+ and Na^+ cesium cation jumping between SO_3^- groups, directly. The main results are published in our recent papers¹⁻⁴.

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UNUSUAL TRIFLIC ACID-PROMOTED OLIGOMERIZATION OF ARABINOFURANOSIDES DURING GLYCOSYLATION

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We discovered an unusual triflic acid-promoted oligomerization of arabinofuranosides during glycosylation of the primary hydroxy group of α -(1 \rightarrow 5)-linked tetraarabinofuranoside bearing 4-(2-chloroethoxy)phenyl aglycone with α -(1 \rightarrow 5), β -(1 \rightarrow 2)-linked tetraarabinofuranoside containing N-phenyltrifluoroacetimidoyl leaving group, which led to octa-, dodeca- and hexadecaarabinofuranosides 1.

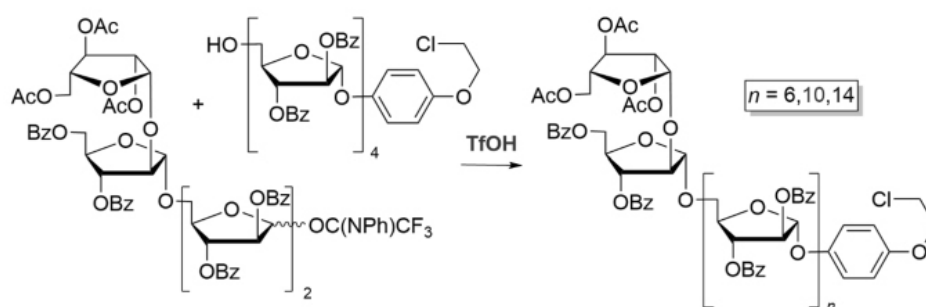


Figure 1. The formation of octa-, dodeca- and hexadecaarabinofuranosides with 4-(2-chloroethoxy)phenyl aglycone during triflic acid-promoted glycosylation.

The choice of promoter was found to be a critical factor for the discovered oligomerization of arabinofuranosides. The obtained octa-, dodeca- and hexadecaarabinofuranosides serve as useful blocks in the synthesis of oligosaccharide fragments of polysaccharides of *Mycobacterium tuberculosis*.

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This work was financially supported by the RSF, Project No. 21-73-20164.

SYNTHESIS OF OLIGOARABINOFURANOSIDES OF MYCOBACTERIUM TUBERCULOSIS USING GLYCOSYL DONORS CONTAINING BULKY SILYL GROUPS

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The synthesis of oligoarabinofuranosides related to the fragments of the mycobacterium cell wall is an important task due to the necessity of the creation of new tuberculosis diagnostics and study the pathways of biosynthesis of glycans from *M. tuberculosis*¹.

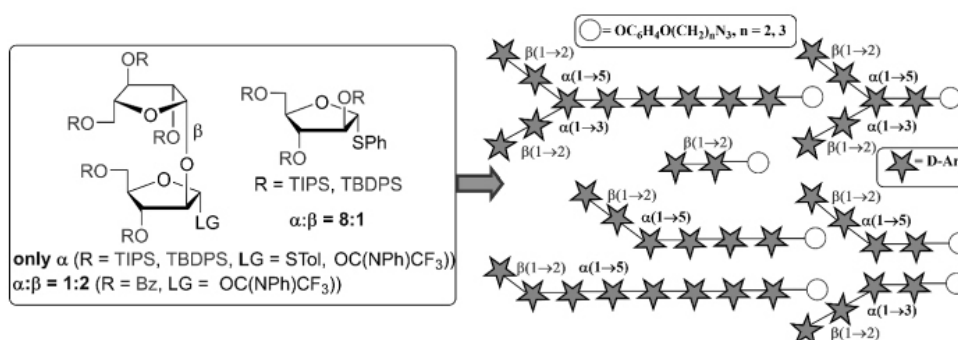


Figure 1. The use of glycosyl donors containing bulky silyl groups in the synthesis of oligoarabinofuranosides of mycobacteria with 4-(ω -azidoalkoxy)phenyl aglycone.

We found that complete stereoselectivity of 1,2-*trans*-glycosylation was achieved for diarabinofuranosides Ara- β -(1 \rightarrow 2)-Ara containing TIPS² or TBDPS groups with formation only α -isomers. In contrast, in the case of the use of benzoyl protected Ara- β -(1 \rightarrow 2)-Ara² or polysilylated *monoarabinofuranosides*, the loss of stereocontrol was observed.

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This work was financially supported by the RSF, Project No. 21-73-20164.

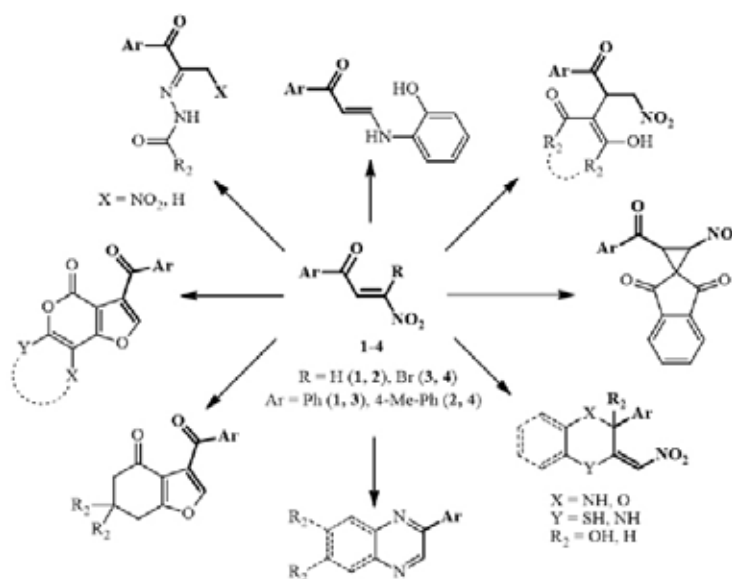
B-AROYL-CONTAINING NITRO- AND *GEM*-BROMONITROETHENES IN THE SYNTHESIS OF OPEN-CHAIN, CARBO- AND HETEROCYCLIC COMPOUNDS

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The heightened reactivity of nitro- and *gem*-bromonitropropenones in reactions with nucleophilic reagents is attributed to the presence of conjugated double C=C bonds within their molecular framework [1, 2]. Additionally, the incorporation of aryl groups and halogen atoms within their molecular structures presents avenues for further transformations, facilitating formation of diverse carbocyclic and heterocyclic compounds.

We have demonstrated that the interaction of aryl-3-nitro- and 3-bromo-3-nitroprop-2-en-1-ones **1-4** with representatives of cyclic CH-acids, aromatic, and aliphatic binucleophilic reagents proceeds to form Michael adducts, which are capable of further transformation, resulting in carbocyclic and heterocyclic structures



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PREDICTION SUITABLE CONDITIONS BY CONDITIONAL VARIATIONAL AUTOENCODER

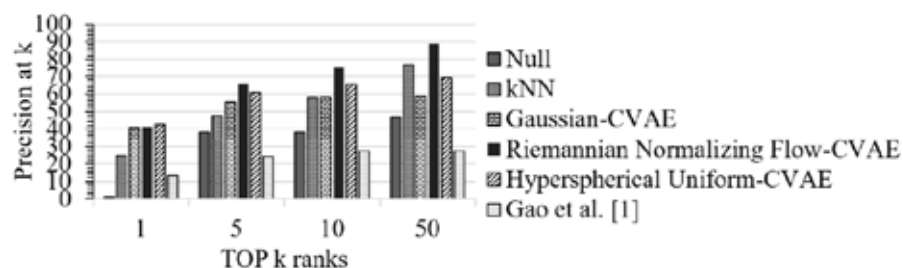
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The main trend of our time is digitalization, penetrating into all areas of our lives, including chemistry. Currently, a large number of automated instruments are available that can perform individual steps of chemical synthesis and are controlled by a computer. The combination of automation and artificial intelligence leads to the possibility of developing a robot chemist capable of synthesizing the required compounds, optimizing reactions and searching for molecules with the desired properties. All of the above tasks require planning a synthesis path. However, choosing the optimal conditions for each of its reactions is almost as complex and important as predicting the path itself. One possible option is to use an artificial neural network with a conditional variational autoencoder architecture. The performance of the approach, which predicts the combination of catalyst, reagent, temperature and pressure most suitable for a particular reaction, was demonstrated using more than 157,000 and 39,000 hydrogenation reactions (training and validation sets) from the Reaxys chemical database.



It significantly outperformed other models used for comparison, including the approach of Gao et al¹.

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GERMYLENES BASED ON DIETHYLENETRIAMINES: SYNTHESIS, STRUCTURE, REACTIVITY

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In recent years, interest in the study of “heavy carbenes” is due not only to the importance of such compounds in fundamental chemical research, but also to the fact that they are the starting point for the synthesis of various organometallic compounds and intermediates¹⁻². These derivatives can be versatile reagents in a number of important reactions of organic substrates, such as oxidation, addition, and intercalation.

Diethylenetriamines are promising ligands for stabilizing the low-valent state of germanium and tin atoms. Previously, germylenes based on diethylenetriamines with pentafluorophenyl substituents on the terminal nitrogen atoms were synthesized and oxidative addition reactions were studied³. The reactivity of these derivatives is determined by the difference in energy between the boundary orbitals. The purpose of this work is the synthesis of germylenes based on diethylenetriamines with substituents of different nature on the terminal nitrogen atoms, determination of the structure using various physicochemical methods, including electrochemical methods and UV spectroscopy, systematic study of their reactivity, allowing us to determine the influence of structural factors on the reaction pathways “heavy carbenes”.

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This work was supported by the Russian Science Foundation № 24-13-00202.

RADICAL C–H FUNCTIONALIZATION OF CYCLIC NITRONES AS A DIVERGENT APPROACH TO THE SYNTHESIS OF PERSPECTIVE AZAHETEROCYCLIC DERIVATIVES

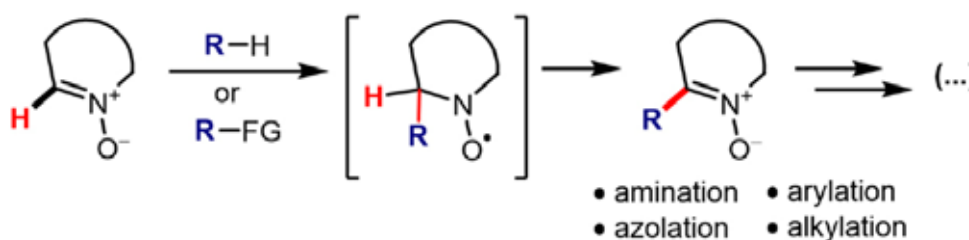
Akulov A.A.,^a Nelyubina A.A.,^a Pershin A.A.,^a Deleva A.A.,^a Chugaev M.V.,^a Varaksin M.V.,^{a,b} Charushin V.N.,^{a,b} Chupakhin O.N.^{a,b}

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The search for effective ways to synthesize azaheterocyclic compounds is known to be one of the key challenges in modern organic chemistry, which is due to the critical role of nitrogen heterocycles in the development of pharmaceuticals and advanced materials. Meanwhile, direct C–H functionalization of organic compounds is considered as one of the most preferred approaches, as it complies with the basic principles of green chemistry.¹

Over the past few years, our research group has studied a number of processes based on the C(sp²)–H bond modification in the structure of cyclic aldonitrones. Among these processes, a special place is occupied by the poorly studied transformations that occur through the formation of intermediate radical adducts (nitroxides) followed by their one-electron oxidation.



To the moment, we have harnessed such transformations to obtain previously undescribed products of amination,² azolation,³ arylation, etc. At the same time, broad prospects for the approach development leave room for its further study.

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This work was financially supported by the Russian Science Foundation, project no. 23-63-10011, <https://rscf.ru/en/project/23-63-10011/>

TRANSFORMATION OF OLIGOSULFANIDES IN THE PRESENCE OF ORGANIC BASES

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Oligosulfanides are newly described ionic compounds that can be prepared by reacting dimethylphosphate-containing ionic liquids with elemental sulfur.¹⁻²

The structure of these compounds with a chain of sulfur atoms and a localized negative charge at the end of this chain explains their promise in the processes of producing organosulfur compounds, including thionation reactions.

This work describes the process of transformation of the oligosulfonide cation using the example of 1,3-dimethylimidazolium (phosphonoxy)oligosulfanide (FOOS) in a medium with organic bases. Based on the results of determining the crystal structure of the formed substance, the formation of dimethylimidazole-2-thione was detected, which probably occurs according to the following scheme (fig. 1).

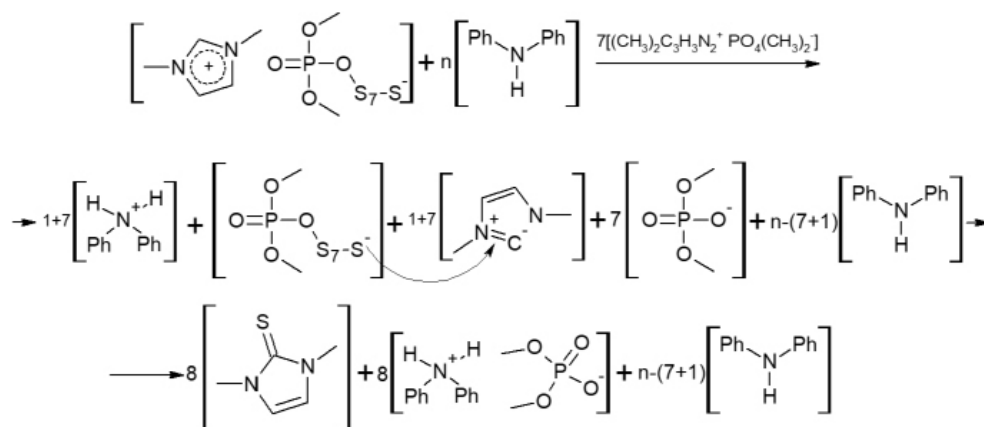


Figure 1. Interaction of FOOS with organic bases using the example of diphenylamine.

The assumption about the mechanism of interaction is consistent with the deprotonation of the imidazolium cation described in the literature during the synthesis using the Morita–Baylis–Hillman reaction³.

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STABILITY OF POLYMERIC MICELLES BASED ON HYDROPHOBIZED HYALURONIC ACID

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Conjugation of low molecular sodium hyaluronan with oleic acid (HA-C18) is known to form polymeric micellar structures in an aqueous medium which allows hydrophobic molecules to be encapsulated. Due to the fact that hyaluronan is able to specifically bind to receptors CD44 expressed by cancer cells, polymeric micelles loaded with drugs can be used as targeted delivery systems. Stability of the structures in physiological environments of the body is important for their medical application. The parameters of micellar structures of HA-C18 (unloaded and loaded with drugs (etoposide, closodecaborate complex (CDB), etc.), their stability upon dilution and over time were studied by dynamic laser light scattering, transmission electron microscopy and spectrofluorimetry. The dependence of sizes, polydispersity and ζ -surface potential on the media components and the nature of the loaded component is shown. It has been established that in distilled water unloaded micelles show a monomodal distribution by volume (379.9 ± 84.9 (100%)), whereas in a medium corresponding to physiological solution (0.9 % NaCl) a bimodal distribution (381.0 (9.5%) and 31.0 (89.8%) nm) is observed. Consequently, micelles are associated, and their association is suppressed with increasing ionic strength of the medium. It has been shown that the stability of micelles in the medium simulating blood plasma (50 mM phosphate buffer + 0.9% NaCl + 4% human serum albumin) depends on the nature of the molecule loaded into the nucleus of the micelle. Unloaded micelles in a medium simulating blood plasma destroy in contrast to the micelles simultaneously loaded with two dyes (DiI+Cy5) or CDB. Thus, the stability of HA-C18 micelles and, consequently, the possibility of their application for targeted transport of drugs depends on the nature of the molecule solubilized by the micellar medium.

The study was supported by the grant of the Russian Scientific Foundation (project No. 23-25-00194).

MIXED CATION SELENITE CHLORIDES WITH COMPOSITION $A_2B(\text{SeO}_3)_2\text{Cl}_2$ AND $A_5B(\text{SeO}_3)_4\text{Cl}_4$: SEARCH AND STUDY OF PHYSICAL PROPERTIES

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The magnetic compounds with reduced dimensionality attract attention of scientific community at recent decade [1]. Such systems are preliminary in fundamental scientific interest; however, low dimensional magnets are considered as future materials for quantum computers [2], controlled heat transfer and spintronics. There is no systematic search for such phases. The synthesis of phases with low-dimensional magnetism is one of the hot topics in modern material science. From this point of view, the family of phases $A_2B(\text{SeO}_3)_2\text{Cl}_2$ ($A = \text{Pb, Sr, Ba}$, $B = \text{d-metal}$) seems to be attractive. The presence of a selenite group in the structure, which has a stereochemically active pair of electrons, as well as halide ions, contributes to the formation of open structures that contribute to the formation of a low-dimensional magnetic subsystem. The purpose of this work is to search for and synthesize phases from this family $\text{Sr}_2\text{Mn}(\text{SeO}_3)_2\text{Cl}_2$, $\text{Ba}_2B(\text{SeO}_3)_2\text{Cl}_2$ ($B = \text{Ni, Cu}$), $\text{Pb}_2\text{Cu}(\text{SeO}_3)_2\text{Cl}_2$, $A_5B(\text{SeO}_3)_4\text{Cl}_4$ ($A = \text{Pb, Sr, Ba}$, $B = \text{Mn, Co, Ni, Cu}$), as well as the study of their physical properties.

The samples were synthesized using the method of solid-phase reactions. Alkaline earth metal selenites ASeO_3 and d-metal chlorides BCl_2 were used as starting materials. In the case of lead compounds, PbO , SeO_2 and CuCl_2 were chosen. The reaction was carried out in sealed silica tubes at different temperatures. The purity of the samples was checked by powder X-ray diffraction (XRD).

As a result of the work, optimal conditions were found for sample preparation, depending on their composition. Crystal structures of new compounds were determined by powder or single crystal XRD. It has been established that new phases crystallize in different structural types. The new structures were characterized by means of IR spectroscopy and thermal analysis. Primary measuring of magnetic properties for $\text{Sr}_2\text{Mn}(\text{SeO}_3)_2\text{Cl}_2$ confirms the presence of a low-dimensional magnetic subsystem in the structure. At a temperature of $T_N = 3.01 \text{ K}$, the substance undergoes antiferromagnetic ordering, which is also observed in the temperature dependence of heat capacity. The structural parameters of the new phases and related ones are compared in presented study.

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FULLERENE DERIVATIVES IN SOLUTIONS – STUDY BY PFG NMR

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The results of a study of association processes of fullerene derivatives in solutions by pulsed field gradient NMR using the Stokes-Einstein model are presented. Figure 1 shows the structures of the studied compounds.

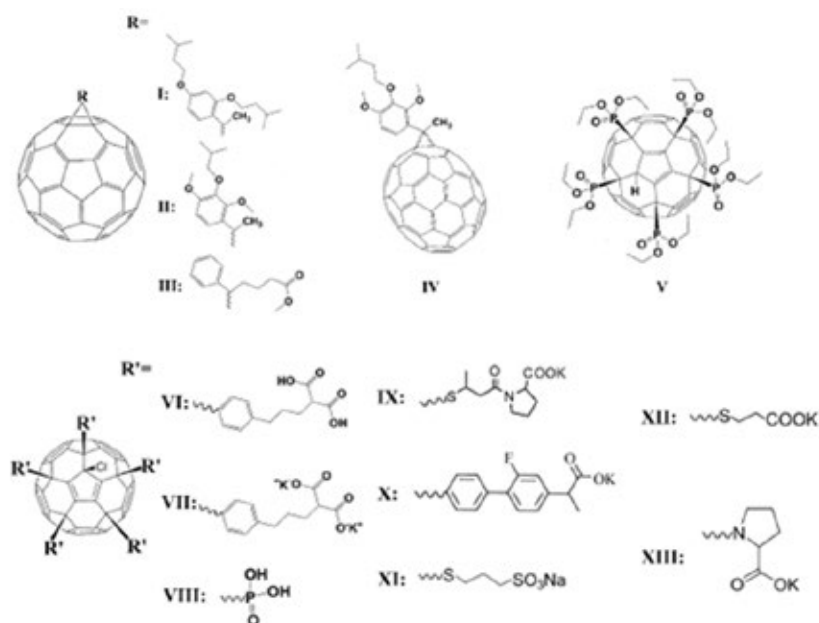


Figure 1. Structures of the studied fullerene derivatives not containing (I-V) and containing polar groups (VI-XIII).

No association is observed for derivatives I-V in CS₂, CDCl₃ and C₇D₈. The hydrodynamic diameters of the molecules are 1.2-1.4 nm. Derivatives containing polar functional groups exhibit a strong association tendency. The diameters of associates vary from 2.2 to 9.6 nm depending on the solvent and temperature. Derivatives VII-XIII in D₂O form stable associates with a diameter of about 5 nm, the number of which increases with increasing solution concentration. The lifetimes of associates were estimated.

This research was performed with the support of State Assignment of the Federal Research Center of Problem of Chemical Physics and Medicinal Chemistry RAS (state registration No 124013000743-3 (FFSG-2024-0008))

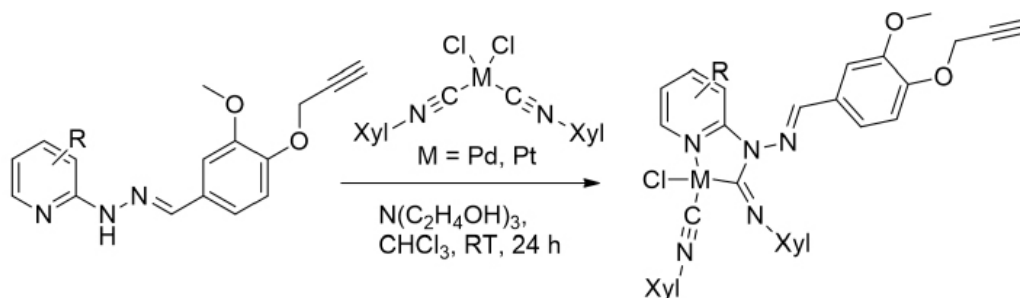
SYNTHESIS OF PLATINUM GROUP METALS COMPLEXES DECORATED WITH C≡C BONDS

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In the last two decades, the functionalization of substances through the copper-catalyzed interaction of the C≡C triple bond with the azide group has become widespread. This method is also applicable in coordination chemistry. But when preparing complexes of late transition metals containing a peripheral triple bond, difficulties arise due to the increased reactivity and coordination ability of triple bonds in the presence of such metal centers. One possible way to overcome this difficulty is to use the ability of coordinated isocyanides to react with *N,N*-polynucleophiles. We recently found that the resulting *C,N*-chelate platinum group metal complexes containing a peripheral triple bond can indeed be isolated and characterized without decomposition. For some of them, we showed that further modification by CuAAC with polysiloxanes containing an azide group can lead to the formation of a number of polymer systems that include a metal center. Moreover, the synthesized metal complexes themselves turned out to be effective catalysts for various reactions.

In this work, we have increased the scope using new organic nucleophiles and also extended our approach to palladium complexes. A series of platinum group metal coordination compounds were prepared by coupling functionalized 2-pyridine hydrazine imines with isocyanide complexes.



This work was supported by a grant from the Ministry of Science and Higher Education of the Russian Federation for large-scale research projects in high priority areas of scientific and technological development (grant number 075-15-2024-553).

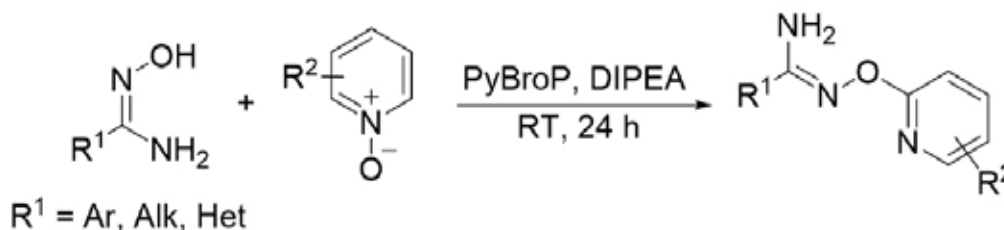
HETARYLATION OF AMIDOXIMES BY PYRIDINE-*N*-OXIDES

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Amidoximes attract the attention of researchers due to the variety of possibilities for their application. They are used for the development of drugs and prodrugs, in particular fungicidal and bactericidal ones¹. In addition, the amidoxime fragment has a special affinity for uranium, so materials based on amidoximes are currently the most promising for cleaning the environment from this heavy metal². Amidoximes also have great synthetic potential for the preparation of various heterocycles³ and complex compounds⁴.

The formation of *O*-(2-pyridyl)-substituted using oximes as nucleophiles in the presence of PyBroP was previously demonstrated⁵. In order to develop this direction, we studied the reactivity of various amidoximes bearing aromatic and aliphatic substituents in a similar reaction. It was found that pyridine *N*-oxides react with amidoximes, forming products substituted at the oxygen atom.



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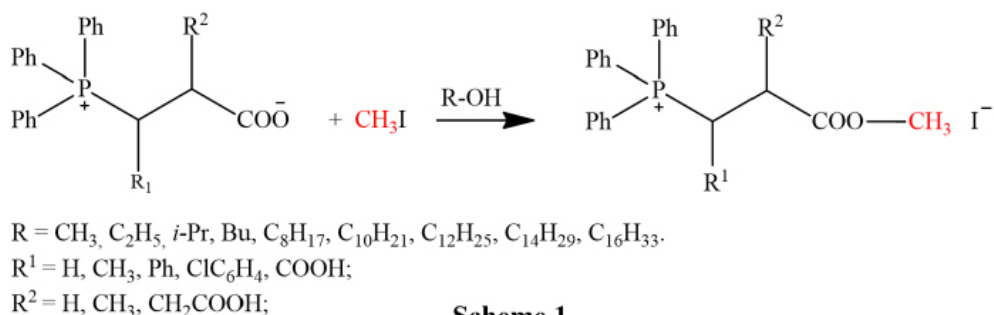
This work was supported by a grant of the Ministry of Science and Higher Education of the Russian Federation for large scientific project in priority areas of scientific and technological development (grant number 075-15-2024-553).

THE FACTORS AFFECTING UNUSUAL COURSE OF THE ALKYLATION REACTION OF CARBOXYLATE PHOSPHABETAINES

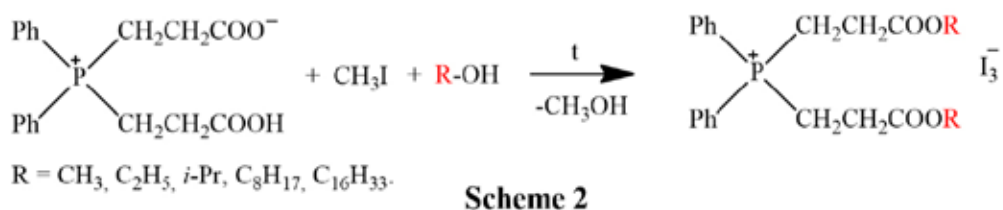
Bakhtiyarova Yu.V., Romanov S.R., Bakhtiyarov D.I., Galkina I.V.

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The alkylation reaction of monocarboxylate phosphobetaines with methyl iodide in an alcoholic medium proceeds according to the classical mechanism and leads to the formation of a phosphonium salt (scheme 1).



Dicarboxylate phosphobetaines in a similar reaction with methyl iodide in an alcoholic medium, are formed compounds in which the ester group contains a radical from an alcohol molecule, and not from a halide alkyl (scheme 2).¹



The structure and composition of all synthesized compounds have been proven by a complex of physical and physico-chemical research methods. It was concluded that the unusual course of this reaction is influenced by the presence of an acidic proton, an onium center, and an excess of both methyl iodide and alcohol is necessary.

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LUMINESCENT PROPERTIES OF NEW ZINC(II) TETRAHALIDE COMPOUNDS WITH TRIPHENYLPHOSPHONIUM CATION

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The investigation of luminescent zinc(II) compounds with phosphine-based ligands has attracted attention due to their optical properties, such as multiband luminescence of various nature, including in the ultraviolet (UV) region of the spectrum.

In this work, new compounds of zinc(II) halides with the general formula $[\text{HL}]_2[\text{ZnX}_4]$ ($\text{X} = \text{Cl}, \text{Br}$, $\text{L} =$ triphenylphosphine) were obtained, exhibiting multiband luminescence in the range from UV-B to visible region. For the $[\text{HL}]_2[\text{ZnBr}_4]$ compound, the luminescence bands can be described within the exciton-phonon model approximation. The temperature dependences of the linewidth and energy of the maximum of the UV-B band of the $[\text{HL}]_2[\text{ZnCl}_4]$ compound are non-monotonic and cannot be described to a first approximation within the aforementioned model. Moreover, up-conversion luminescence with a maximum at $\lambda = 305$ nm was detected for $[\text{HL}]_2[\text{ZnCl}_4]$ upon irradiation with a $\lambda = 405$ nm laser. The purpose of the investigation was to elucidate the main processes leading to multiband luminescence, and especially those causing up-conversion luminescence. A combination of experimental methods and quantum-chemical calculations was used to understand the complex mechanisms of light absorption, energy transfer and relaxation processes. The influence of non-covalent interactions on photoexcitation processes, in particular leading to up-conversion photoluminescence, is shown.

The unusual combination of luminescent properties of relatively inexpensive zinc(II)-based compounds with phosphonium cations makes them attractive candidates for a variety of applications, including bioimaging, biomedicine, solar energy conversion, and optoelectronics. The results of the work expand the understanding of the nature of up-conversion luminescence in zinc(II) compounds, which in the future may make it possible to optimize the characteristics of compounds for specific tasks by selecting the ligands and structural design.

This research was funded by the Russian Science Foundation for the funding project № 23-73-01102.

IMMUNOANALYSIS OF BISPHENOL A USING NON-POLAR OR-GANIC SOLVENTS

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Bisphenol A (Fig. 1A) is a low molecular weight compound that is used in the production of polymer packaging and household materials (coatings, resins, etc.) and therefore ends up in water and food. Due to its estrogen-like effects, bisphenol A is regulated and requires effective means of detection. Immunochemical methods that combine specific recognition of the analyte by antibodies with simple and productive testing are promising for these purposes.

To implement these techniques, conjugates of a bisphenol A derivative - 4,4-bis(hydroxyphenyl)valeric acid (Fig. 1B) with proteins were synthesized, animals were immunized, and specific polyclonal antibodies were obtained.

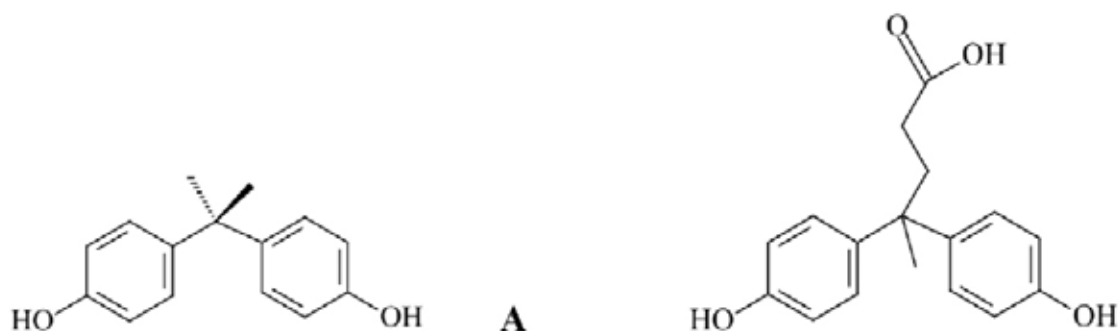


Figure 1. Structure of bisphenol A (A) and 4,4-bis(hydroxyphenyl)valeric acid (B)

The possibilities of effective immunodetection of bisphenol A in the systems of buffer solution with organic solvent have been demonstrated. Under the optimized conditions of the competitive enzyme immunoassay, the following detection limits (LOD) and working ranges (WR) were achieved:

- phosphate buffer – LOD 77 ng/ml, WR 185–3700 ng/ml;
- phosphate buffer + hexane – LOD 18.5 ng/ml, WR 545–2145 ng/ml;
- phosphate buffer + toluene – LOD 8.7 ng/ml, WR 38–5900 ng/ml.

The characteristics achieved for two-component systems make it possible to control the excess of maximum permissible levels of bisphenol A in environmental monitoring and control of consumer products.

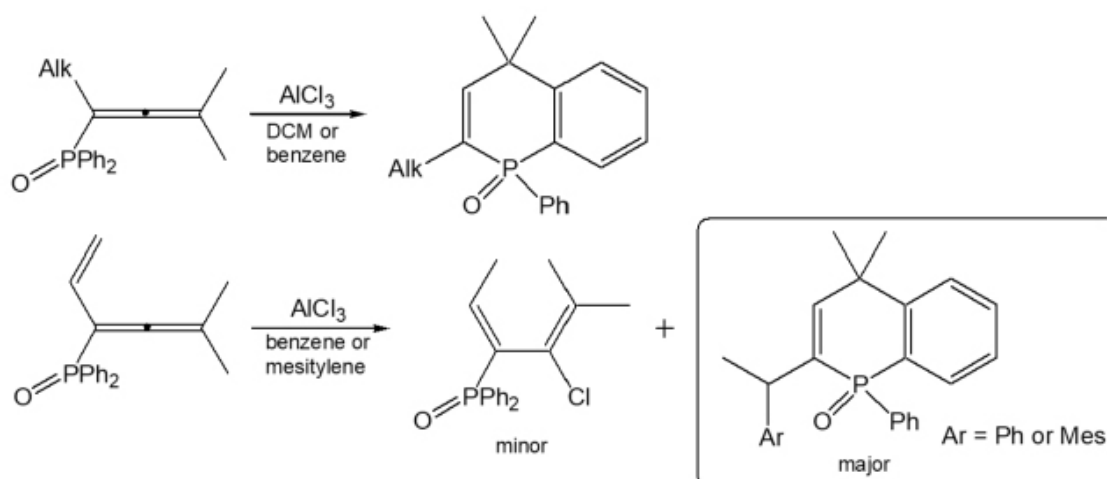
This work was financially supported by the Russian Science Foundation, project 22-13-00293 (<https://www.rscf.ru/project/22-13-00293/>).

“DOUBLE ARYLATION” IN AlCl_3 -PROMOTED TRANSFORMATION OF VINYL(DIPHENYLPHOSPHORYL) ALLENES IN BENZENE AND MESITYLENE

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It was previously reported that AlCl_3 , as a Lewis acid, can promote an intramolecular cyclization of allenyl(diphenyl) phosphine oxides into 1,4-dihydrophosphinolin-1-oxides in dichloromethane. In this work transformations of allenyl(diphenyl)phosphine oxides in the presence of AlCl_3 in benzene and mesitylene were studied. It was shown that vinylallenyl phosphine oxide transforms into a mixture of compounds and the major product forms in a result of “double arylation”, i.e., hydroarylation of vinyl C=C bond and intramolecular 6-*endo*-trig cyclization. The reaction mechanism is currently under investigation.



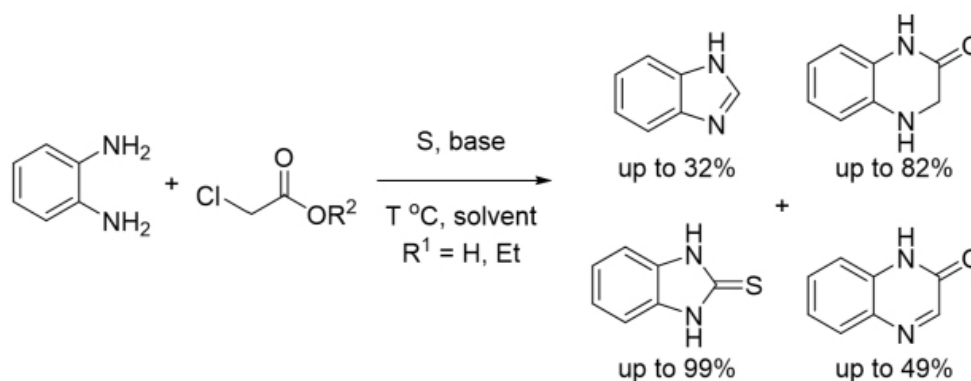
STUDY OF THE HETEROCYCLIZATION REACTION OF 1,2-PHENYLENEDIAMINE AND CHLOROACETIC ACID DERIVATIVES IN THE PRESENCE OF SULFUR

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The use of a combination of molecular sulfur and DMSO is an effective approach to promote oxidative coupling of dicarboxylic acids and amines as nucleophiles for the synthesis of aza-heterocycles¹. In the case of some substrates, for example 2-amino(thio)phenols, it is possible to use water as a more convenient reaction medium².

We noticed that a reaction between 1,2-phenylenediamine and chloroacetic acid or its ester derivatives in the presence of base and sulfur leads to the formation of various heterocyclic products depending on the solvent. A mixture of benzimidazole and 3,4-dihydro-1H-quinoxalin-2-one was forming when reagents were boiled in water and only 2-mercaptobenzimidazole was observed when the reaction was carried out in DMSO.



It was shown that the promotion of heterocyclization by sulfur is not suitable for the synthesis of 2-carboxyl-substituted benzimidazoles in the same way that it effectively allows the synthesis of various 2-phosphoryl- and 2-carbomoyl- benzannulated 1,3-azoles.

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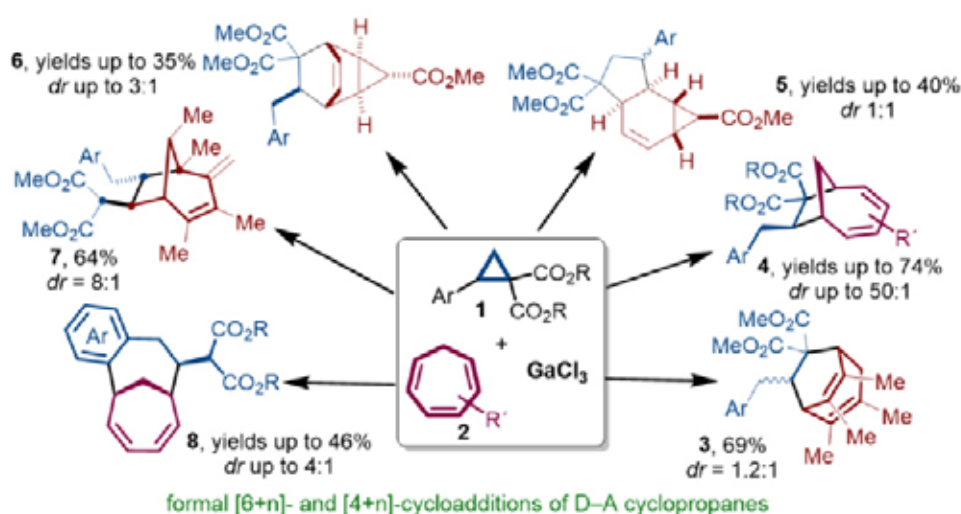
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REACTIONS OF CYCLOHEPTATRIENE SYSTEMS WITH ZWITTERIONIC COMPLEXES OF DONOR-ACCEPTOR CYCLOPROPANES

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Donor-acceptor cyclopropanes (DAC, **1**) are widely used as three-carbon synthons in modern organic synthesis.¹ They usually react in the form of 1,3-zwitterionic intermediates with various substrates in the presence of Lewis acids. The use of gallium halides makes it possible to obtain stable 1,2-zwitterionic complexes that are capable of entering into various reactions with unsaturated compounds.^{2,3}



In the current work we demonstrated the interaction of DAC **1** with substituted cycloheptatrienes **2** in the presence of gallium halides. Such transformations were studied in detail for the first time and as result we developed a number of selective processes of formal [6+n]- and [4+n]-cycloaddition/annulation involving both 1,3- and 1,2-zwitterionic intermediates. We obtained a wide range of polycyclic compounds **3–8**, which are usually formed in good yields and diastereoselectivity. The mechanisms of the developed processes and some modifications of bicyclic products **4** were also presented.

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SYNTHESIS AND STUDY OF THE PROPERTIES OF NEW PHOTOCHEMICALLY ACTIVE NITROSORUTHENUM COMPLEXES

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Coordination compounds with a nitrosyl ligand are an interesting class of compounds to study because they have photoinduced bond isomerism of the nitrosyl group. This group can be coordinated in at least three ways: through a nitrogen atom (GS), through an oxygen atom (MS1), and η^2 -(NO) (MS2).

In addition, all three structural isomers have characteristic absorption spectra, making it possible to selectively photoexcite and convert one isomer to another using light radiation in a solid compound, and, as a result, it is possible to create molecular switches and data storage devices based on holography.

Among nitrosyl complexes of various metals, such as Fe, Ni, Mn, Pt, Os, Ru, ruthenium complexes have the highest thermal stability and MS1 occupancy, which also exhibit anticancer properties. The most electronegative ligand (in the series SH-<OH-<Cl-<F-) in the trans position and the least π -donor ligands (in the series I->Br->SCN->Cl->NH₃) in equatorial positions also provide the highest MS1 decay temperatures.

Based on many studies, it can be concluded that for further study, compounds with the trans coordinate F-Ru-NO and with N-donor equatorial ligands should be selected. The work presents the synthesis of previously known and new structures with such a ligand environment, the composition of which was established and confirmed using monocrystal X-ray diffraction, powder X-ray diffraction and elemental analysis. In addition to the synthesis, the above-described properties of this class of compounds in solids are demonstrated through a series of IR spectra recorded as the temperature changes. For some compounds, decay temperatures and physicochemical parameters (activation energy and pre-exponential factor) were determined.

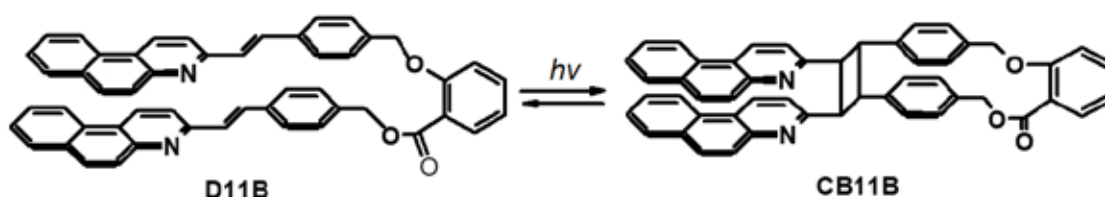
The work was carried out with the financial support of the Russian Science Foundation, project 22-43-09001.

COLOR-CORRELATED PHOTOSWITCH BASED ON A NEW PHOTOCHROMIC PAIR OPERATING VIA THE [2+2] PHOTOCYCLOADDITION MECHANISM

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Biphotochromic dyad **D11B** undergoes a reversible [2+2] photocycloaddition reaction to form cyclobutane **CB11B**:



The absorption and luminescence spectra of **D11B** and **CB11B** are significantly different, so the photochromic pair **D11B**–**CB11B** can serve as a color-correlated photoswitch, Figure 1. The input signals of the switch are irradiation with light with $\lambda = 397$ nm (in1) and 260 nm (in2), and the output is fluorescence I ($\lambda_{\text{exc}} = 333$ nm) at wavelengths of 354 nm (out1) and 396 nm (out2). Exposure to in1 results in the formation of **CB11B** (I_{354} maxima and I_{396} minima). Exposure to in2 results in partial opening of **CB11B** and the formation of a mixture of **CB11B** and various geometric isomers of **D11B** (I_{354} minima and I_{396} maxima).

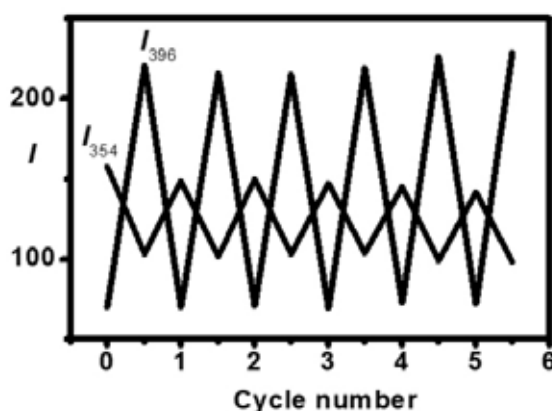


Figure 1. Change in fluorescence intensity I of the system at wavelengths 354 nm and 396 nm upon alternate irradiation with 260 nm light for 500 s and 397 nm light for 600 s.

The work was performed in accordance with the state task No. 124013000686-3 with the financial support of the Russian Science Foundation, project 22-23-00482.

AN UNUSUAL REARRANGEMENT OF PYRAZOLE NITRENE: HETEROCYCLIC RING-OPENING/ RECYCLIZATION CASCADE

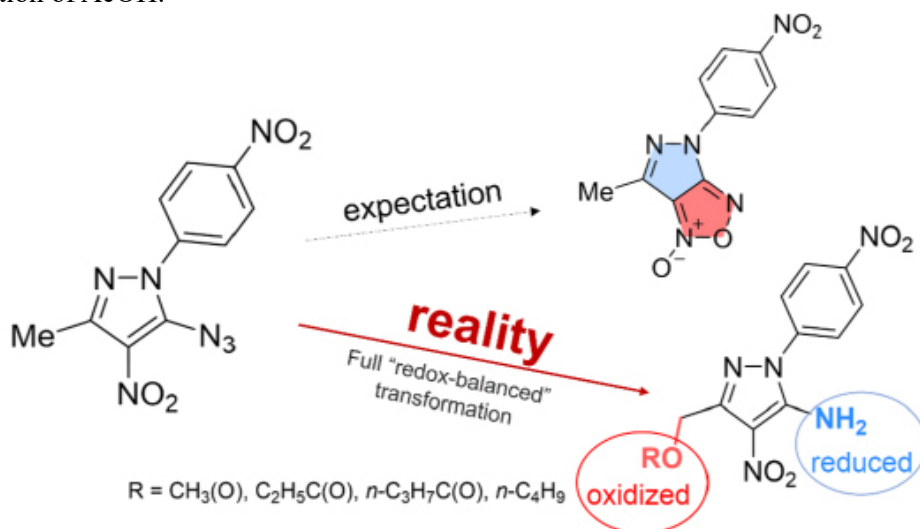
**Burilov A.R.,^a Chugunova E.A.,^a Gazizov A.S.,^a Matveeva V.I.,^a
Akylbekov N.I.,^b Tonkoglažova D.I.,^c Alabugin I.V.^{a,c}**

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We obtained an interesting “redox-balanced” transformation where two functional groups separated in space undergo simultaneous redox transformations in opposite directions: the Me group is oxidized while the nitrene moiety is reduced. The absence of usual furoxan products in this case can be attributed to the combination of two factors: the lower aromaticity of pyrazole relative to benzene and the accumulation of strain upon the fusion of the two five-membered rings. The interplay of electronic effects due to the presence of multiple nitrogen atoms in pyrazole activates the fast Grob fragmentation into a functionally rich acyclic nitro nitrile, which can recyclize after prototropic isomerization and the Michael-like addition of AcOH.¹



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Research was supported by the Ministry of Science and Higher Education of the Russian Federation at FRC Kazan Scientific Center (grant No. 075-15-2022-1128).

ZnFe₂O₄: COMPARATIVE ANALYSIS OF SYNTHESIS METHODS FOR ELECTRODE MATERIALS

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The developing field of hydrogen energy requires economically affordable efficient electrode materials, optimal use of zinc ferrite-based ceramics due to excellent functional properties. The paper analyzes the data of the ZnFe₂O₄ material obtained by the most common synthesis methods: sol-gel autocombustion, dehydration of layered double hydroxide (LDH) and mechanochemical. The density of ceramics is shown (Table 1), each sample is characterized by a decrease in grain size with an increase in sintering temperature.

Table 1. Ceramic density indicators Fe₂O₃/ZnFe₂O₄

Synthesis method	Sintering temperature, °C	Density, g/cm ³
Sol-gel autocombustion	1000	4,0943
	1100	4,7232
Mechanochemical	1000	4,4203
	1100	5,0962
LDH dehydration	1000	4,3709
	1100	4,8048

The highest value of specific capacity is observed for ceramics with a lower density (sol-gel 1000). The correlation of the above data suggests the possibility of using sol-gel ceramics as cathode materials.

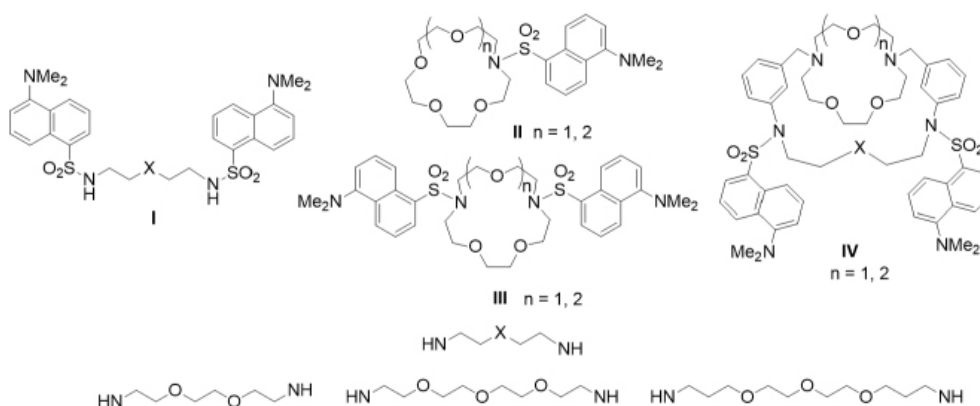
*The work was performed within the framework of the state assignment of Sakhalin State University
No. FEFF-2024-0001*

DANSYL-CONTAINING LINEAR AND MACROCYCLIC POLYOXADIAMINES AS FLUORESCENT DETECTORS OF METAL CATIONS

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The development of fluorescent sensors for metal cations is a current trend in modern chemistry. Our research makes extensive use of palladium-catalyzed amination techniques to form C-N bonds macrocyclic and macrobicyclic compounds modifications. In this way, compounds based on diazacrown ethers¹ and triazacycles^{2,3} were obtained. This work combines data on the capabilities of fluorescent detection of metal cations by derivatives of linear and macrocyclic polyoxadiazamine derivatives containing 5-(dimethylamino)naphthalene-1-sulfonyl (dansyl) group as a fluorescent fragment. It has been shown that the selectivity of the metal cations detection depends on the structure of the fluorescent sensor. The studied compounds are most suitable for detection of Cu(II), Al(III), Hg(II).



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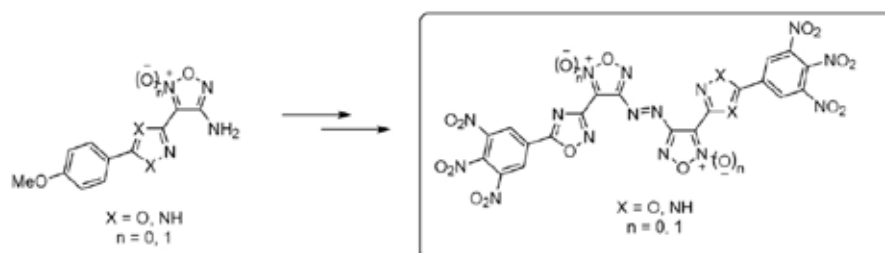
POLYHETEROCYCLIC POLYNITROPHENYL DERIVATIVES OF AZO-1,2,5-OXADIAZOLES

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Nowadays, requirements for safety of high-energy density materials (HEDM) make the demand in research in the field of HEDM one of the highest. Among the strategies for synthesis of new HEDM combining 1,2,5-oxadiazol heterocycles with another heteroatomic moieties, such as azo-bridges, can provide compounds with high thermostability.^{1,2} Incorporating trinitrophenyl and aminodinitrophenyl moieties with nitrogen-rich heterocycles yields to HEDM with insensitivity to friction.^{3,4}

In this work are presented novel azo-bridged 1,2,5-oxadiazoles containing another heterocyclic and polynitrophenyl moieties, which are insensitive to friction and possess high thermostability and low sensitivity to friction.



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ALIPHATIC N,N'-DIOXIDES AS LIGANDS FOR THE CONSTRUCTION OF FUNCTIONAL METAL-ORGANIC FRAMEWORKS

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Aliphatic and aromatic N,N'-dioxides represent a rare class of ligands in the chemistry of metal-organic frameworks (MOFs). Such features as affinity for a wide range of both soft and oxophilic metal centers¹, conformational flexibility² and electrical neutrality, scarce for O,O'-donor ligands, can be highlighted for this class. In general, these properties deserve a great interest in the design of adsorbents and sensors for toxic anionic substrates, as well as in the preparation of multifunctional ionic inclusion compounds³.

The chemistry of MOFs based on aliphatic N,N'-dioxides has been extensively developed in recent years by our group, with selective adsorption, sensing an "synthesis-structure"⁴ correlations as main working directions. Examples of selective and reversible sorption of I⁻ (Fig. 1)⁵ and luminescent sensors for nitrates, nitrites, chromates, and dichromates were discovered. Synthetic methods for new aliphatic N,N'-dioxides, previously not reported, have been elaborated.

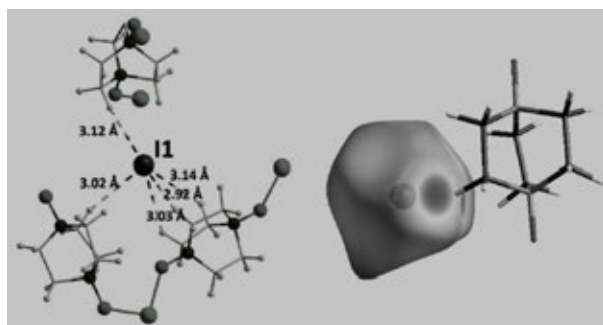


Figure 1. I atom position in $[\text{Co}_2(\text{H}_2\text{O})(\text{NO}_3)(\text{odabco})_5]\text{I}_2(\text{NO}_3) \cdot 1.85\text{H}_2\text{O}$ inclusion compound, and its Hirshfeld surface.

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A SERIES OF METAL-ORGANIC COORDINATION POLYMERS WITH ENHANCED SORPTION CHARACTERISTICS

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Metal-organic coordination polymers (MOCPs) are a relatively new class of compounds with wide possibilities for tuning sorption and magnetic, catalytic and luminescent properties. This is achieved, among other things, by using various carboxylate and N-donor ligands, as well as metal ions or clusters. Thus, it becomes possible to fine-tune the structure and properties of coordination polymers^{1,2}.

We have synthesized two- and three-dimensional coordination polymers based on dicarboxylic acids and transition metal ions. Chelated and bridged N-donor ligands were used to complicate the architectures of the obtained coordination polymers. The structures of the MOCPs were established using single-crystal X-ray diffraction analysis. The chemical and phase compositions are determined by a number of physico-chemical methods.

Activation conditions were selected for MOCPs, which made it possible to establish their textural and sorption characteristics. Sorption measurements of adsorption isotherms of gases CO₂, N₂, O₂, CO, CH₄, C₂H₂, C₂H₄, C₂H₆ and vapors of benzene, cyclohexane were carried out for activated compounds. While some frameworks are distinguished by significant indicators of sorption capacity, others demonstrate increased selectivity with respect to carbon dioxide and ethane.

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The research was supported by Russian Science Foundation, project № 23-13-00310.

COORDINATION POLYMERS BASED ON DERIVATIVES OF 2,1,3-BENZOCALCOGENADIAZOLES AS A LUMINESCENT SENSORS FOR H_2PO_4^- ANIONS AND CATIONS OF THREE-CHARGED METALS

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Coordination polymers (CPs) are a class of porous materials assembled from metal ions which are connected by organic molecules (linkers) into a polymeric structure. Luminescent polymers are of particular interest among CPs, since they can be used as sensors to detect metal cations, anions, antibiotics and various organic pollutants in food and the environment.

One of the approaches to the synthesis of luminescent CPs is the use of organic fluorophores, for example, derivatives of 2,1,3-benzochalcogenadiazoles. In this work, coordination polymers based on 4,7-di(carboxypyrazole-1-yl)-2,1,3-benzochalcogenadiazoles (H_2LX , where $\text{X} = \text{O}, \text{S}, \text{Se}$) and zinc(II) or cadmium(II) cations were obtained. All coordination polymers have demonstrated intense luminescent properties. Ethanolic suspension of $[\text{Zn}_2(\text{bpy})(\text{H}_2\text{O})_2(\text{L}_\text{O})_2]$ ($\text{bpy} = 4,4'$ -bipyridine) has demonstrated luminescent response (increase of intensity) to different metal cations (Al^{3+} , Ga^{3+} , In^{3+} , Fe^{3+}) and H_2PO_4^- anion (fig. 1). Limit of detection for Ga^{3+} and H_2PO_4^- were determined as 0,14 and 0,18 μM , respectively.

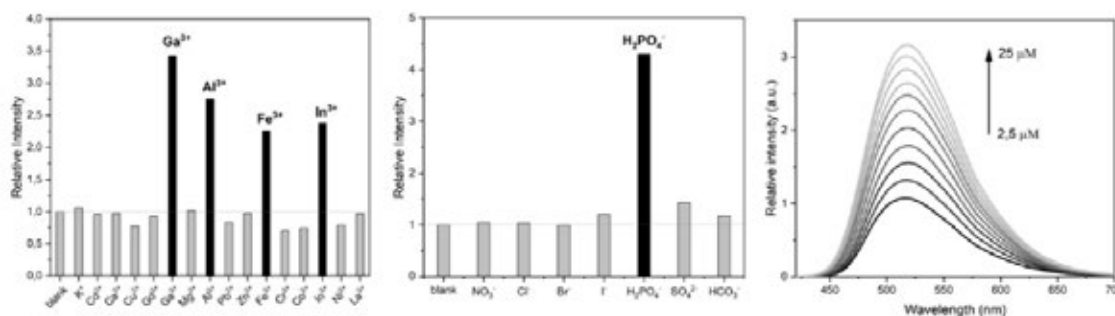


Figure 1. The luminescent response to cations of various metals and anions in solution (left) and the dependence of the luminescence intensity on the concentration of H_2PO_4^- anion (right) for CP $[\text{Zn}_2(\text{bpy})(\text{H}_2\text{O})_2(\text{L}_\text{O})_2]$.

This work was supported by the Russian Science Foundation, grant No. 23-43-00017, <https://rscf.ru/project/23-43-00017/>.

METAL-ORGANIC COORDINATION POLYMERS FOR ADSORPTION AND SEPARATION OF LIGHT HYDROCARBONS

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Microporous adsorbents allow the separation of mixtures into individual components with high selectivity and low energy consumption, in comparison with more common distillation technologies. Metal-organic coordination frameworks (MOFs) are a modern type of microporous adsorbents that feature a number of advantages over traditional materials (nanocarbon materials, zeolites).

This report will present recent results on the preparation and investigation of microporous and mesoporous MOFs with unique adsorption characteristics towards saturated and unsaturated C1, C2, C3 hydrocarbons. Relationships between the crystalline structure of the porous framework and its adsorption properties are systematically studied. An unusual “inverted” selectivity with respect to saturated hydrocarbons over the unsaturated ones was discovered experimentally and rationalized using quantum chemical calculations. Record-high selectivity values have been achieved for a number of industrially important gas mixtures. The preparative separation of multicomponent mixtures of hydrocarbons has been demonstrated under conditions closely simulating industrial technological processes [1-3]. The effective separation of the practically-relevant systems (methane-ethane-propane, ethane-ethylene, propane-propylene, etc.) is a necessary step towards the broad use of the natural gas as an accessible chemical feedstock, as well as in the production of important polymers.

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This work was supported by Russian Science Foundation (Grant № 23-13-00310).

FEATURES OF OBTAINING NITRO-SUBSTITUTED 6H-INDOLO[2,3-B]QUINOXALINES

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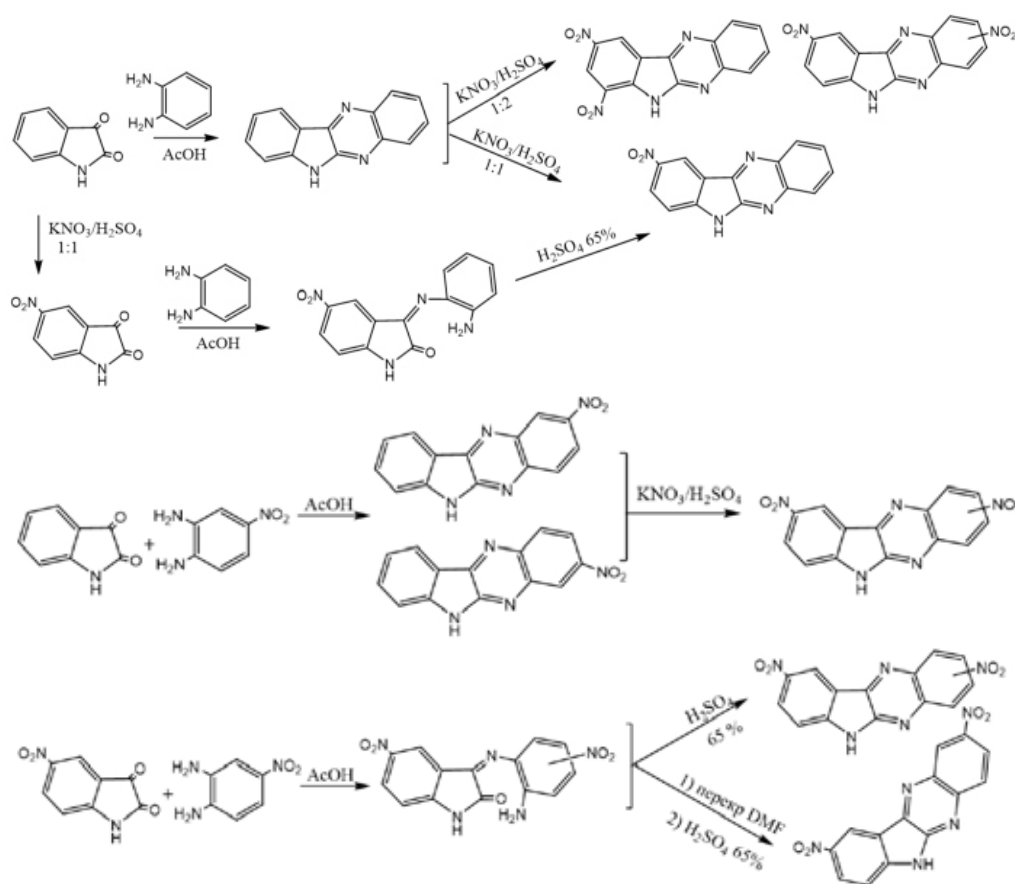
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The conditions for the preparation of nitro-substituted 6H-indolo[2,3-b]quinoxaline derivatives, which are valuable precursors in the synthesis of the corresponding amines containing the 6H-indolo[2,3-b]quinoxaline fragment, have been studied and optimized. Amines obtained by reduction of nitro compounds synthesized in this work can be used in the synthesis of new classes of organic dyes and compounds with semiconductor properties.



The work was carried out with the financial support of the Russian Science Foundation, project 03-01-00001

VOLUMETRIC PROPERTIES OF GLYCEROL + DIMETHYLSULPHOXIDE MIXTURE AT ATMOSPHERIC PRESSURE

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To predict the effectiveness of cryoprotectant and cryo-preservative compositions in preventing the formation of ice in biological objects and protein denaturation under conditions of high compression, data on their properties is needed. Many of the molecular mechanisms by which cryoprotectants stabilize and protect molecules and cells, along with inhibiting ice formation, are still not fully understood. Therefore, to understand these mechanisms, it is first necessary to know the physicochemical properties of these systems.

The volumetric properties of binary mixtures are directly related to the packing of the component molecules and changes in this packing when the composition and external parameters of the state are varied. Of great interest are mixtures characterized by the presence of a network of hydrogen bonds. These include mixtures of glycerol (GL) with dimethyl sulfoxide (DMSO). As is known, both GL and DMSO are classified as penetrating antifreeze agents in cryomedicine. Their mixtures are actively used in fundamental re-search as cryoprotective solutions that completely prevent water crystallization in biological objects. Also, these mixtures protect biological cells from exposure to high pressure, i.e. are baroprotectors.

In the report, based on the measured densities of the binary mixture glycerol + dimethyl sulfoxide in the entire range of compositions of the liquid state in the temperature range from 278.15 to 333.15 K and atmospheric pressure, the apparent and partial molar volumes of the components of the mixture are discussed, including their limiting values, excess molar volumes, molar isobaric thermal expansion of the mixture. It has been shown that the formation of a mixture of GL + DMSO occurs with a decrease in the volume of the mixture at all temperatures; the maximum partial molar volumes of GL and DMSO increase with increasing temperature.

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THERMAL AND PRESSURE CHARACTERISTICS GLYCEROL MIXTURES OF NON-ELECTROLYTES

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Glycerol, like water and diols, is a solvent with three-dimensional net of hydrogen bonds and is characterized by the presence of some specific properties, namely: small coefficients of isothermal compressibility and isobaric thermal expansion, high viscosity, strongly dependent on temperature, the ability to remain in a state hypothermia, relatively large free volume, etc.

Glycerol-based mixtures in cryobiology and cryomedicine are used as penetrating antifreeze agents that prevent water crystallization in biological objects. In addition, glycerol mixtures protect biological cells from exposure to high pressure, i.e. are baroprotectors.

In solutions characterized by the presence of a developed network of hydrogen bonds, the decisive role in intermolecular interactions belongs to strong H-bonds. And fluctuations in volume, first of all, will depend on changes in both the energy of these H-bonds and their number.

To understand the role of hydrogen bonds in molecular processes occurring in liquid glycerol systems, it is important to know the properties of such mixtures, because the mechanism of the influence of glycerol H-bonds on the processes of ice crystallization in biological objects is still not clear.

The report examines the thermal and pressure characteristics of glycerol and its mixtures with non-electrolytes, also characterized by the presence of a network of hydrogen bonds.

The study was supported by a grant from the Russian Science Foundation No 24-23-00058

NEW FUNCTIONALIZED PHOSPHONATES WITH PHOTO-SWITCHABLE INHIBITORY ACTIVITY AGAINST CHOLINESTERASE ENZYMES.

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The search for compounds on the basis of which the concept of photoswitching biological activity can be realized has become a subject of interest in modern fundamental science and medicine. Research on photoexposure to phosphonates is a new, little-studied area, and the problems of modern pharmacology determine the importance of the synthesis of new compounds with anticholinesterase action as drugs for the treatment of a wide range of diseases. To solve current problems of photopharmacology, we have synthesized new families of photoactive substances that simultaneously have biological activity and the ability to change the amount of biological activity after optical exposure.

Thus, we demonstrated the possibility of laser-induced changes in biological activity using the example of inhibition of butyrylcholinesterase (BChE) by different groups of the phosphonate family: phosphorus functionalized thiazolotriazole molecules (PFT), phosphorylated 2-arylamino malonates (PhAM) and dialkyl[(Z)-2-chloro-2-phenylethenyl]phosphonates (VP).

Thus, a systematic study of the photo-switchable properties of phosphonates allowed us to synthesize new groups of compounds with photo-controlled biological activity

The study was carried out at the expense of the Russian Science Foundation No 22-13-00082, <https://rscf.ru/en/project/22-13-00082/>. Authors are grateful to "Centre for Optical and Laser Materials Research", "Interdisciplinary Resource Centre for Nanotechnology" of St. Petersburg State University Research Park for technical support.

PHASE EQUILIBRIA OF THE $LREPO_4$ - YPO_4 QUASI-BINARY SYSTEMS ($LRE = La, Gd$)

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Speaking of phase equilibria in single- and multicomponent systems of rare earth orthophosphates, one cannot fail to note the variety of structural types that form these compounds: rhabdophane, churchite, monazite, xenotime and anhydrite¹. Despite the enormous interest in functional materials based on multicomponent rare earth orthophosphates in the field of optical luminescence, thermal insulation ceramics and immobilization of radioactive waste, the phase equilibria of such systems still remain poorly understood.

The study of $LREPO_4$ - $HREPO_4$ systems ($LRE = La \rightarrow Gd$, $HRE = Tb \rightarrow Lu$, Sc, Y), in which limited solubility of the components in each other in the solid state is obviously observed, is of fundamental interest for calculating phase diagrams and predicting the behavior of materials, which is necessary for the applied use of multicomponent materials.

In this work, materials were synthesized using soft chemistry methods and subsequent heat treatment in air at $T=1000$ - 1600°C in the quasi-binary systems $LaPO_4$ - YPO_4 and $GdPO_4$ - YPO_4 . The results of studies of X-ray phase and X-ray structural analysis, scanning electron microscopy, thermal behavior and high-temperature mass spectrometry are presented. The limits of miscibility of solid solutions based on the phase with the monazite structure and with the xenotime structure in the $LaPO_4$ - YPO_4 system were obtained: the maximum solubility of YPO_4 in the phase with the monazite structure is 46 mol.% at $T=1600^\circ\text{C}$, $LaPO_4$ is practically insoluble in the xenotime structured phase over the entire temperature range studied. It has been shown that the $GdPO_4$ - YPO_4 system is kinetically “frozen” and does not reach a state close to equilibrium under the given synthesis conditions.

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SYNTHESIS OF NEW CARBORANYL-CARBENE COMPLEXES OF RHODIUM

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Carboranes are polyhedral boron-carbon molecular clusters that are attractive as ligands due to their unique geometry, electronic properties and wide functionalisation options¹.

Despite the worldwide popularity of N-heterocyclic carbene ligands, carboranyl-carbene ligands are rather poorly studied, although they can exhibit interesting catalytic and bioactive properties^{2,3}.

In this work, we have synthesised rhodium carborane-carbene complexes based on the icosahedral 1, 2-dicarba-closo-carborane (ortho-carborane) (Figure 1) and 7,8-dicarba-nido-carborane.

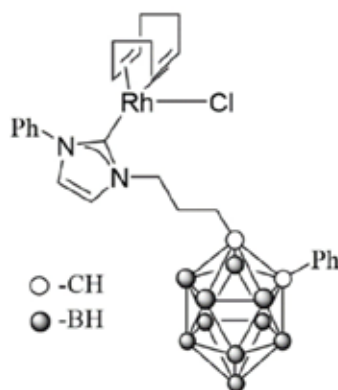


Figure 1. An example of a rhodium complex prepared.

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PREPARATION OF NEW COORDINATION POLYMERS BASED ON CLUSTER COMPLEXES OF RHENIUM AND COPPER (I) OR SILVER (I)

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Systematic study of cluster chalcogenide cyanocomplexes of rhenium $[\text{Re}_4\text{Q}_4(\text{CN})_{12}]^{4-}$ and $[\text{Re}_6\text{Q}_8(\text{CN})_6]^{4-}$ (Q = S, Se, Te) has led to the production of a large number of new compounds with different geometries and properties. The interest in these cluster complexes is due to their physico-chemical properties, such as high resistance to thermal and chemical influences, and the possibility of formation of polymer structures. It is shown that such cyanocomplexes are convenient "building blocks" for the construction of new coordination compounds with a given geometry and properties, due, among other things, to the peculiarities of the cluster core¹⁻⁵. A new tetrahedral cluster complex of rhenium⁶ $[\{\text{Re}_4\text{As}_2\text{S}_2\}(\text{CN})_{12}]^{6-}$ has recently been obtained, which is capable of forming coordination polymers with transition metal cations, which makes it an interesting object for research.

The paper discusses the results of the synthesis of new metal-organic coordination polymers based on tetrahedral and octahedral cluster chalcogenide complexes of rhenium with complex cations of copper (I) and silver (I). The new compounds were synthesized under hydrothermal conditions at 150°C using as precursors: $[\text{Re}_6\text{Q}_8(\text{CN})_6]^{4-}$, $[\text{Re}_6\text{Q}_8(\text{OH})_6]^{4-}$, $\text{trans-}[\text{Re}_6\text{S}_8(\text{CN})_2(\text{OH})_4]^{4-}$ and $\text{trans-}[\text{Re}_6\text{Se}_8(\text{CN})_4(\text{OH})_2]^{4-}$, $[\text{Re}_4\text{Q}_4(\text{CN})_{12}]^{4-}$, $[\{\text{Re}_4\text{As}_2\text{S}_2\}(\text{CN})_{12}]^{6-}$, CuCN, AgCN, bpy (2,2'-bipyridyl), 4,4'-bpy (4,4'-bipyridyl), dpe (1,2-di(4-pyridyl)ethylene). The obtained metal-organic coordination polymers were studied by a set of physico-chemical methods.

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FORMATION OF METASTABLE BIMETALLIC SOLID SOLUTIONS IN Cu-Rh, Cu-Ru AND Ni-Ru SYSTEMS DURING THERMAL DECOMPOSITION OF COMPLEX COMPOUNDS

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The development of methods for producing metastable solid solutions is of fundamental and practical scientific interest. When one metal is replaced by another in the crystal lattice, a synergistic effect may occur, for example, an increase in catalytic activity compared to monometallic samples.

In this work, we synthesized various complex compounds containing water, oxalate ion, ammonia, ethylenediamine and imidazole as ligands: $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2][\text{RuNOCl}_5]$, $[\text{Ni}(\text{NH}_3)_6][\text{RuNOCl}_5]$, $[\text{Cu}(\text{En})_2][\text{RuNOCl}_5]$, $[\text{Ni}(\text{En})_3][\text{RuNOCl}_5]$, $[\text{Cu}(\text{Im})_4][\text{RuNOCl}_5]$, $[\text{Ni}(\text{Im})_6][\text{RuNOCl}_5] \cdot \text{H}_2\text{O}$ and $[\text{RuNO}(\text{NO}_2)_4\text{OHNi}(\text{En})_2]$. The process of their thermal decomposition was studied with the establishment of intermediate and final products of thermolysis.

In the Cu-Ru system, the maximum incorporation of copper into the ruthenium structure was 5 at.% during thermolysis of $[\text{Cu}(\text{En})_2][\text{RuNOCl}_5]$ in both inert and reducing atmospheres.

In the Ni-Ru system, it was possible to obtain a single-phase metastable solid solution $\text{Ni}_{0.50}\text{Ru}_{0.50}$ (HCP, $a = 2.6137$, $c = 4.2012 \text{ \AA}$, $V/Z = 12.437 \text{ \AA}^3$) with slow heating (1 K/min) of the $[\text{RuNO}(\text{NO}_2)_4\text{OHNi}(\text{En})_2]$ in a hydrogen atmosphere up to 205 °C. The $\text{Ni}_{0.50}\text{Ru}_{0.50}$ nanoalloy prepared on a support (Al_2O_3) showed activity in the CO methanation reaction higher than its monometallic analogues. It was found that the nanoalloy retains its structure during the catalytic reaction without showing signs of separation.

The kinetics of decomposition of the metastable $\text{Ni}_{0.50}\text{Ru}_{0.50}$ solid solution was studied under isothermal conditions using *in situ* X-ray diffraction. It has been shown that this separation occurs at temperatures above 500 °C according to a binodal mechanism.

The work was financially supported by Russian Science Foundation (project number 21-73-20203) <https://rscf.ru/project/221-73-20203/>

DBU-PROMOTED TRANSFORMATIONS OF 4-ALKYL-2-AZABUTA-1,3-DIENES INTO DERIVATIVES OF PYRROLE AND 1H-CYCLOPENT[C]PYRID-1-ONE

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2-Azabuta-1,3-dienes are effective substrates for the construction of a wide range of heterocyclic structures. A convenient approach to the synthesis of 2-azabutadienes is the Rh(II)-catalyzed reaction of diazo compounds **1** with 2H-azirines **2**.¹

We have recently shown that 4-alkyl-2-azabuta-1,3-dienes **3**, under the action of the base DBU, enter into 1,5-cyclization to form 1-pyrroline derivatives **4** with high yields and a wide range of introduced substituents (Fig.1, *path a*). When the cyclopentyl substituent was introduced into the fourth position of azabutadiene **3'**, under the action of DBU other cyclizations took place – cyclopentapyridone derivatives **5** and 3-hydroxypyrrole **6** were obtained as products (Fig. 1, *path b*). With moderate yields, it was possible to synthesize a number of pyridone derivatives, but reaction turned out to be limited in terms of the introduced substituents. The mechanisms of formation of pyrrolines **4**, pyridones **5** and pyrroles **6** were proposed with the aid of control experiments and quantum chemical calculations.

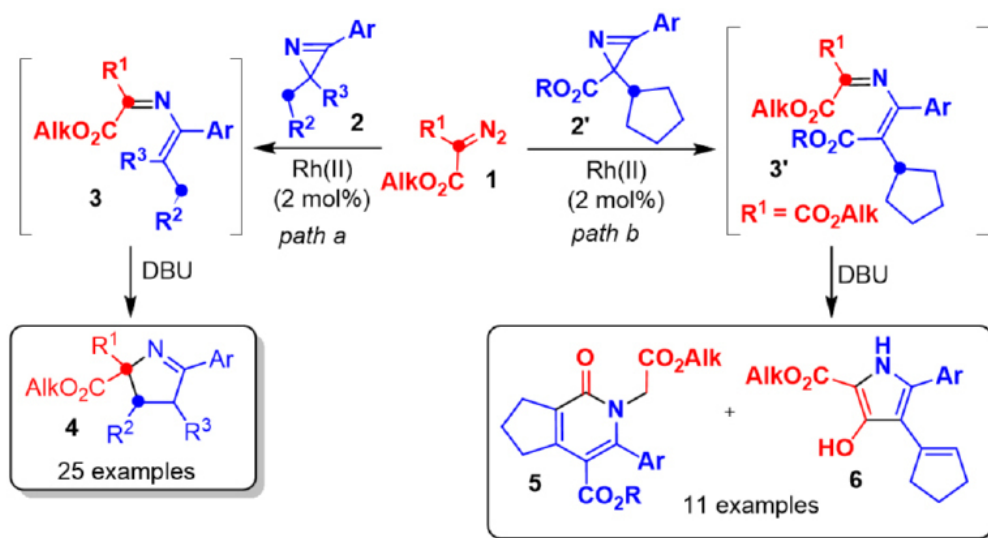


Figure 1. DBU-promoted cyclizations of 4-alkyl-2-azabuta-1,3-dienes

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MACHINE LEARNING PREDICTION OF QUANTUM CHEMICAL DESCRIPTORS OF CHLORINATED POLYCYCLIC AROMATIC HYDROCARBONS

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Chlorinated polycyclic aromatic hydrocarbons (Cl-PAH) are common organic pollutants exhibiting toxic and carcinogenic properties. The features obtained from quantum chemical calculations can be used to estimate various physicochemical properties of Cl-PAH or as descriptors in QSAR correlations. However, high-precision quantum chemistry methods are computationally expensive, which prevents them from being used to generate descriptors for large sets of molecules. An interesting approach aimed to reduce the computational costs is the Δ -machine learning¹, which refines the results of low-cost semi-empirical methods using a model pre-trained on the data calculated using *ab initio* methods.

We performed calculations for more than 3000 Cl-PAH molecules including geometry optimization and energy and vibrational frequency calculations using the semi-empirical GFN2-xTB method, as well as geometry optimization and energy calculations at the DFT level with a range-separated hybrid functional. Using the resulting dataset, a number of machine learning models including Δ -learning based artificial neural networks have been tested. The accuracy of prediction of the quantum chemical properties calculated at the high level of theory has been compared. The performance of descriptors calculated using the considered models in prediction of the toxicity of compounds and their affinity to the aromatic hydrocarbon receptor AhR was analyzed.

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FUNCTIONAL COORDINATION POLYMERS BASED ON THE OCTAHEDRAL CYANIDE CLUSTERS

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In recent years, research of metal-organic coordination polymers (MOCP) has progressed from fundamental work to industrial applications in catalysis, fine chemical synthesis, gas storage and separation of gas mixtures, and as sensor materials¹. The physicochemical properties of these compounds are largely determined by the properties of individual “building blocks,” primarily metal cations. Chalcogenide clusters $[\text{Re}_{6-x}\text{Mo}_x\text{Q}_8(\text{CN})_6]^{n-}$ (Q = S or Se; x = 0–3) and halide clusters $[\text{Mo}_6\text{X}_8(\text{CN})_6]^{2-}$ (X = Br or I) exhibit bright luminescence in the red and near-IR regions as well as the electrochromic effect in solutions and solid salts. These properties make such compounds promising candidates for the preparation of functional MOCPs with sensor properties².

This work reports recent discoveries in the chemistry of MOCPs based on octahedral rhenium and molybdenum cyanocluster anions. It was shown that these clusters can be included in the crystalline matrices of MOCPs, coordinating through the nitrogen atoms of CN groups to transition metal or lanthanide cations. In this case, the properties of each cluster can be significantly enhanced by selecting the cationic part and additional organic ligands.

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A SYSTEMATIC STUDY OF HETEROMETALLIC OCTAHEDRAL CLUSTERS $[\text{Re}_{6-X}\text{M}_X\text{Se}_8\text{L}_6]$

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Octahedral clusters of metals of groups 5-7 are characterized by an isorecticular structure and similar sizes of complexes, which are preserved during redox transformations, pH changes, and ligand substitution. This makes them promising competitors of mononuclear complexes as building blocks for the design of various polymer materials and coatings. Metal substitution in the metal core is a promising tool for fine control of the functional properties of cluster complexes, due to the fact that it affects the spectroscopic characteristics, redox behavior, the presence of unpaired electrons, charge, solubility and other properties of the compounds.

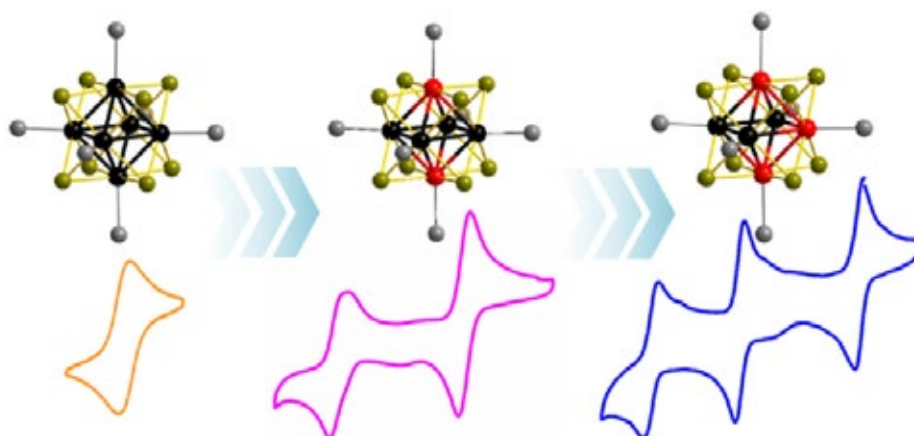


Figure 1. The examples of structure and CV curves for $[\text{Re}_6\text{Se}_8\text{L}_6]^n$, $[\text{Re}_4\text{Mo}_2\text{Se}_8\text{L}_6]^n$, $[\text{Re}_3\text{Mo}_3\text{Se}_8\text{L}_6]^n$ cluster complexes.

We report on the preparation and detailed study of heterometallic octahedral rhenium clusters – products of non-isovalent “substitution” of rhenium by atoms of groups 5, 6 and 8 in the cluster core. The study includes an assessment of the influence of the nature of metal heteroatoms and the degree of substitution on the redox behavior, spectroscopic characteristics and electronic structure of molecular cluster complexes.

The work was carried out with the financial support of the Russian Science Foundation, project 22-73-10181.

THE CYCLIZATION OF DIPHENYLPHOSPHINYLATED THIOSEMICARBAZIDES OF ACETIC AND FORMIC ACIDS

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Krutov I.A.,^a Samigullina A.I.^b**

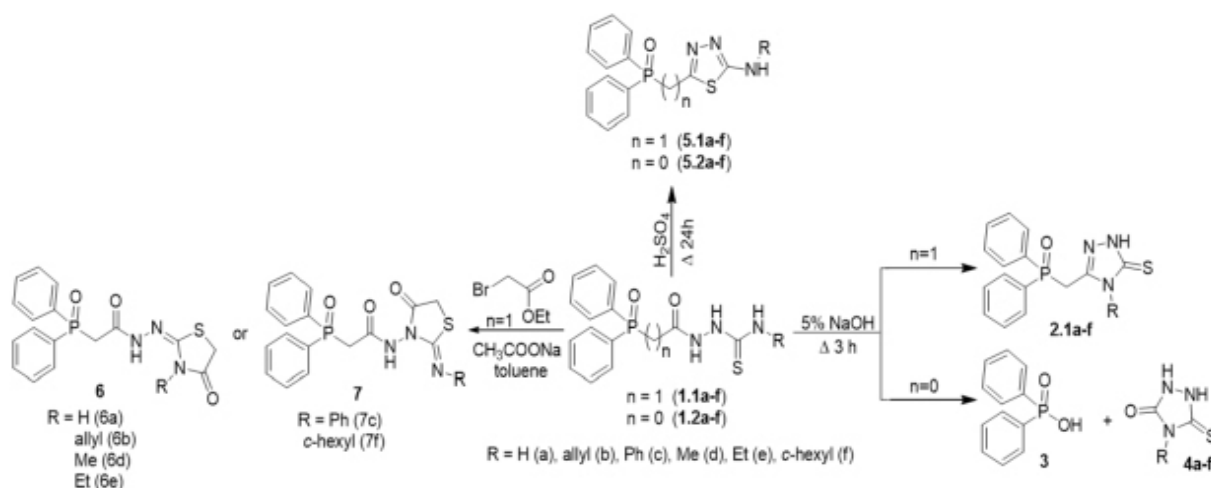
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Heterocyclic systems such as triazolethiones are favored structures in medicinal chemistry, with significant potential for the development of new drugs. Phosphorus-containing 1,2,4-triazolethione heterocycles are little known. While the phosphorus atom, which is involved in many biological processes occurring in living organisms, can reduce toxicity and increase bioavailability. We have studied the cyclization of diphenylphosphinylated thiosemicarbazides of acetic and formic acids under various conditions in order to obtain 1,2,4-triazolethione heterocycles:



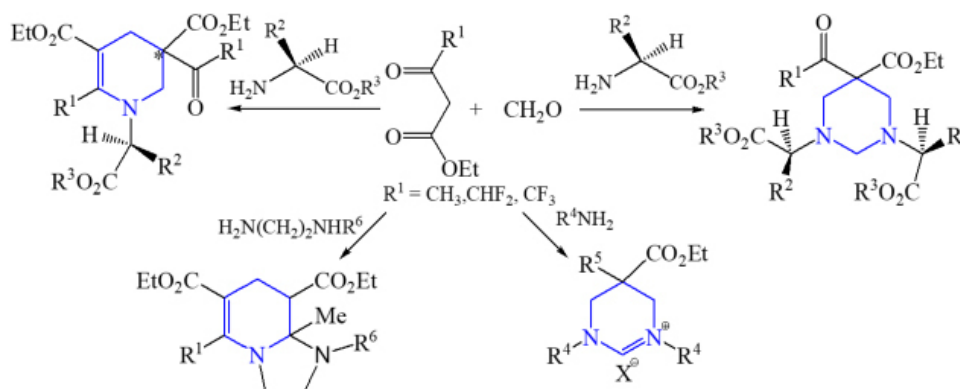
It was shown that, depending on the cyclization conditions, heterocycles of various structures are formed. The structure of compounds 2, 3, 4, 5, 6, 7 was confirmed by X-ray diffraction data.

POLYFUNCTIONAL SIX-MEMBERED NITROCYCLES BASED ON FORMALDEHYDE: SYNTHESIS AND BIOLOGICAL ACTIVITY

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The paper presents the results of a study on the development of routes for the synthesis of heterocyclic compounds containing hexahydropyrimidine, 1,2,3,4-tetrahydropyridine and imidazo[1,2-a]pyridine fragments, based on the interaction of formaldehyde with CH-acids and primary amines ^{1,2}. The influence of the fluorine atom on the reactivity of 1,3-dicarbonyl compounds, the structure of primary amines and natural amino acids, aqueous solutions of electrolytes and carbohydrates on the yield and composition of the resulting condensation products was studied. Methods for the synthesis of optically pure di- and trifluoro derivatives of hexahydropyrimidine have been proposed. The transformations of the resulting compounds were studied, including those leading to the formation of 3,4,5,6-tetrahydropyrimidinium salts. Pd-promoted hydrolytic selective cleavage of the C–N bond in 1,3,5-triazinanes was established.



The cytotoxic activity *in vitro* on cells of tumor origin and a conditionally normal cell line of the synthesized compounds was studied.

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AUTOMATION OF MOLECULE SYNTHESIS WITH DESIRED PROPERTIES

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Fatykhova A.A., Khakimova A.A., Gimadiev T.R.**

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Synthetic chemistry continually aims to develop molecules tailored to human needs. However, this process often encounters difficulties and errors, consuming significant time and resources. In pharmaceutical chemistry, rapid synthesis of numerous compounds is crucial for discovering biologically active molecules. The limited set of validated reactions commonly used by synthetic chemists constrains the search for new promising compounds.

Modern instrumentation technologies offer new opportunities for automating chemical processes. Various computer-controlled tools, including sample selection, automated reactors, and analytical methods, can be integrated to create a chemical compound synthesis conveyor. Our project focuses on developing technologies for creating robot chemists capable of automating molecule synthesis and optimization processes, as well as conducting searches for molecules with specified properties. Three components are necessary for the system to operate: artificial intelligence, a robotic experimental platform, and a results analysis and feedback system. This will improve efficiency and resource savings in synthetic chemistry, opening up new prospects for scientific research and industrial production. Currently, we are developing an experimental system based on an industrial robot and conducting trial syntheses.

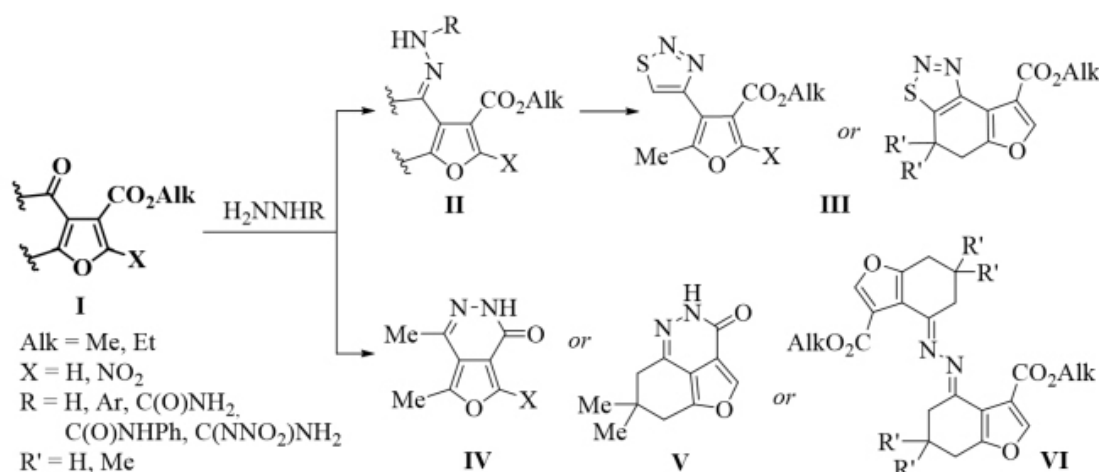
This work was supported by a subsidy allocated to Kazan Federal University to fulfill the state task in the field of scientific activity FZSM-2024-0002.

SYNTHESIS OF NEW HETEROCYCLIC COMPOUNDS BASED ON CARBONYL-CONTAINING FURAN-3-CARBOXYLATES

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Carbonyl-containing furan-3-carboxylates and their 2-nitro-substituted representatives **I** [1, 2] are promising substrates for functionalization in reactions with polynitrogen nucleophiles and the construction of new heterocycles [3].



It has been shown that reactions of furan-3-carboxylates and their 2-nitro-substituted representatives **I** with phenylhydrazines, semicarbazide, phenylsemicarbazide and nitroaminoguanidine lead to the production of a wide range of corresponding *E*-isomeric substituted hydrazones **II**.

Synthesized semicarbazones **II** under the conditions of the Hard-Mori reaction are converted into the original thiadiazole furancarboxylates **III**.

At the same time, based on the reactions of hydrazine with monocyclic furan-3-carboxylates **I**, pyridazinones **IV** are obtained, and with benzofuran carboxylates **I**, furocinnolinone **V** or bis-hydrazones **VI** are obtained. The products structure has been proven by a complex of physico-chemical methods.

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The research was supported by an internal grant of the Herzen State Pedagogical University of Russia (project № 3VG).

EQUILIBRIUM STRUCTURE OF CHEMISORBED LAYERS OF UNSATURATED CYCLIC HYDROCARBONS ON A SILICON SURFACE

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Organic thin films deposited on semiconductor surfaces are active elements of the organic semiconductor devices, such as organic field-effect transistors, solar panels, and LEDs¹⁻⁴. The advantage of using semiconductor surfaces as a support is the possibility of covalent attachment of unsaturated organic molecules². This is a direct path to incorporating molecular functionality into conventional semiconductor technology. Electronic properties of an organic thin film largely depend on its quality and morphology, which are determined by the balance between “molecule-surface” and “molecule-molecule” interactions at the initial stage of organic film growth^{1,4}. The first few monolayers of organic film play an important role in charge transport in organic field-effect transistors^{1,3}.

This work shows the capabilities of modern statistical methods for studying organic/semiconductor interfaces within the framework of lattice models parameterized by quantum chemistry methods. Particularly, we are focused on the tensor renormalization group (TRG) we are developing^{5,6}. Here we demonstrate the applications of TRG for revealing the equilibrium structure of 1,4-cyclohexadiene and pentacene monolayers on Si(001) surface. The effect of intermolecular interactions on structural and thermodynamic characteristics of the chemisorbed layers is discussed.

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HIGH TEMPERATURE SUPERCONDUCTIVITY IN CLATHRATE Ca–Y HYDRIDES

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Achieving room-temperature superconductivity remains one of the most challenging tasks in modern science. Significant progress has been made in this field over the past decade: a multitude of superconducting binary and ternary hydrides have been theoretically predicted¹ and experimentally studied².

In this study, we report on the theoretical investigation of superconducting ternary hydrides in Ca–Y–H system under high pressures. Modern computational chemistry methods, including the evolutionary algorithm USPEX and Phonopy package, were employed to examine the thermodynamic and dynamic stability of the obtained structures, taking into account the energy of zero-point vibrations. Electronic density of states and band structures of the predicted hydrides were analyzed using VASP. Matrix elements of electron-phonon interaction were calculated with Quantum ESPRESSO to evaluate the superconducting properties of clathrate Ca–Y hydrides through the numerical solution of isotropic Migdal–Eliashberg equations.

The results predict ternary thermodynamically and dynamically stable, as well as metastable, Ca–Y–H hydrides at pressures of 150–400 GPa. These hydrides consist of characteristic CaH_6 ¹ and YH_6 ², CaH_9 ¹ and YH_9 ² polyhedra. For the superhydrides based on CaH_6 – YH_6 , a critical temperature T_c (Eliashberg) = 200–240 K is predicted at pressures of 180 and 200 GPa. The P - $6m2$ – CaYH_{18} , composed of CaH_9 and YH_9 polyhedra, exhibits a superconducting temperature range from 282 to 303 K at a pressure of 300 GPa.

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The work was carried out with the financial support of Russian Science Foundation, grant 19-72-30043, grant 21-73-10261.

THERMODYNAMIC PARAMETERS OF PROTOLYTIC AND COORDINATION EQUILIBRIA IN SOLUTIONS OF SOME AMINOACIDS AND COMPLEXONES

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This work presents results of potentiometric, spectrophotometric and calorimetric investigations of the acid-base interaction and magnesium(II), calcium(II), zinc(II), cadmium(II), copper(II), nickel(II), cobalt(II), manganese(II) complexation processes in solutions of L-alanine, L-serine, L-homoserine, D,L-threonine, D-asparagine, L-aspartic, L-glutamic, glycyl-L-glutamic, glycyl-L-aspartic, ethylenediamine-N,N'-disuccinic, ethylenediamine-N,N'-diglutaric, ethylenediamine-N,N'-bis-(α -propionic), ethylenediamine-N,N'-bis-(β -hydroxy- α -propionic), N-methylimino-N,N'-diacetic, N-(β -hydroxyethyl)-ethylenediamine-N,N',N'-triacetic, ethylenediamine-N,N,N',N'-tetrapropionic, ethylenediamine-N,N'-diacetic-N,N'-dipropionic, ethylene-diamine-N,N,N',N'-tetraacetic, 2-hydroxypropylene-1,3-diamine-N,N,N',N'-tetraacetic, trimethylenediamine-N,N,N',N'-tetraacetic, tetramethylenediamine-N,N,N',N'-tetraacetic and hexamethylenediamine-N,N,N',N'-tetraacetic acids.

Thermodynamic parameters ($\log K$, ΔG , ΔH , ΔS) for the relevant equilibria have been determined at 298.15 K and ionic strength values from 0.1 up to 1.5 M. The results obtained were compared with the reference data on some related aminocarboxylates (amino acids, monoamine complexones, dipeptides). The influence of background electrolyte character and concentration on the protolytic and coordination equilibria was under consideration. The standard thermodynamic parameters have been evaluated for the corresponding reactions. A plausible explanation of changes in these quantities has been suggested in view of the metal ion and ligand structures (type of coordination, denticity, presence of hydrophobic and hydrophilic fragments, solvation features of the zwitter ions).

This research was funded by the Ministry of Science and Higher Education of the Russian Federation in accordance with a state assignment (project FZZW-2023-0010).

REGIO- AND DIASTEREOSELECTIVE SYNTHESIS OF α -AMINO ACID DERIVATIVES STARTING FROM NI(II) COMPLEX OF GLYCINE

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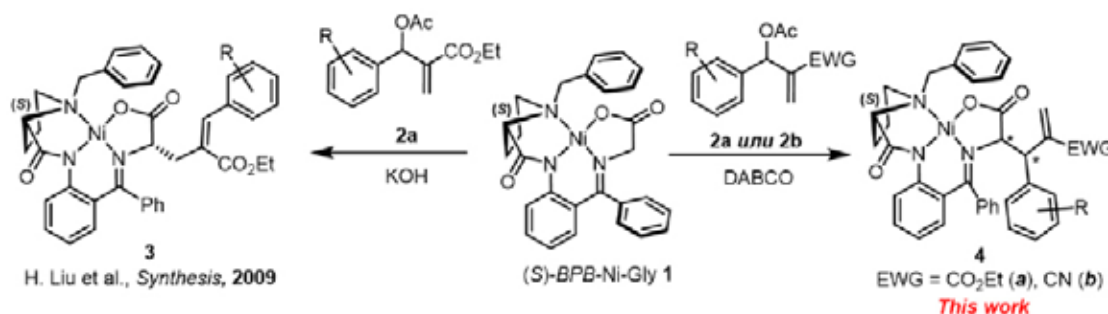
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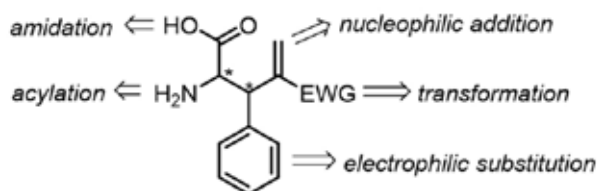
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The synthesis of new chiral compounds is a significant challenge in modern chemistry due to the difficulty of their preparation. Their widespread use in biochemistry, medicinal chemistry, and pharmaceutical chemistry demonstrates their significant importance.¹ In particular, derivatives of glutamic acid are structural components of various types of glutamate receptors.

We have developed a method for the regio- and diastereoselective addition of Morita–Baylis–Hillman acetate **2** to the glycine Ni(II) complex **1** (Scheme).



Depending on the nature of the base, regioselective formation of either complex **3**² or **4** occurs. Products **4** are obtained in yields of 70–92% and with diastereoselectivities of 5:1 and have a high potential for further modification (Figure).



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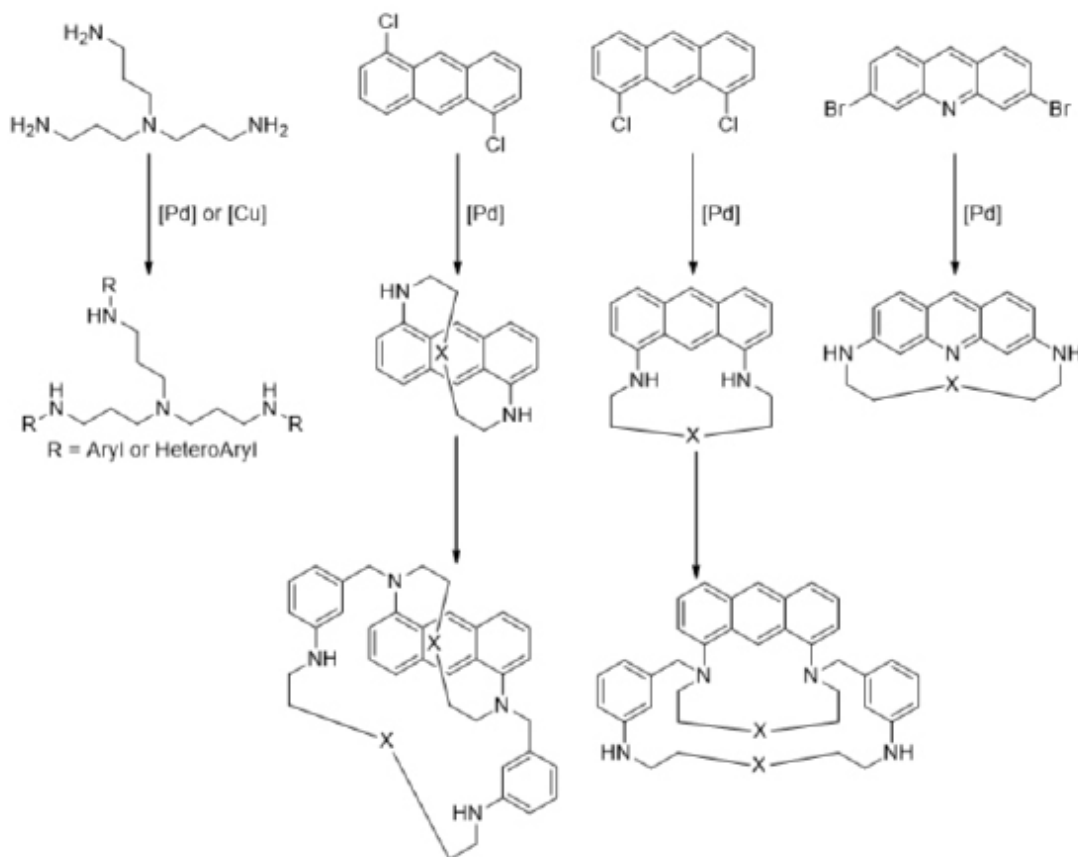
Pd AND Cu-CATALYZED AMINATION IN THE SYNTHESIS OF FLUORESCENT DETECTORS – POTENTIAL CHEMOSENSORS

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An actual problem of modern chemistry is the search for highly sensitive and reliable methods for detecting various charged and neutral analytes, such as metal cations, anions, and polar organic molecules. One of the most effective methods employs the coordinating abilities of compounds with fluorescent properties, which provide changes in absorption and emission spectra during complexation. This approach has been actively developed in the Laboratory of organoelement compounds of the Department of Chemistry of the Lomonosov MSU.

In this work, various fluorescent N-aryl derivatives of branched structure based on tris(3-aminopropyl)amine, as well as series of macrocyclic and macrobicyclic derivatives comprising 1,5- and 1,8-diaminoanthracene and 3,6-diaminoacridine moieties with various endocyclic oxadiazine and polyamine structural fragments were synthesized and their detecting ability was studied. Many of the obtained compounds showed optical response towards various metal cations, such as Cu^{2+} , Zn^{2+} , K^+ , In^{3+} , Cr^{3+} , Al^{3+} , Ga^{3+} .



FORMATION OF A TRANSITION PHASE STATE IN THE THIN LAYERS OF ORGANIC SYSTEMS

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The formation of a phase state that has a cluster shape and combines the properties of the liquid and solid phases was discovered inside thin layers in the near-surface area of the metal-complex catalysis.¹

In the presented work, the formation of a transition phase state (TPS) near a solid surface for organic systems, in which the spectral characteristics of the gas and liquid phases appear, was discovered for the first time. Several groups of organic liquids with different mechanisms of intermolecular interaction were considered, including chloroalkanes, compounds with the general formula CH_3X , where $\text{X} = \text{Br}, \text{I}, \text{CN}, \text{OH}, \text{O}=\text{CCH}_3$, compounds with aromatic properties: C_6H_6 , $\text{C}_5\text{H}_5\text{O}$, $\text{C}_5\text{H}_5\text{S}$, $\text{C}_6\text{H}_6\text{N}$, as well as group analogues in the Periodic Table of chlorine-substituted methane – chlorosilanes.

It was found that when the thin layers are generated in the near-surface area, bands are simultaneously observed in the IR spectrum that relate to vibrations of an unbound molecule (gas phase) and to a system of bound molecules (liquid phase). Since in the IR spectrum with a thickness of the measured layer of 1 mm, bands of the equilibrium gas state cannot be observed due to its low intensity, the observed absorption indicates the formation of a transition molecular system. The relationship between phase properties can change over time and under the influence of temperature.

The cluster structure of the TPS was confirmed within the framework of *ab initio* quantum chemical calculations using the density functional theory, which also considers the dispersion interactions.

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This work was supported by the Ministry of Science and Higher Education of the Russian Federation as part of the scientific project No. FSWR-2022-0008.

SYNTHESIS AND OPTICAL PROPERTIES OF PLASMONIC CORE/SHELL/FLUOROPHORE NANOSTRUCTURES WITH CONTROLLED EMISSION

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Recently, a fairly large number of works have appeared on the study of the enhanced fluorescence effect of dyes near plasmonic nanoparticles, as well as its use for solving practical problems. It is shown, in particular, that the magnitude of this effect strongly depends on the distance between the plasmonic nanoparticle and the fluorescent molecule, the degree of their optical coupling, and the quantum yield of the dye.

At the same time, a number of questions related to the synthesis of plasmonic particle/fluorophore structures and the control of their emission remain open. First of all, we are talking about understanding the features of nonradiative resonant energy transfer in such systems and evaluating the possibility of creating "cascade" structures using several fluorophores of different nature.

In this research, an attempt is made to answer some of these questions using model spherical composite nanoparticles (CNPs) with a gold core and an organosilica shell containing a fluorophore. The main results of the work are as follows.

The effect of the distance between fluorophore molecules in the shell of plasmonic CNP on their radiative properties is analyzed. At the same time, two different approaches to the synthesis of such particles based on the introduction of a dye into the reaction system during shell growth or its chemisorption at the end of this process are compared.

Systematic information has been obtained on the features of embedding two dyes of different nature into the CNP shell (including those capable of interacting by the donor-acceptor mechanism) and the main ways to control the optical properties of such structures have been determined.

THE LATTICE EFFECTS ON THE SUPRAMOLECULAR STRUCTURE AND MAGNETIC PROPERTIES OF THE BICOMPONENT $[\text{Mn}^{\text{III}}(5\text{-Hal-sal}_2\text{323})]_2[\text{Re}^{\text{IV}}\text{Cl}_6]$ COMPLEXES

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The cationic complexes of Mn(III) with the 5-Hal-sal₂323 (Hal = Cl, Br, F) ligands and a paramagnetic doubly charged counterion $[\text{ReCl}_6]^{2-}$ have been synthesized: $[\text{Mn}(5\text{-Cl-sal}_2\text{323})]_2[\text{ReCl}_6]$ (**1**), $[\text{Mn}(5\text{-Br-sal}_2\text{323})]_2[\text{ReCl}_6]$ (**2**) and $[\text{Mn}(5\text{-F-sal}_2\text{323})]_2[\text{ReCl}_6]$ (**3**). Their crystal structures and magnetic properties have been studied. The isostructural two-component ionic compounds (**1**) and (**2**) show a thermally induced spin transition at high temperature associated with the cationic subsystem and a field-induced frequency dependent *ac* magnetic susceptibility at low temperature, associated with the anionic subsystem. Compound **3** has the same composition as **1** and **2**. A study of the dc and ac magnetic properties showed that the complex **3** exhibits no spin transition and field-induced single-ion magnetism. To understand the reasons for such a strong difference in the properties of the 5F and 5Cl/Br hybrid systems, quantum-chemical calculations of $[\text{Mn}^{\text{III}}(5\text{-Hal-sal}_2\text{323})]$ cations. It was established that the nature of the halogen in the 5-position of the phenyl ring has no effect on the value of the splitting between the triplet (S=1) and quintet (S=2) states of the complexes compared. This means that the main factor determining the stabilization of spin states and the character of spin transformations in $[\text{Mn}(5\text{-Hal-sal}_2\text{323})]^+$ complexes is the crystal packing. The stabilization of the high-spin state and the suppression of single-ion magnetism in the F-substituted complex are associated with strong π - π stacking between the phenyl rings of Mn cations and shortened Mn...Re and Re...Re distances, respectively. Magnetic data correlate well with the results of X-ray analysis.

Until now, only one case of the manifestation of single-ion magnetic behavior of the $[\text{Re}^{\text{IV}}\text{Cl}_6]^{2-}$ anion has been known in the literature.¹ The compounds **1** and **2** are the first examples of the coexistence of spin crossover and field-induced slow magnetic relaxation in the family of known $[\text{Mn}^{\text{III}}(\text{sal}_2\text{323})]$ cationic complexes with various counterions.

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Acknowledgments: The work was carried out on the topic of the State assignment for FRC PCP MC RAS, state registration number 124013100858-3.

SERUM ALBUMINS FIBRIL FORMATION IN THE PRESENCE OF LIGANDS WITH DIFFERENT AFFINITY

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Amyloid fibrils are protein aggregates with an ordered cross-beta structure. Studying the influence of different substances on the process of fibril formation is an urgent task associated with the search for compounds with anti-amyloid activity and their possible use for the treatment of currently incurable diseases, such as Alzheimer's disease and others.

In this work, fibril formation of serum albumins from bovine and human organisms was studied. Fibrils were prepared by incubating protein solutions at elevated temperature with the addition of varying amounts of substances with different affinities for albumin. Using the method of differential scanning calorimetry, albumin denaturation curves were recorded in the presence of the same substances and the fraction of the denatured form of the protein was determined at the incubation temperature.

Analysis of the obtained kinetic curves of fibril formation showed that the process is of first-order with respect to the protein. The final yield of fibrils in the absence of ligands is also proportional to the initial protein concentration. In the presence of high-affinity ligands, which shift the denaturation peak to a high-temperature region, a decrease in the yield of fibrils and their growth rate is observed. In this case, the initial growth rate of fibrils is directly proportional to the fraction of the denatured form of albumin, and their final yield shows a pronounced nonlinear correlation with this value.

Hence, compounds that bind tightly to the native form of the protein effectively inhibit fibril formation. This is due to a thermodynamic factor - a decrease in the equilibrium fraction of the denatured form of the protein involved in the process of fibril growth, as well as a shift in the equilibrium between fibrils and monomeric protein, which determines the final yield of fibrils. Such substances may become promising inhibitors of amyloid aggregation of globular proteins. The differential scanning calorimetry method can be used for their identification and screening.

The research was carried out with the financial support of the RSF, project No.23-23-10084.

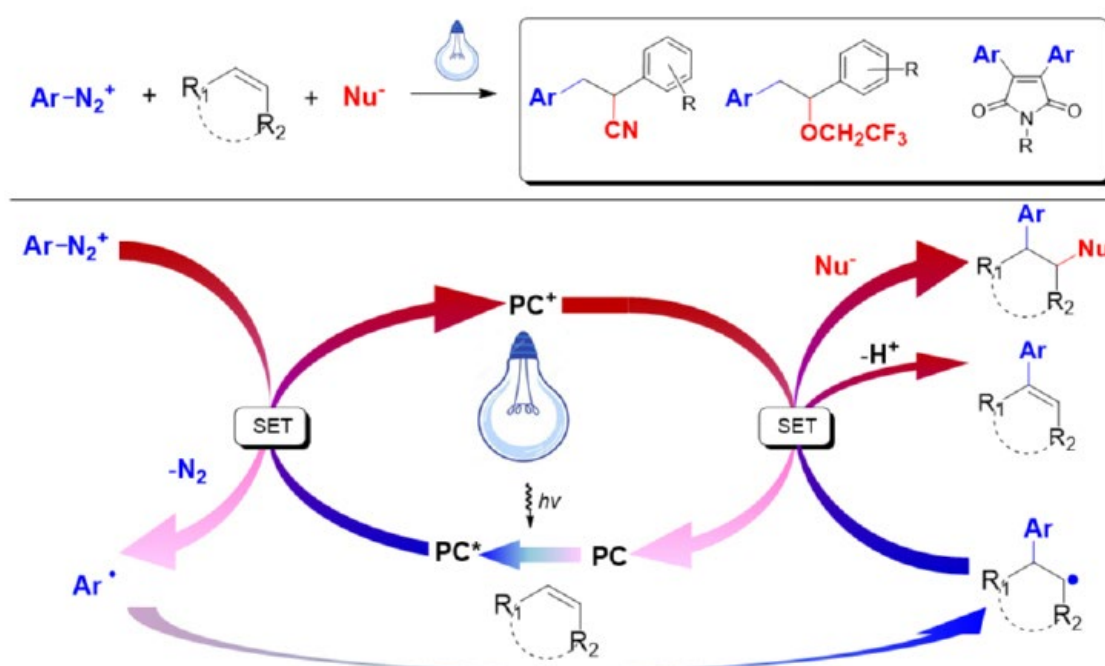
RADICAL BIFUNCTIONALIZATION OF OLEFINS UNDER VISIBLE LIGHT IRRADIATION

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Bifunctionalization of olefins is a convenient method for preparing sophisticated molecules, since it allows the introduction of two different substituents into the structure of a molecule in one step. In recent years, photocatalytic methods have been actively used in this area, which allow radical reactions to be carried out under mild conditions under visible light irradiation and use a wider scope of substrates compared to classical approaches.

In this work, the photoredox-catalyzed radical arylation reaction of various styrenes and maleimides with diazonium salts was studied (Meerwein reaction, Scheme 1).



Scheme 1. Mechanism of the photoredox-catalyzed Meerwein reaction.

Conditions for the bifunctionalization of styrenes with diazonium salts using cyanide anion and trifluoroethanol as nucleophile under visible light irradiation in the presence of photocatalyst have been found. It was also revealed that photoinduced diarylation of maleimides can be performed under soft conditions without photocatalyst, which makes it possible to obtain diaryl-substituted maleimides, including biologically active compounds precursors.

The work was financially supported by the Russian Science Foundation (grant no 24-43-00069).

RATIOMETRIC SINGLET OXYGEN SENSOR BASED ON BODIPY-DPA DYAD

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Compounds based on 9,10-diphenylanthracene (DPA) **1** (Fig. 1, A) are often used in biological research, due to their optical properties: photostability, high quantum yield and high extinction coefficient. It was found that singlet oxygen (¹O₂) effectively binds to 9,10-diphenylanthracene **1** (Fig. 1, A)¹. On account of it DPA derivatives can be exploited as sensors for detection of ¹O₂.

BODIPY **3** (Fig. 1, B) and many of its derivatives are used as fluorescent dyes with unique properties: high fluorescence quantum yield, high solubility in many solvents, as well as low toxicity to tissues².

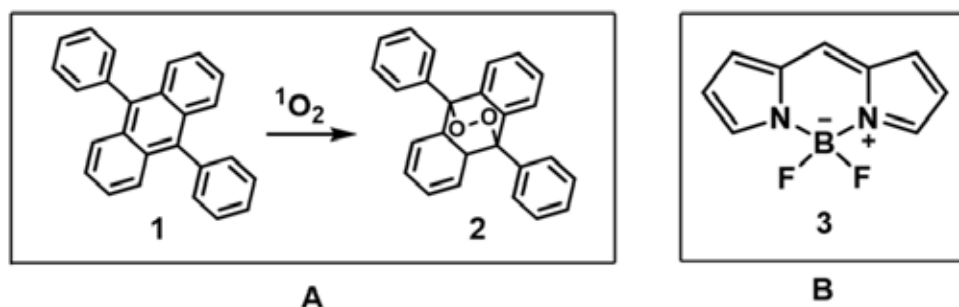


Figure 1. A - the interaction of 9,10-diphenylanthracene **1** with singlet oxygen.
B - Chemical structure of BODIPY **3**

In the present work, a BODIPY-DPA dyad was synthesized. In this dyad, the DPA unit acts as a highly specific oxygen sensor, whereas BODIPY acts as a reference fluorophore. This allows the BODIPY-DPA dyad to be used as a ratiometric sensor of singlet oxygen

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THE EFFECT OF ELECTRON IRRADIATION ON THE INITIATION OF THE RELAXATION PROCESSES IN ALUMINUM HYDRIDE CRYSTALS

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Aluminum hydride is a high perspective compound for use in nuclear and rocket engineering due to its high volumetric and gravimetric hydrogen densities. It is of interest to study changes in the physical-chemical properties of the aluminum hydride crystals exposed to ionizing radiation. Under irradiation, the factors that contribute to the appearance of an abnormal changing the dielectric properties of α -modification of AlH_3 into the frequency range of more than 5 MHz are partial covalence of the $\text{Al}\cdots\text{H}$ bond and the relatively low decomposition temperature of AlH_3 .¹

In this research work, the influence of impurities (γ -modification of AlH_3 and metallic aluminum) on the dielectric characteristics of α -modification of aluminum hydride AlH_3 arising from irradiation with electrons with an energy of 7 MeV was studied by methods of dielectric spectroscopy, potentiometric titration, scanning electron spectroscopy and X-rays phase analysis. It was found that γ -modification of AlH_3 , if its content in α -modification of AlH_3 is 20 wt.%, completely suppresses the occurrence of Debye type relaxation process in the frequency range of an electric field of more than 1 MHz caused by exposure to electron irradiation with the absorbed doses up to 50 kGy at the temperature of 293–298 K. Alternatively, the presence of metallic aluminum in the crystals of α -modification of AlH_3 leads to the appearance of dielectric relaxation, moreover, with an increase in the content of metallic aluminum from 1 to 7 wt.% the maximum of dielectric losses is shifted to the lower frequency range.

The reasons for the appearance of an abnormal frequency dispersion of the dielectric constant as a result of the relaxation process in α - AlH_3 are discussed, which is assumed to be associated with the possibility of formation of dipoles arising from a violation of the symmetry of hexagonal elementary cells under the influence of ionizing radiation.

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ELECTROCHEMICAL INVESTIGATION ON INTERACTION OF ANTIOXIDANT FLAVONOIDS WITH DNA

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The study of the interaction of many naturally occurring antioxidants with DNA is an active area of research in chemistry and biology, which leads to the understanding of the interaction of antioxidants with DNA and, as a result, to the development of new effective drugs targeted to DNA. Due to the central role and complex structure of dsDNA, different ways of binding antioxidants to DNA are possible.

In this study, plant-derived polyphenols - flavonoids (quercetin, rutin, and morin) were used as ligands, which have a wide range of biological activity.

The aim of the work is to study the different modes interaction and to determine binding parameters (K - binding constant and n - number of bases corresponding to one site of binding) of selected flavonoids with DNA using square-wave voltammetry method. To determine the binding parameters, the binding curve of ligands with DNA was transformed into Scatchard coordinates according to the neighbor exclusion model of McGhee and von Hippel¹.

Table 1. Value of binding parameters (K and n) of flavonoids with DNA.

Flavonoid	$K_1 \text{ M}^{-1}$	$K_2 \text{ M}^{-1}$	n_1	n_2
Rutin	4.65×10^5	6.09×10^3	4-6	1-2
Quercetin	9.58×10^5	4.06×10^4		
Morin	9.79×10^5	4.49×10^4		

Thus, different types of binding of flavonoids with DNA were quantitatively characterized and interpreted.

It has been identified that the values of K_1 and n_1 correspond to strong intercalative interactions, while K_2 and n_2 correspond to weak electrostatic interactions.

Regularities in the variation of quantitative binding parameters of selected flavonoids with DNA have been identified depending on the molecular structure of bioflavonoids.

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FEATURES OF FORMATION OF [2+1] CARBONYL-DIKETONATE COMPLEXES OF TECHNETIUM (I)

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Recently, the diketonate-phosphine system has been actively studied for the introduction of a technetium into an organic molecule in the form of $\text{Tc}(\text{CO})_3$ fragment. For this purpose the water ligands in $[\text{Tc}(\text{CO})_3(\text{H}_2\text{O})_3]^+$ precursor are substitute by three dentate- of combination of mono and bidentate ligands (2+1 approach). One of the promising systems for the latter approach are acac-PPh₃, acac-PPh₂Cy, acac-PCy₂, hfa-PPh₃. Our preliminary studies have shown that complexation with these systems can be complicated by formation of side dicarbonyl complexes.

The aim of the work is to find out to what extent the formation of dicarbonyl complexes depends on the donor properties of the diketonate ligand. In this connection, the following systems were studied: acac-PPh₃, acac-Py, acac-Imd, hfa-PPh₃, hfa-Py, hfa-Imd. Acetylacetone (acac) acts as a strong-donor diketonate ligand, and hexafluoroacetylacetone (hfa) acts as a weak-donor ligand.

We found that the formation of a mixture of dicarbonyl and the target [2+1] tricarbonyl complexes is observed even at the equimolar ratio of acac-PPh₃. Only when hexafluoroacetylacetone is used instead of acetylacetone the pure [2+1] complex is formed.

If the monodentate ligand exhibits weak π -acceptor properties or pure δ -donor properties (Py, Imd), no dicarbonyl technetium complexes are also formed.

Thus, the use of diketonate ligands in the framework of the [2+1] approach for introduction of $\text{Tc}(\text{CO})_3$ fragment into biomolecules requires combination of weakly donating diketonate ligands and monodentate ligands with weak π -acceptor properties or pure π -donor properties.

The study was financially supported by the Russian Science Foundation (project no. 22-13-00057).

EXPLORING THE IMPACT OF CONCENTRATION AND EXPOSURE TIME ON CYTOTOXIC ACTIVITY OF IMIDAZOLIUM IONIC LIQUIDS

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Ionic liquids (ILs) find wide applications in many fields of modern science and industry, including interphase catalysis, organic synthesis, electrochemistry, biotechnology, pharmaceuticals, analytical chemistry, extraction, etc.¹ For a long time, ILs had been considered low-toxic compounds; however, according to recent studies, ILs often can be more toxic than traditional organic solvents.² Despite active research on the effects of ILs on various biological objects, the mechanisms of their toxicity remain poorly understood which hinders the development of safe compounds of this class.

The aim of this study is investigating the cytotoxic effects of imidazolium ILs on normal and tumor cell cultures. Three common imidazolium ILs with side alkyl chains of different lengths (2, 4, or 16 carbon atoms) in the cation were examined. The mechanism of cell death induced by these substances was established, and the dependence of cytotoxicity on the exposure time was comprehensively studied for the first time.

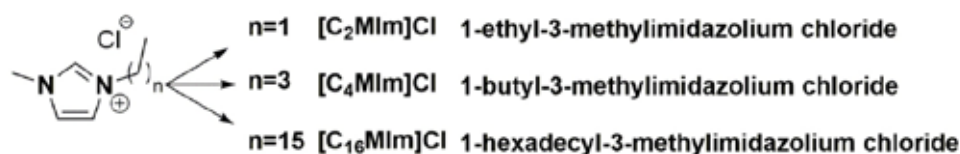


Figure 1. Ionic liquids studied in this work.

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PREDICTING CARBON DIOXIDE CAPTURE BY DEEP EUTECTIC SOLVENTS

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Industrial growth significantly increases the demand for energy, which in turn leads to the emission of large amounts of greenhouse gases, especially carbon dioxide (CO_2). Current CO_2 capture technologies use different types of solvents, realising both physical and chemical adsorption processes, which in most cases are not characterised by high efficiency. Therefore, the development of new CO_2 capture technologies, including the search for new solvents, is an important aspect in reducing greenhouse gas emissions.

In recent years, deep eutectic solvents (DES) have been widely investigated as potential solvents for CO_2 capture. Unlike volatile organic compounds, DES have many attractive properties such as low vapor pressure, wide liquid state range and easily tunable properties.

The aim of this study was to develop regression models that can predict CO_2 absorption in DES as a function of temperature and pressure. Several global models using nonlinear machine learning techniques to estimate CO_2 uptake were created that can be applied to a wide range of DESs capable of both physical and chemical absorption. The data set for model development consisted of 2505 points for 162 unique DESs. A rigorous "component" validation protocol was shown to provide a more accurate assessment of model performance. Model interpretation was performed using a SHAP approach. A quantitative structure-property relationship model was also created to predict CO_2 solubility in choline chloride-based physical absorbents at low pressures. In this model, the experimental conditions of pressure and temperature were used as independent variables; and the free volume of the liquid was used as a molecular descriptor reflecting the structure features of DES. Evaluation of the model on the test set showed good statistical parameters: $R^2 = 0.90$; RMSE = 0.10; AARD = 4%.

The study was supported by a grant from the Russian Science Foundation No 23-13-00118, <https://rscf.ru/project/23-13-00118/>

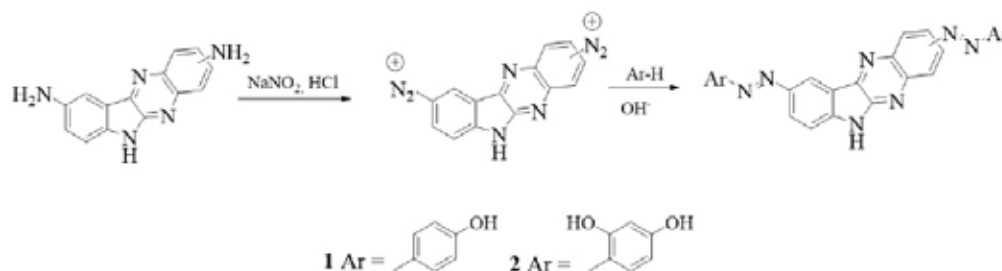
PROSPECTS OF APPLICATION OF HALOCHROMIC DISAZO DERIVATIVES OF 6N-INDOLO[2,3-B] QUINOXALINES IN MEDICAL DIAGNOSTICS

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The halochromic properties of cellulose dressings stained with disazo dyes, which are derivatives of 6H-indolo[2,3-b]quinoxaline, have been studied. Antimicrobial properties, mutagenic, mitosis-modifying and toxic effects of the dyed materials were evaluated in relation to meristem cells of *Allium cepa* (*Allium* test). The absence of growth of microorganisms colonies within the boundaries of the fragment of the stained material in contact with the pre-sown nutrient medium was established. The mutagenic, mitosis-modifying and toxic effects of the dyed materials are comparable to those of materials treated with brilliant green and methylene blue, or are expressed to a lesser extent.



Dyed dressing materials in the conditions of research according to GOST 9733.6 (Method I) showed high color stability to the action of salt solutions imitating sweat and blood plasma.

Dressing materials with reversible color indication, obtained with the use of compound 1, are distinguished by color diversity in a wide range of pH values, and are promising for use in surgery.

The focus of our study is on the color change of the material in the alkaline region, which occurs as a result of the multiplication of pathogens in a clean wound.

The results obtained on the application of dressing material with halochrome dye as an information resource in monitoring the wound process showed high informativeness of this method.

The work was financially supported by RSF, project 23-25-00021

PALLADIUM CARBOXYLATE COMPLEXES CONTAINING HALOALKYL ACIDS ANIONS

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Palladium carboxylate complexes are traditional objects of fundamental coordination chemistry, and also act as precursors of homogeneous and heterogeneous catalysts for transformation processes in organic compounds. The synthesis and study of the structure and properties of new palladium carboxylate complexes is an urgent task of modern chemistry.

Palladium carboxylate complexes containing alkylcarboxylic acid anions have been studied in detail, but there is practically no data on similar compounds with haloalkanoic acid anions. In the present work, we describe binary carboxylates $[\text{Pd}(\text{RCO}_2)_2]_n$ and carbonyl carboxylates $[\text{Pd}(\text{CO})(\text{RCO}_2)]_n$ containing the anions $\text{C}_2\text{F}_5\text{CO}_2^-$ and $\text{C}_3\text{F}_7\text{CO}_2^-$.

The above formulas are assigned to the resulting compounds based on the results of elemental analysis. Using IR spectroscopy, it was shown that all ligands in the resulting complexes have bridging coordination. The frequencies of stretching vibrations of carbonyl groups lie in the range of $2000\text{--}1900\text{ cm}^{-1}$, and the difference in the frequency of asymmetric and symmetric stretching vibrations of carboxylate groups is $200\text{--}300\text{ cm}^{-1}$. The assignment of bands in the spectra is consistent with the results of quantum chemical modeling within the framework of density functional theory (Priroda v. 19 software package, PBE/L11). The applicability of the chosen calculation method is confirmed by the coincidence of the calculated and experimental structural and spectral characteristics for the obtained compounds and previously characterized trifluoroacetate complexes. Based on the totality of experimental and theoretical data, the resulting complexes can be assigned a structure with bridging coordination of all ligands. For binary carboxylates, trimeric or polymeric structures are possible; for carbonyl carboxylates, the most likely is a 4-nuclear structure.

The work was carried out with the support of the Russian Science Foundation – project No. 23-73-00123.

PALLADIUM CARBOXYLATE COMPLEXES CONTAINING BENZOIC ACIDS ANIONS

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Palladium carboxylate complexes are traditional objects of fundamental coordination chemistry, and also act as precursors of homogeneous and heterogeneous catalysts for transformation processes in organic compounds. Synthesis and study of the structure and properties of new palladium carboxylate complexes is an urgent task of modern chemistry.

Palladium carboxylate complexes containing anions of alkyl and, to a lesser extent, alkenylcarboxylic acids have been studied in detail, while data on the corresponding compounds with benzoic acid anions are practically absent. In the present work, we describe a wide range of binary carboxylates $[\text{Pd}(\text{RCO}_2)_2]_n$ containing anions of trifluoromethylbenzoic and halobenzoic acids and carbonylcarboxylates $[\text{Pd}(\text{CO})(\text{RCO}_2)]_n$ containing anions of trifluoromethylbenzoic acids (Fig. 1).

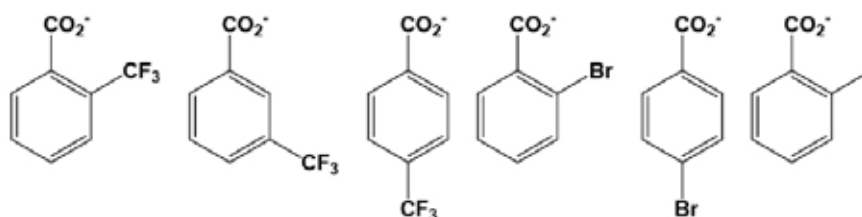


Figure 1. Anions of trifluoromethylbenzoic and halobenzoic acids.

The complexes were characterized by elemental analysis, IR and NMR spectroscopy, and quantum chemical modeling was performed within the framework of density functional theory (Priroda v. 19, PBE/L11 software package). Based on the totality of experimental and theoretical data, the resulting complexes can be assigned a structure with bridging coordination of all ligands. For binary carboxylates, trimeric or polymeric structures are possible; for carbonyl carboxylates, the most likely is a 4-nuclear structure.

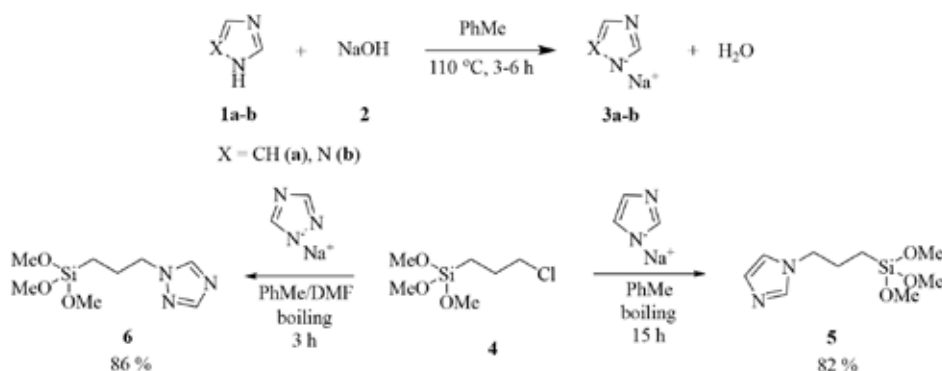
The work was carried out with the support of the Russian Science Foundation – project No. 23-73-00123.

PRACTICAL SYNTHESIS 1-(3-(TRIMETHOXYSILYL) PROPYLAZOLES

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Carbofunctional trialkoxysilanes play a key role in the production of materials using sol-gel technologies, siloxane polymers, and surface functionalization of oxide materials. Using them, it is possible to obtain materials for separation and concentration technologies, heterogeneous catalysts, and coatings. We have proposed an effective one-pot preparative synthesis of 1-(3-(trimethoxysilyl)propyl)-1H-imidazole^{1,2} **5** and 1-(3-(trimethoxysilyl)propyl)-1H-1,2,4-triazole **6**, based on metalation of azoles by the action of sodium hydroxide in toluene medium followed by alkylation with (3-chloropropyl)trimethoxysilane, providing a yield of target substances of 82% and 86%, respectively.



It should be noted that the alkylation of the Na derivative of imidazole reacts in a toluene medium, while the alkylation of the Na derivative of 1,2,4-triazole is possible only in a toluene-dimethylformamide medium (1:1).

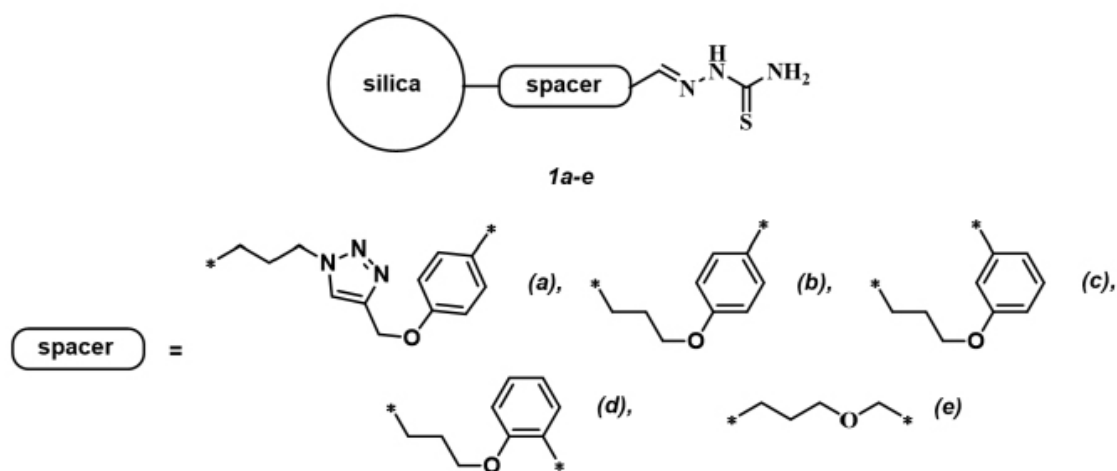
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Konshin V.V., Konshina Dzh.N.

Modification of various matrixes with N,S-ligands creates the opportunity to synthesize effective materials for the concentration of transition metals. One of the simplest and most accessible N,S-ligands is thiosemicarbazide, which by itself and in the form of derivatives effectively coordinates many metals, which is used in various methods for the isolation and determination of a wide range of elements. We have obtained a series of materials 1a-e based on thiosemicarbazone-silica gels^{1,2}, which are formed by condensation of aldehyde-silica gels³ with thiosemicarbazide.



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ELECTRON TRANSPORT AND THERMOELECTRIC PROPERTIES IN (Pb,Ho)-MODIFIED MANGANITES WITH PEROVSKITE-TYPE STRUCTURE

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Electron-doped perovskite-type $\text{CaMnO}_{3-\delta}$ manganites constitute promising materials for all-oxide thermoelectric generators (TEG) for converting heat into electricity. New manganites $\text{Ca}_{0.5}\text{Sr}_{0.45-x}\text{Pb}_{0.05}\text{Ho}_x\text{MnO}_{3-\delta}$ ($0.05 \leq x \leq 0.20$) with orthorhombic (SG *Pbnm*) perovskite-type structure have been synthesized. The thermoelectric properties of these compounds depend on the combination of holmium content and oxygen non-stoichiometry, as both factors result in Mn^{3+} ion formation, causing n-type conductivity. The replacement of Sr by heavier Pb and Ho atoms contributes to the low thermal conductivity values and the increase in holmium concentration shifts the onset of oxygen removal from the manganites towards the high temperature range. The n-type conductivity is explained by an adiabatic model with small radius polaron hopping. The increase in the absolute value of the Seebeck coefficient with rising temperature is the result of the decrease in the concentration of Mn^{3+} ions caused by their disproportionation into Mn^{2+} and Mn^{4+} ions. The equilibrium constants of the disproportionation reaction, carrier concentration and mobility have been derived from the temperature dependencies of $S(T)$ and $\sigma(T)$ in the conditions when $\delta \approx 0$. The content of Mn^{3+} ions is close to the value of x in $\text{Ca}_{0.5}\text{Sr}_{0.45-x}\text{Pb}_{0.05}\text{Ho}_x\text{MnO}_{3-\delta}$ near the ambient temperature. The mobility of the carriers has been demonstrated to decrease due to the increase in their concentration. The best values of the power factor ($S^2\sigma$) up to 1000 K have been determined for the $\text{Ca}_{0.5}\text{Sr}_{0.3}\text{Pb}_{0.05}\text{Ho}_{0.15}\text{MnO}_{3-\delta}$ manganite. This composition has the highest ZT values together with low thermal conductivity in the $\text{Ca}_{0.5}\text{Sr}_{0.45-x}\text{Pb}_{0.05}\text{Ho}_x\text{MnO}_{3-\delta}$ series over a wide temperature range, which is an important factor for the applications in all-oxide TEGs.

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PHOTOCHEMISTRY OF NEW RUTHENIUM NITROSYLS WITH TRANS NO-RU-F COORDINATE

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Photochemical transformations of ruthenium nitrosyl complexes in solid phases are accompanied by photoisomerization of the nitrosyl group (Ru-NO) with the formation of two new metastable bond isomers Ru-ON (MS1) and Ru- μ_2 (NO) (MS2). Switching between isomers can be realized photochemically, in addition, a return to the ground state can be carried out with increasing temperature. The achieved population and thermal stability of the resulting isomers are determined primarily by the ligand environment of the ruthenium center. MS stability temperatures have previously been shown to correlate with the electronegativity of the trans ligand at the position to NO. Based on this, the most thermally stable bond isomers should be observed for nitrosyl complexes with the trans-NO-Ru-F coordinate.

Simple methods have been proposed for the synthesis of $[\text{RuNOL}_x\text{F}]$ complexes with various N-donor ligands (L), starting from hydroxo- or nitrate-complexes as precursors. The formation of bond isomers was confirmed by NMR and IR spectroscopy, and the activation parameters of the transitions were determined using DSC or IR spectroscopy. The two-photon mechanism of formation of the MS1 bond isomer has been experimentally confirmed. It has been shown that the thermal stability of photoinduced bond isomers in complexes with the trans coordinate NO-Ru-F is the highest among all known nitrosyl complexes of transition metals, in particular for various salts of the complexes $[\text{RuNO}(\text{Py})_4\text{F}]^{2+}$ and $[\text{RuNO}(\text{NH}_3)_4\text{F}]^{2+}$ the stability temperatures for MS1 are in the range of 290-310 K.

This work was supported by the Russian Science Foundation project 22-43-09001.

DEVELOPMENT OF CURCUMIN-LOADED PLGA NANOPARTICLES USING FACTORIAL DESIGN OF EXPERIMENT

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Due to the large number of parameters affecting the technological process, the conditions for the production of nanoparticle-based drug delivery systems (DDS) are usually selected empirically. The development process can be optimized using methods of design of experiments, which allow identifying the most significant parameters (factors) affecting the properties of the product¹.

The aim of this work was to obtain PLGA nanoparticles with high curcumin (Cur) loading. The NPs were prepared by the nanoprecipitation method; the following parameters were varied: polymer structure (i.e. lactic and glycolic acid monomer ratio [LA/GA], end groups structure [EG], molecular weight [Mw]), polymer and curcumin concentrations (C_{PLGA} and C_{Cur}), organic phase to aqueous phase addition rate (v), and stirring rate (ω).

Fractional factor design of the experiment was used to identify the process parameters exerting the most considerable influence on the encapsulation efficiency (EE) and the drug content in the nanoparticles (DL) and to determine the optimal conditions for nanoparticle preparation. This method enables evaluating of the influence of > five parameters (factors) and significantly reduces the number of experiments required to select the optimal technique². The factors were varied at 2 levels.

C_{PLGA} and LA/GA ratio were shown to be the main determinants of the EE and DL values, respectively. The method optimization resulted in a significant increase in the encapsulation efficiency (from 16% to 76%) and curcumin content in the nanoparticles (1% to 2%).

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The research was carried out within the state assignment of Ministry of Science and Higher Education of the Russian Federation (project FSSM-2022-0003).

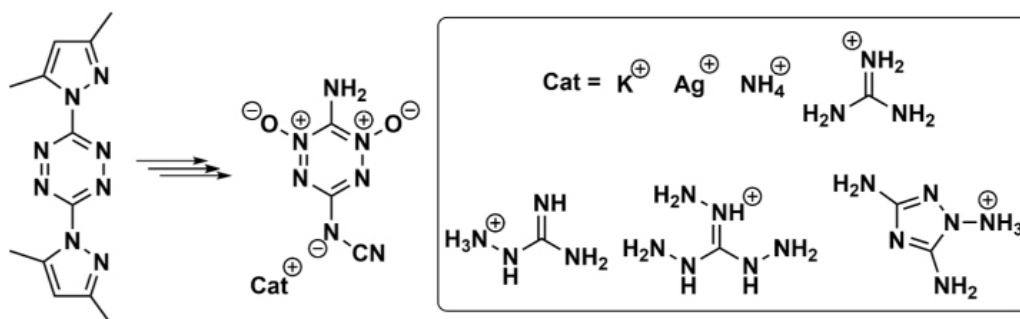
NEW METHODS FOR DIRECT FUNCTIONALIZATION OF THE TETRAZINE CORE

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Despite more than a century of study of s-tetrazine, the current status of this area of organic chemistry is still poorly investigated, contrary to the importance of this heterocyclic fragment in obtaining practically important substances and materials. The key applications of s-tetrazine derivatives include photoactive elements, biological markers, pharmaceuticals and high energetic materials. Creation and study of new molecular systems based on s-tetrazine remains one of the demanded tasks of synthetic organic chemistry.



Scheme 1. General scheme for the preparation of ionic salts of 3-cyanamide-6-amino-1,2,4,5-tetrazine-1,5-dioxide

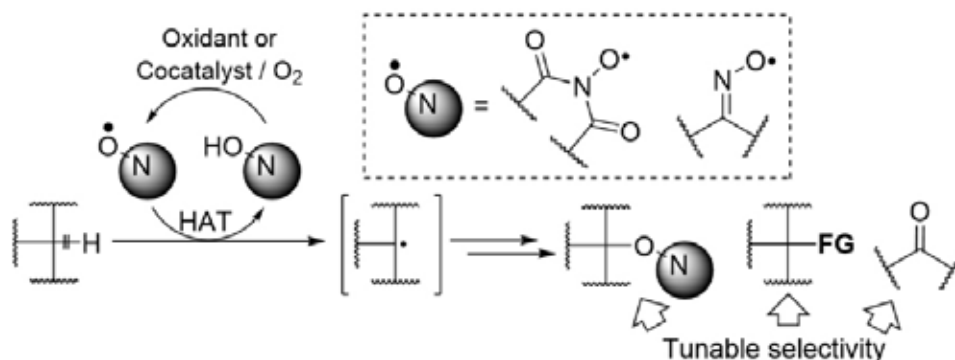
In this work, we have developed an approach to obtain new high-energy salt structures based on s-tetrazine with different cations. Based on successive transformations of the available 3,6-bis(1,5-dimethyl-1H-pyrazol-1-yl)-1,2,4,5-tetrazine, we have prepared energetic structures containing the fragment 3-cyanamide-6-amino-1,2,4,5-tetrazine-1,5-dioxide as an anionic component. The proposed method, unlike the existing ones, has a small number of stages and is characterized by high conversions and yields.

ELECTRON-DEFICIENT N-OXYL RADICALS IN ORGANIC SYNTHESIS

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Electron-deficient N-oxyl radicals are one of the most widely used redox organocatalysts for the selective free radical CH-functionalization of organic compounds.¹ They are formed under mild oxidative conditions from the corresponding N-hydroxy compounds and act as highly efficient hydrogen atom acceptors in C–H bond cleavage:



Depending on the synthesis conditions, N-oxyl radicals can serve for the selective aerobic oxidation of CH-reagents,² for the introduction of various functional groups,^{1,3} or additionally act as an O-components for the oxidative C–O coupling^{1,4,5}. In addition to CH functionalization, N-oxyl radicals are widely used in the radical difunctionalization of C=C bonds.⁵

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The work is carried out with the financial support of the Russian Science Foundation, project 24-43-00111.

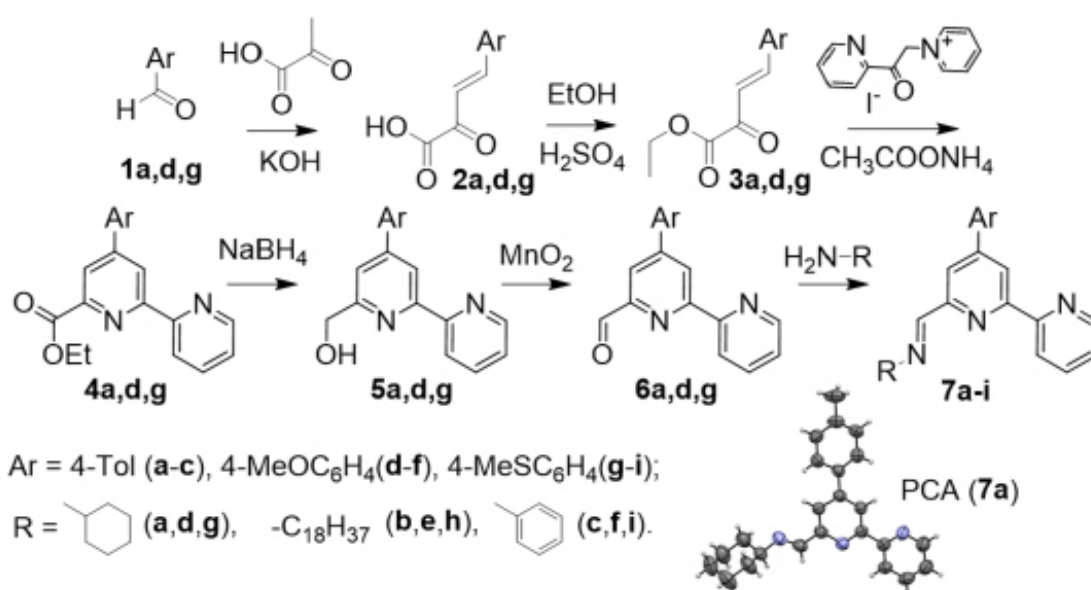
SYNTHESIS AND PHOTOPHYSICAL PROPERTIES OF AZOMETHINES BASED ON 4-ARYL-2,2'-BIPYRIDINE-6-CARBALDEHYDES

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Schiff bases and their metal complexes are of considerable interest due to their catalytic and ferromagnetic properties, as well as their biological activity in a wide range.

We have implemented the synthesis of azomethines based on 4-aryl-2,2'-bipyridine-6-carbaldehyde. For this purpose, the Knoevenagel condensation of aromatic aldehydes **1** and the pyruvic acid salt obtained in situ was realized. Further esterification of acid **2** was allowed to obtain ethyl ether **3**. The construction of the central pyridine ring of compounds **4** was performed using the Kröhnke method. Due to further modifications of the ester group, the corresponding aldehydes **6** were obtained, on the basis of which the corresponding ligands **7** were synthesized. Their structure was confirmed, including XRD analysis data.



Compounds **7** luminesce in acetonitrile solutions, with quantum yields reaching 43%. We also recorded a luminescent response to the addition of zinc(II) cations.

This work was supported by the Ministry of Science and Higher Education of the Russian Federation, Agreement # 075-15-2022-1118 dated 29.06.2022.

SYNTHESIS OF GALLIC ACID DERIVATIVE

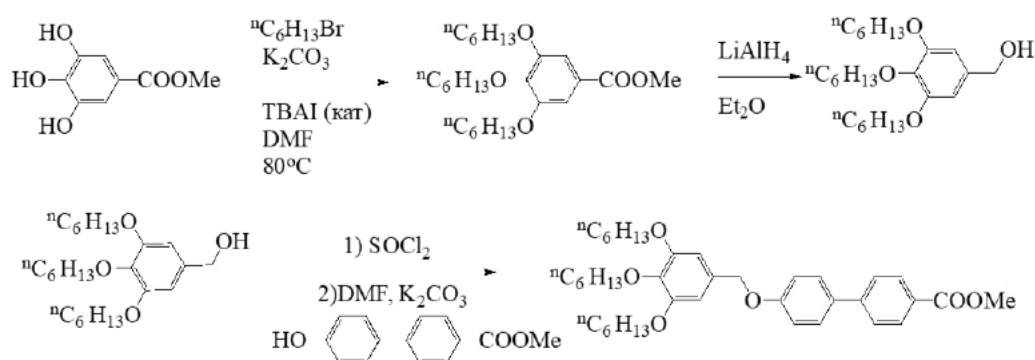
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Gallic acid is a well-known natural phenolic antioxidant that occurs naturally in tea, oak bark, and tanning extracts. This accessible acid is used in the synthesis of dyes and the creation of electrochemical devices. Today, multifunctional derivatives, including those containing flexible fragments of alkylated gallates and rigid biphenyl groups, are of particular importance, because such compounds are used to create liquid crystals and liquid crystalline polymers.

The goal of this work was to develop an effective synthesis of methyl 4'-((3,4,5-tris(*n*-hexyloxy)benzyl)oxy)-[1,1'-biphenyl]-4-carboxylate, (*n*-HexO)₃C₆H₂CH₂O[C₆H₄]₂COOMe.

The target compound was obtained as a result of a three-step synthesis; all synthesis stages are optimized.



At each stage, the compounds were isolated individually and characterized by NMR spectroscopy, mass spectrometry, and IR spectroscopy.

SYNTHESIS OF TRIARYLPHOSPHINES FROM ARYL FLUORIDES AND RED PHOSPHORUS: DFT STUDY

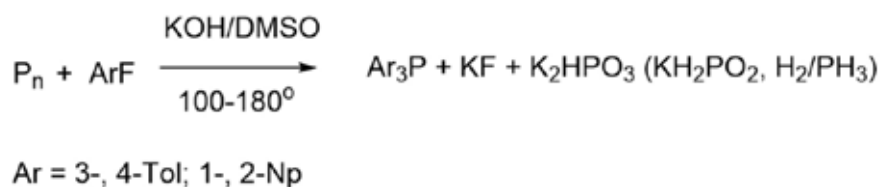
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Tertiary phosphines with sterically hindered aryl substituents and their chalcogenides are widely used for the design of metal complexes exhibiting biological¹, luminescent² and catalytic³ properties. New synthesis methods are being developed, in particular those corresponding to the principles of Green chemistry⁴, due to the high demand for phosphine ligands.



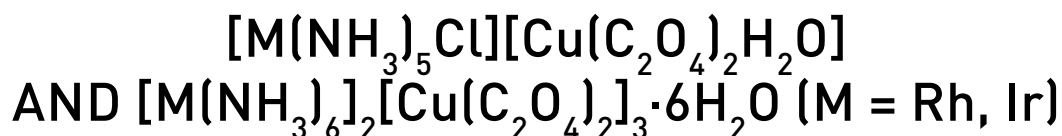
The reactions mechanisms for the production of phosphines with three 3-, 4-methylphenyl and 1-, 2-naphthyl substituents from red phosphorus and aryl fluorides were studied using the methods of quantum chemistry DFT B3PW91/Def2-TZVPP. The structure of reagents and products was established, transition states were localized, energy parameters of all stages were calculated using quantum chemical calculations.

The reaction includes three stages of sequential addition of aryl substituents to phosphorus, which are initiated by the cleavage of phosphorus–phosphorus bonds by the hydroxide anion and proceed according to the mechanism of aromatic nucleophilic substitution. It should be noted that each subsequent transition state is characterized by a lower energy barrier, which is consistent with experimental data on the formation of only triaryl-substituted phosphines⁴.

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SYNTHESIS AND STUDY OF THE THERMAL PROPERTIES OF THE DOUBLE COMPLEX SALTS



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Bimetallic nanoparticles (nanoalloys) have many useful properties, of which catalytic properties are of particular interest. This interest in nanoalloys is due to the synergy of properties, i.e. the properties of bimetallic nanoparticles are often superior to their monometallic counterparts. In addition, the use of nanoalloys can reduce the cost of the resulting catalysts by partially replacing expensive precious metals (which are most commonly used in catalysts) with base metals. There are many methods of producing nanoparticles, one of which is the thermal decomposition of complex precursor compounds. This method has proved to be a promising way of obtaining nanoparticles with specific properties. When planning the synthesis, it is possible to choose the central atoms – metals – and to select ligands that are easily removed during thermal decomposition. The central atoms and the ligand environment influence the composition of the resulting metal products, their structure, and the decomposition temperature. And in thermal experiments, the atmosphere, heating regime, annealing time and temperature can be varied, affecting the size, atomic ordering and morphology of the nanoparticles formed.

In the course of this work the double complex salts $[M(NH_3)_5Cl][Cu(C_2O_4)_2 \cdot H_2O]$ and $[M(NH_3)_6]_2[Cu(C_2O_4)_2]_3 \cdot 6H_2O$ (M = Rh, Ir) were synthesized. The obtained compounds were characterized by a series of physicochemical methods (PXRD, IR spectroscopy, elemental analysis), single crystals were obtained for all compounds and their crystal structure was determined. The formation of metastable solid solutions M_xCu_{1-x} (M = Rh, Ir) was detected during the study of the thermal destruction process of the obtained compounds in a reducing atmosphere by *in situ* and *ex situ* PXRD methods. Thus, for the Rh-Cu system it was possible to obtain a solid solution with a maximum copper content of 28 at.%, and for the Ir-Cu system a series of solid solutions with different Ir:Cu ratios (2:3, 1:1 and 2:1) were obtained.

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<https://rscf.ru/project/21-73-20203/>*

RELATIVISTIC CORRECTIONS THEORY OF HYDROGEN-LIKE SYSTEMS AS THE BASIS FOR CONSTRUCTION FINAL VARIANT PERIODIC SYSTEM D.I. MENDELEEV OF CHEMICAL ELEMENTS

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Development Periodic system of chemical elements D.I.Mendeleev's method is based on solving problems that involve performing rather complex calculations and depends on the form of description of quantum phenomena^{1,2}. Thus, despite the fact that in 1923, regularities were obtained between the radius of the first shell of an atom (*K*-shell) and the charge of the nucleus *Z*, due to a number of unresolved problems of an epistemological nature at that time it was impossible to construct the final version of the Periodic Table of Chemical Elements. The development the theory of hydrogen-like systems, taking into account relativistic corrections to the groundstate *E*, was carried out by Dirac³ using perturbation theory: $E/\mu = -Z^2/2 - Z^4/8c^2$. Here *E* is the energy of a hydrogen-like atom; *μ* – reduced electron mass; *c* – is the speed of light in the atomic coordinate system, equal to 137.03604 atomic speed units. Later, an exact equation was obtained for calculating the energy of a hydrogen-like system in the ground state (the traditional representation of an atomic system is the atomic nucleus and electron shells outside the nucleus)⁴⁻⁶:

$$E/\mu = c\sqrt{c^2 - Z^2} - c^2.$$

The final version of the Periodic Table of Chemical Elements D.I. Mendeleev was proposed by of 137 elements. All elements are placed in eight periods and eight groups. The last three periods – the sixth, seventh and eighth form families consisting of 14 elements, in which 4*f*, 5*f*, 6*f*- subshells are filled. According to the configuration of the electronic shells, the last two elements 136, 137 can be classified as *d*-elements.

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THERMODYNAMICS OF CAVITY FORMATION IN INDIVIDUAL AND MIXED LIQUIDS

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The concept of cavity formation is widely used to explain the solvation properties of solvents, predict solubility, and analyze protein structure. According to this concept, the process of solvation of a substance can be divided into two stages: 1) the formation of a cavity in the solvent and 2) the transfer of a substance from the gas phase into this cavity.

Using test particles insertion method into trajectories obtained by all-atom molecular dynamics, we calculated the thermodynamic functions of cavity formation ($\Delta_{cav}f$) in various individual molecular solvents¹, ionic liquids², aqueous-organic mixtures, and mixtures of solvents with inorganic salts³. It was shown that associated solvents (water, glycerol, ethylene glycol, and formamide) are characterized by higher free Gibbs energies and lower entropies of cavity formation compared to non-associated solvents.

For $\Delta_{cav}f$ in aqueous-organic mixtures, the same patterns are observed as for the thermodynamic functions of solvation of non-polar compounds. It was shown that the weakening of the hydrophobic effect upon addition of an organic solvent is associated with a decrease in $\Delta_{cav}G$ and an increase in $\Delta_{cav}H$ due to the reorganization of the solvent around the cavity.

For protic ionic liquids with nanoheterogeneous structure, the calculated $\Delta_{cav}G$ values are lower compared to ionic liquids that do not have such structure. The cavities formation occurs mainly in the nonpolar domains of ionic liquids.

Increasing the salt concentration in mixtures of solvents with inorganic salts leads to an increase in $\Delta_{cav}G$. This result is consistent with the “salting-out” of low-polar compounds when salt is added to an organic solvent or water.

Thus, the hydrophobic effect and its weakening upon addition of an organic solvent, as well as solvophobic effects in non-aqueous media, can be explained by thermodynamic features of cavity formation.

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CREATION OF NEW FLUORINE-CONTAINING AMINOPHOSPHONATES WITH MULTIFUNCTIONAL ACTION

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One fluorine atom is present in at least 25% of newly developed pharmaceuticals and more than 30% of agrochemicals used in agriculture. The presence of fluorine in an organic molecule leads to increased bioactivity, lipophilicity and increased potential for use in medicinal chemistry and agricultural chemistry.

Previously, we obtained monofluoro-substituted aminophosphonate derivatives that showed local anesthetic and growth-stimulating properties, demonstrating the promise of using this class of compounds for medical as well as agricultural purposes. Synthesized monofluorosubstituted AP at a concentration of 0.001-0.0001% during pre-sowing seed treatment increases the yield of tomatoes by 19%, corn biomass by 21% and potatoes by 24%. The results of biological studies have shown that monofluorosubstituted AP is a low-toxic drug, and its safety indicator is 5.4 times higher than that of lidocaine^{1,2}.

Currently, to enhance bioactivity, work is underway to improve the structure of new trifluoro-substituted heterocyclic α -APs under Kabachnik-Fields condensation conditions.

The addition of 3 fluorine atoms should accordingly increase the bioactivity of the molecules as a whole and lead to an expansion of the list of new aminophosphonates containing fluorine atoms, as well as their complexes with multifunctional action.

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The research was funded by the Science Committee of the Ministry of Science and Higher Education of the Republic of Kazakhstan (Grant No. AP22685628).

GROUP 13 METAL COMPLEXES AS INITIATORS FOR POLYMERIZATION OF CYCLIC ESTERS

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Currently, due to the rapid growth in the production of traditional synthetic polymers due to their chemical inertness, a number of problems arise that are associated with both the depletion of fossil resources and environmental pollution. The detrimental environmental impacts and man-made waste problems of this magnitude have sparked interest in biodegradable and economically feasible alternatives, many of which are derived from renewable sources of raw materials. It is important to improve the characteristics of the resulting biodegradable polymers through their controlled synthesis, which expands subsequent areas of application, namely: in medicine as a suture material, scaffolds for tissue engineering, in pharmaceuticals for use in long-acting drugs. Ring opening polymerization (ROP) of cyclic esters in the presence of metal complex initiators can be used to create biodegradable polyesters such as poly- ϵ -caprolactone (PCL), polylactide (PLA) and their copolymers in a controlled manner¹. Today, research on the search for new stable in industrial conditions and less toxic initiators based on non-transition metal complexes (compared to those currently used based on tin), which at the same time exhibit high catalytic activity in the synthesis of these polymers, is one of the important problems of modern polymer chemistry.

In the course of this work, a synthesis was carried out based on dianionic tri- and tetradentate ligands of aluminum and gallium complexes stabilized by intramolecular nitrogen–element interactions, and the influence of the ligand structure on the type of complexes obtained and their activity in the homo- and copolymerization of ϵ -caprolactone and lactide was studied.

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THE ROLES OF ARTIFICIAL INTELLIGENCE IN CHEMICAL RESEARCH

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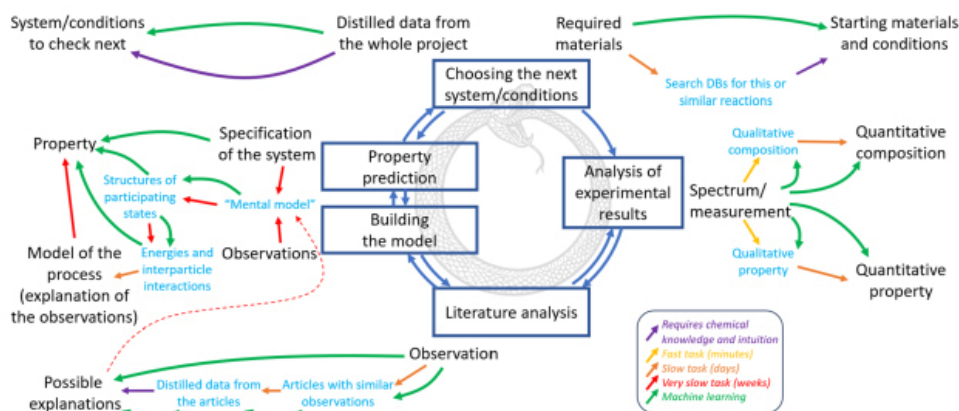
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Machine learning (ML), the pillar of nowadays artificial intelligence (AI), is the field at the interface of computer sciences and mathematics, which uses computers to find trends in data and use them to solve tasks, which generally cannot be solved *via* programs based on sets of rules. With the rise of available computing power and development of new techniques (e.g., transformers, graph neural networks, diffusion models, etc.), now AI can do things which were recently considered impossible: hold a human-like conversations, draw realistic paintings, write computer codes, etc.

With these recently acquired powers, AI transforms Sciences just like Sciences transform human lives. In this contribution we will discuss applications of AI that significantly accelerate various stages of chemical research: enhance analysis of experimental results, guide literature review, allow one to model chemical processes and predict properties. We will identify tasks which benefit from AI the most and analyze AI's ability to accelerate them and possibilities to improve this acceleration even further.



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STRUCTURE OF NIKEL-DIAMOND COATING OBTAINED FROM A VIBRATION-LIQUEFIED ELECTROLYTE-SUSPENSION

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Composite electrochemical coatings (CECs) have significant advantages over coatings consisting of a single phase, and their potential applications cover almost all industries, which proves the relevance of research in this direction¹.

Among the numerous composite systems, the nickel-diamond system stands out, promising for producing wear-resistant coatings. However, when obtaining CECs, there is a problem of ensuring suspension stabilization, without solving which it is impossible to obtain coatings with a uniform distribution of the reinforcing phase.

In this work, a vibrational method of stabilization of an aggregate electrolyte suspension is applied and its advantages are shown. A study of the influence of the concentration of diamond powders of various dispersions showed that this method makes it possible to obtain CECs from electrolytes with relatively large diamond particle sizes of 5–7 μm and achieve a significant volume fraction of the reinforcing phase up to 50% with a microhardness of 1450 HV. Studies of the structure of coatings using the EBSD method revealed a significant grain refinement of the matrix metal compared to a metallic nickel coating. It has been shown that high microhardness is due not only to the large volume fraction of diamond, but also to the strengthening of the coating matrix due to grain crushing.

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The presented material was obtained within the framework of the grant of the Russian Science Foundation "Conducting research by world-class scientific laboratories within the framework of the priorities of scientific and technological development of the Russian Federation" of the Presidential program of research projects implemented by leading scientists, including young scientists under agreement No. 21-73-30019.

PARAMETRIZATION OF ELECTROSTATIC INTERACTIONS IN MOLECULAR MECHANICS BASED ON ELECTRON DENSITY DESCRIPTORS

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Molecular mechanics is a valuable tool widely used in biology and materials science, as it provides possibility to model systems of hundreds and thousands of atoms¹⁻². Noncovalent (electrostatic and dispersion) interactions are of a great importance for most systems of interest.

Common way to describe electrostatic interactions is to use Coulomb law with point charges, located at the atomic positions. This representation is computationally effective, but sometimes is unable to reproduce charge distribution around an atom, the most common example being halogen atoms³. The so-called sigma hole at line connection carbon atom and heavy heteroatom can be described by an additional virtual charge, improving the quality of approximation. The positions for such virtual sites are usually chosen based on chemical intuition or quantum mechanical data. It is also important to choose correct values of atomic charges as they are not a measurable in quantum mechanics.

This work suggests analyzing the electron density topology to locate virtual sites positions. The method helps to make virtual sites localization automatic and provides physical argumentation for their positions. We also describe electron density descriptors, which can be used to improve charge fitting. It is shown that virtual sites fitted using our procedure improve the description of noncovalent interactions in biological molecules and halogenated molecules.

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This work was supported by the RSF (22-73-10124).

STUDY OF MAGNETIC PROPERTIES OF Fe(II)- AND Co(II)-CONTAINING HEXAAZATRIPHENYLENE-BASED COMPLEXES WITH VARIOUS CHARGE STATES OF A CENTRAL LIGAND AND DIFFERENT AMOUNT OF COORDINATED METAL ATOMS

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In this work we have obtained a series of hexaazatriphenylene-based (HAT) coordination complexes of Fe(II)¹⁻³ and Co(II)^{2,3}. The compounds contain different amount of coordinated metal atoms and the central HAT-ligand possess various reduction states – from neutral to radical trianionic. The crystal structure and magnetic properties of the obtained compounds were investigated. We have found that trianionic trinuclear Fe(II) complexes form high-spin systems due to strong Fe-HAT and weak Fe-Fe antiferromagnetic exchange interactions which lead to parallel alignment of metal spins while in Co(II) complexes magnetic moment suppression is observed. Meanwhile, the metal-ligand antiferromagnetic exchange value in binuclear radical anionic complexes sharply increases in comparison to trinuclear radical anionic ones – so, that these complexes keep their high-spin states even at room temperature. Theoretical calculations using DFT and CASSCF methods were conducted for several compounds and they support the results obtained in this work.

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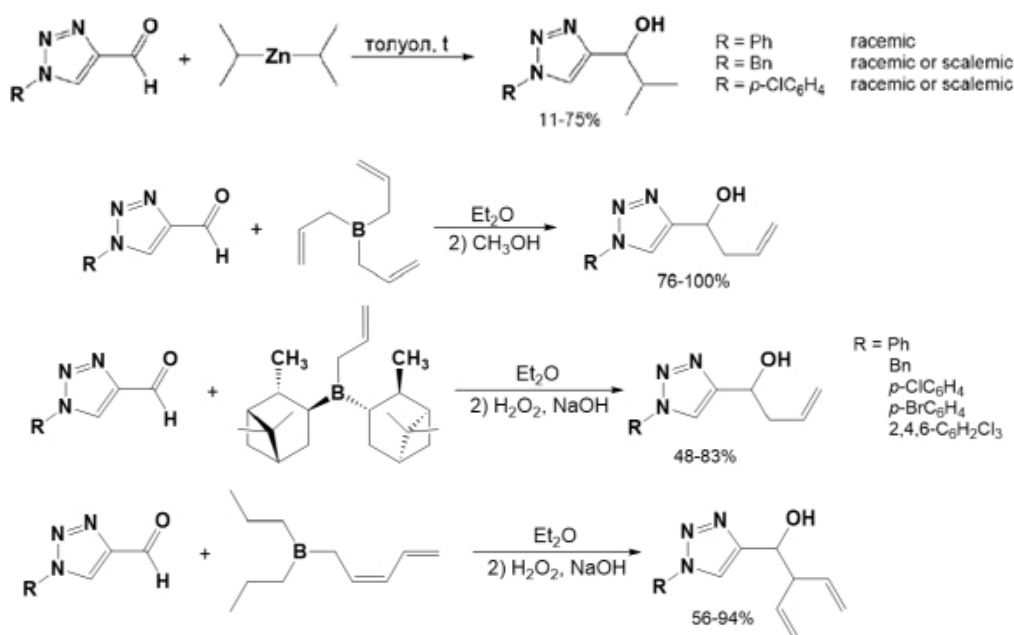
The work was supported by the Russian Science Foundation (№ 24-13-00060).

REACTIONS OF 1,2,3-TRIAZOLIC ALDEHYDES WITH DIISOPROPYL ZINC AND ALLYLBORANES

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Alkylation of 1,2,3-triazolic aldehydes with diisopropyl zinc afforded corresponding alcohols. In some reactions spontaneous generation of chirality was observed.¹



Allylboration of 1,2,3-triazolic aldehydes with triallylborane and pentadi-enyl(dipropyl)borane yielded corresponding homoallylic alcohols prone for further modification.

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The work was supported by the RSF grant 22-13-00275.

SIMULATION OF MANGANESE(III) INTERACTIONS IN THE BINUCLEAR OXO-CARBOXYLATE STRUCTURAL FRAGMENTS

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Research and theoretical modeling of the magnetic properties of manganese complexes has been actively developing since the production of the first single-molecule magnets¹. Interesting attempts have been made in the literature to identify empirical correlations between the structural parameters of manganese oxoclusters and their magnetic properties². However, theoretical quantum chemical calculations to date provide only good qualitative results in predicting the nature of the interaction of Mn³⁺ ions in complexes, while the numerical values of J often turn out to be completely unrealistic³.

In this work, an attempt was made to systematically calculate the spin-spin interaction constants J in the family of binuclear Mn(III) complexes containing the Mn-O-Mn fragment and two carboxylate bridges $[\text{Mn}^{\text{III}}_2(\mu_2\text{-O})(\mu_2\text{-RCOO})_2\text{L}_n]^{\pm+}$, using different levels of theory (DFT functionals, such as B3LYP, TPSSh, wB97x), as well as different basis sets (including def2-SVP, def2-tzvp, 6-311G*). To compare the calculation results with experimental data, complexes that were not previously modeled but studied experimentally⁴ were used. Based on the results of the calculations, the best method for modeling such systems was selected and a correlation between the calculated values of J and experimental measurements was proposed.

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THERMODYNAMIC AND KINETIC PERCULIARITIES FOR THE ESTERIFICATION REACTION: THE ETHYL ACETATE SYNTHESIS REACTION

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The essence of coupled processes is in combining the synthesis reaction of a required substance with the phase transition, which plays the role of a purification stage, within one technological process. Development and implementation of such coupled technologies require not only data on chemical reaction kinetics but also information about phase equilibria that are simultaneously realized in the system.

In this work, some peculiarities of the esterification reaction (synthesis of ethyl acetate) kinetics are discussed together with thermodynamic properties of the acetic acid – ethanol – ethyl acetate – water system in terms of patterns determining relationship between thermodynamic and kinetic properties. A considerable amount of experimental data on phase and chemical equilibria for this system has been obtained by us earlier^{1,2}, critical analysis of the literature information on thermodynamic properties of the system has been also carried out³. At the same time, such comprehensive study of relationships between thermodynamic and kinetic properties are rather limited in the modern literature.

The rate of the ethyl acetate synthesis reaction was studied at 313.15 K and under atmospheric pressure. The equilibrium vapour pressures were measured by the dynamic flow method. Equilibrium compositions of the liquid and vapour phases were determined by gas chromatography. Activity coefficients of the components in liquid phase were estimated based on the experimental vapour-liquid equilibrium (VLE) data. The experimental results were compared with the data obtained by the calculation with the group model UNIFAC.

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The work was carried out with the financial support of the Russian Science Foundation, project 23-23-00227.

DIRECT C-H FUNCTIONALIZATION OF AZAHETEROCYCLES AS A “GREEN” METHOD FOR THE SYNTHESIS OF PROMISING PHYSIOLOGICALLY ACTIVE COMPOUNDS AND FUNCTIONAL MATERIALS

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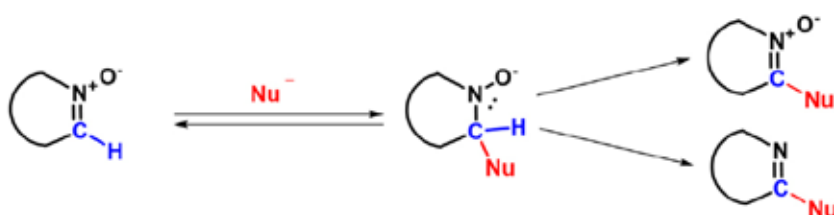
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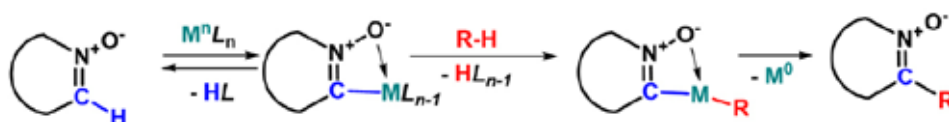
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The C–H functionalization methodology is one of the effective synthetic methods for obtaining promising biologically active substances and functional materials that can be realized in the following ways.¹⁻³

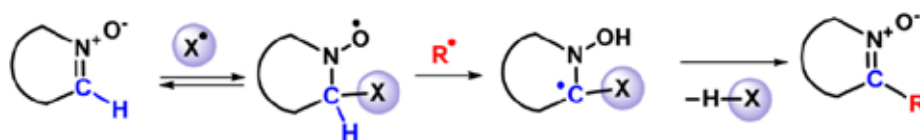
1. Reactions of nucleophilic substitution of hydrogen (SNH);



2. Metal-catalyzed cross-dehydrogenative coupling reactions;



3. Radical-induced cross-dehydrogenative coupling reactions.



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The work was financially supported by the Russian Science Foundation (project No. 23-63-10011, <https://rscf.ru/en/project/23-63-10011/>).

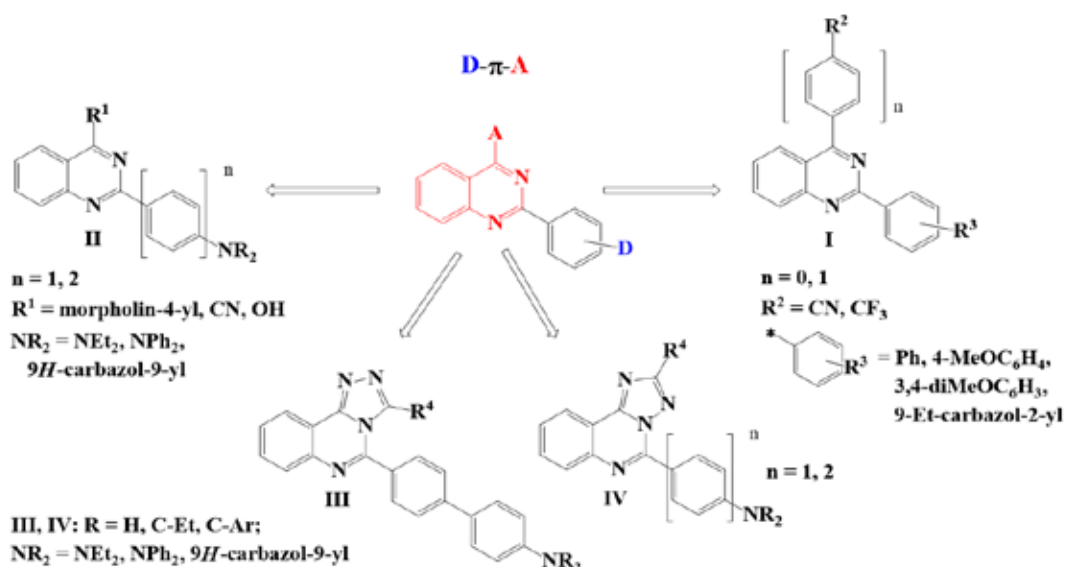
DONOR- π -ACCEPTOR STRUCTURES BASED ON 2-ARYLQUINAZOLINE OR 5-ARYL[1,2,4]TRIAZOLOQUINAZOLINE

Moshkina T.N., Kopotilova A.E., Ivan'kina M.A., Permyakova J.V., Nosova E.V.

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Quinazoline core is a planar aromatic heterocyclic fragment with π -deficient character that can be used as electron-withdrawing part in push-pull structures.¹

Three types of fluorophores were prepared based on quinazoline. To obtain target compounds Pd-catalyzed cross-coupling of corresponding bromo-derivative with arylboronic acid or its pinacol ester was applied.



The influence of substituents on photophysical properties was studied.²⁻⁴ The obtained structures can be considered as the effective luminophores with solution/solid state emission, fluorosolvatochromism, pH-sensitivity, AIE/AIEE effect, and have significant impact on pure and applied chemistry.

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This work was supported by the Russian Scientific Foundation (project 23-73-01147), the research funding from the Ministry of Science and Higher Education of the Russian Federation (Ural Federal University Program of Development within the Priority-2030 Program)

FEATURES OF SILVER(I) COMPLEXATION WITH BENZIMIDAZOLE DERIVATIVES OF VARIOUS MODIFICATIONS IN THE PRESENCE OF BORON CLUSTER ANIONS $[B_nH_n]^{2-}$ ($n = 10, 12$)

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The process of silver(I) complexation with benzimidazole derivatives containing various linker groups ($-N=N-$ (L^1), $-CH=N-$ (L^2), $-CH_2-NH-$ (L^3) or $-N=CH-$ (L^4)) in the presence of boron cluster anions $[B_nH_n]^{2-}$ ($n = 10, 12$) both in the system $AgNO_3 / [B_nH_n]^{2-} / L$ and $\{Ag_2[B_nH_n]\}_m / L$ has been studied for the first time.

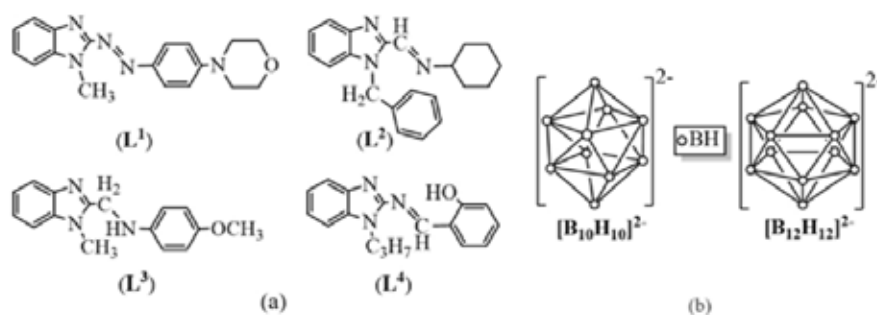


Figure 1. Organic (a) and inorganic (b) ligands used in this work.

As a result, depending on the type of linker group in the organic ligand, new binuclear complexes $[Ag_2L_2[\mu-B_nH_n]]$ ($n = 10, 12$; $L = L^1, L^2$), cationic-anionic compounds $[Ag(L^3)_2][Ag[B_{10}H_{10}]]_m$ and $[Ag(L^3)_2][B_{12}H_{12}]$, as well as polymers $\{Ag_2(Bz-NH_2)_2[\mu-B_nH_n]\}_m$ ($n = 10, 12$) with 1-propyl-2-aminobenzimidazole ($Bz-NH_2$) – a fragment of degradation of ligand L^4 at the linker group $-N=C-$, have been selectively isolated and characterized by various physicochemical methods of analysis, including X-ray diffraction analysis. The structural features of the obtained compounds have been analyzed, in particular, various bonding or positional ways of coordination of boron cluster anions.

This work was supported by the Ministry of Science and Higher Education of the Russian Federation as part of the State Assignment of the Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences in the field of fundamental research.

GRAPH NEURAL NETWORKS BASED HIGH-YIELD REACTIONS SEARCH WITH TRANSFER AND ACTIVE LEARNING

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The prognosis of chemical reaction outcomes is a critical aspect of research in organic chemistry synthesis planning¹. The ability to predict reaction yields in advance makes it possible to pinpoint high-yield reactions for a complex synthetic process.

In this study, we leveraged the established high-throughput experimentation (HTE) Buchwald-Hartwig (BH) and Suzuki-Miyaura (SM) datasets, comprising 4599 Pd-catalyzed C-N coupling reactions and 5760 cross-coupling reactions. Our model is built upon the Chytorch RxnMap² pretrained graph-based encoder. To utilize active learning with a regression model the network architecture with self-uncertainty prediction was adopted³. The model showed high performance with R² up to 0.9678 on BH and 0.8548 on SM datasets.

Our active learning approach simulates a realistic scenario with a constrained initial budget of 16 training and 32 validation labeled reactions. In each cycle, 16 reactions were queried from the pool, iteratively expanding training and validation sets. We explored various data sampling techniques, including random, highest uncertainty, stratified and K-means batch sampling. Results demonstrated effectiveness in imitating real experimental reaction searches. High-quality predictions with R² more than 0.8 were attainable with only 500 reactions starting from just 16. With specific querying strategies the model showed an ability to precisely indicate high-yield reactions (above 50%).

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This work was funded by the subsidy allocated to Kazan Federal University for the state assignment in the sphere of scientific activities FZSM-2024-0002

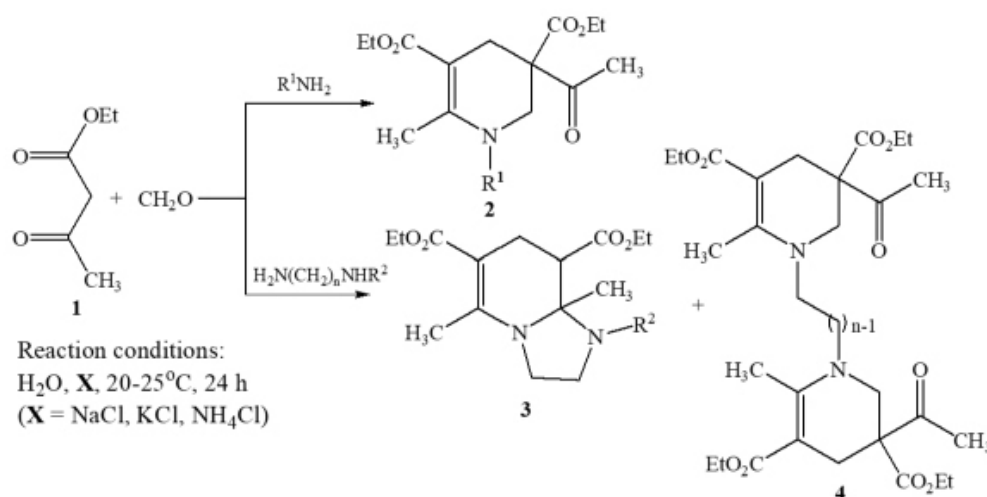
SYNTHESIS OF 1,2,3,4-TETRAHYDROPYRIDINES AND HEXAHYDROIMIDAZO[1,2-A]PYRIDINES IN AQUEOUS SOLUTIONS OF ELECTROLYTES

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Nitrogen heterocycles of the tetrahydropyridine and hexahydroimidazo[1,2-a]pyridine series exhibit antibacterial, antimalarial, insecticidal, analgesic and anti-inflammatory activities¹.

We have developed a new one-pot method for the synthesis of 1,2,3,4-tetrahydropyridine derivatives based on a three-component reaction of acetoacetic ester **1** with an aqueous solution of formaldehyde and amines, occurring in an aqueous solution of salts at room temperature. The presented synthesis method is characterized by mild reaction conditions and allows the selective preparation of penta-substituted polyfunctionalized 1,2,3,4-tetrahydropyridines **2** without isolation and purification by column chromatography. When diamines are used in the reaction along with bistetrahydropyridines **4**, hexahydroimidazo[1,2-a]pyridine derivatives **3** are formed.



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POLYTHERMAL STUDY OF THE LITHIUM ACETATE - CESIUM ACETATE - WATER TERNARY SYSTEM

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The development of highly concentrated water-salt electrolytes is a rather promising area for the design of new lithium-ion batteries.¹ The ternary system lithium acetate - cesium acetate - water has shown good electrochemical properties,² but the literature does not provide data on the temperature range of the liquid state.

In this research work, a series of various concentrations of cesium acetate in the ternary system 7 m LiOAc - x m CsOAc - H₂O were chosen to study their cooling and/or heating behavior using a constructed instrument based on copper-constantan thermocouples and an Arduino platform. The use of inexpensive analogue low-temperature thermal analysis equipment makes it possible to study the temperature behavior of a large number of different electrolytes and other liquid systems over a wide temperature range, which is cost-effective, technically simple for electrolytes being developed for industrial applications.

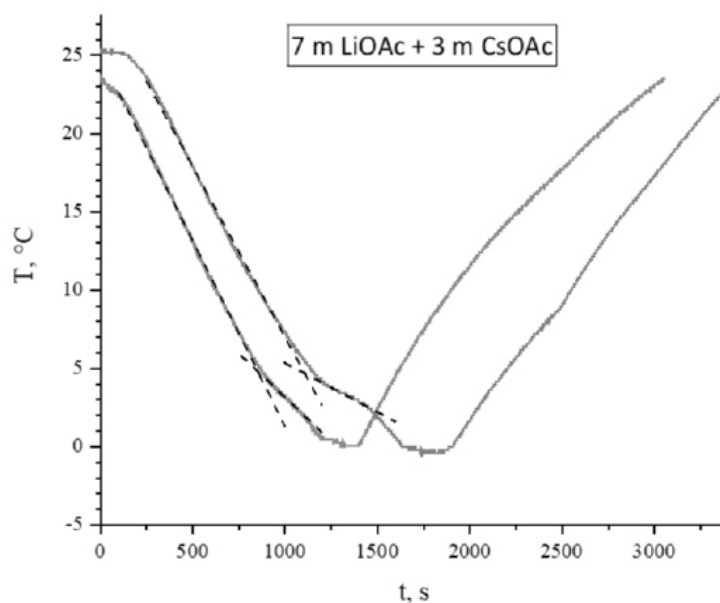


Figure 1. Cryoscopic curve for one of the ternary system samples.

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SYNTHESIS AND PHOTOPHYSICAL PROPERTIES NEW ORGANOBORON LUMINOPHORES

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Chupakhin O.N.^{a,b}, Dmitrishin S.A.^a**

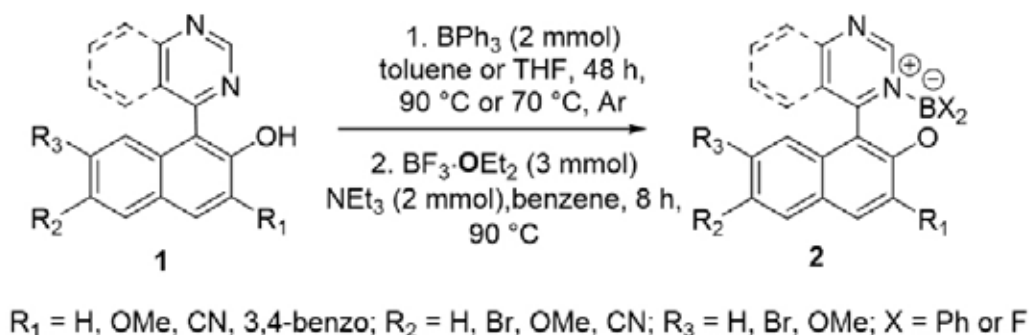
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Interest in the development of new fluorescent organoboron compounds has been aroused due to the discovery of applied properties in optoelectronic applications, as sensors and switches, or in bioimagine. In particular, the focus was on tetracoordinated boron(III) compounds with bidentate chelating ligands. The coordination saturation of the boron center provides increased chemical stability and rigidity, which is often accompanied by significantly high fluorescence quantum yields.

One of the promising boron complexes are six-membered 1,3,2-oxazaborinine containing the *N,B,O*-fragment, due to their synthetic availability, a variety of ligand structures, and the possibility of subsequent modification of substituents.

In the present study, chelating heterobiaryl ligands **1** were synthesized to form new organic luminophores. Complexes **2** were synthesized in the presence of triphenylborane or boron trifluoride ether.



Studies of the photophysical characteristics were carried out both in solution and in the solid state.

The work was supported by the Russian Science Foundation (grant No. 22-13-00298)

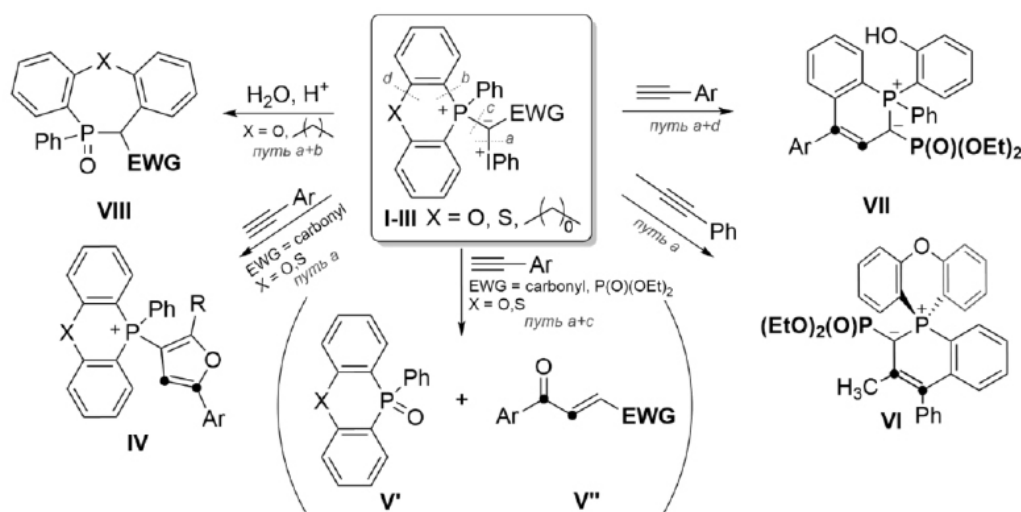
MIXED YLIDES BASED ON CYCLIC PHOSPHINES AS AN EFFICIENT PLATFORM FOR THE SYNTHESIS OF PHOSPHORUS-CONTAINING HETEROCYCLIC SYSTEMS

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The distinctive properties of mixed phosphonium-iodonium ylides stem from their unique structural hybridity, combining elements of both phosphonium ylide and iodonium salt. This structural amalgamation results in an unexpected array of reactions that extend beyond the mere additive properties of the individual onium groups.

In our current study, we delve into the impact of modifying the phosphonium fragment of mixed ylides. This modification involves conformational constraints imposed on aromatic substituents at the phosphorus atom, achieved by their incorporation into a tricyclic system. This modification has facilitated the exploration of several promising transformations utilizing ylides **I-III**. These transformations encompass diverse reaction pathways, including various interactions with alkynes resulting in the formation of compounds **IV-VII**, as well as the hydrolysis reaction with cyclization leading to the formation of phosphinoyide **VIII**.



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This work was financially supported by the Russian Science Foundation (Project No. 23-23-00166).

SYNTHESIS, CRYSTAL STRUCTURE AND LUMINESCENT PROPERTIES OF METAL-ORGANIC COORDINATION POLYMERS BASED ON 4-BROMOISOPHTHALIC ACID AND BIS(IMIDAZOL-1-YL)METHANE

Nesterova A.I.^{a,b}, Potapov A.S.^{a,b}

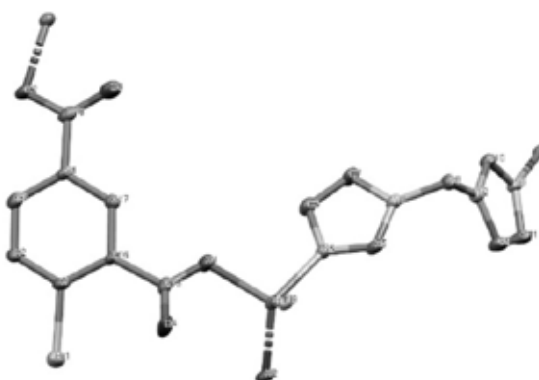
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Metal-organic coordination polymers (MOCP) are a type of crystalline porous materials consisting of metal ions connected by organic ligands. An approach based on a combination of carboxylate ligands with an aromatic π -system and a N,N-donor linker is widely used, which makes it possible to obtain new luminescent MOCP.

In this work, new two-dimensional coordination polymers based on Zn^{2+} and Cd^{2+} were synthesized with the formulas $\{[\text{M}(\text{bim})(\text{Br-ipa})]\cdot\text{DMF}\}_n$ (bim = bis(imidazole-1-yl)methane, Br-ipa = 4-bromoisophthalic acid). Their luminescent properties in the solid state were investigated, and the dependence of the emission maximum on the excitation wavelength is observed in two compounds.



Scheme 1. Asymmetric unit of of coordination polymers.

The crystal structures were established by X-ray diffraction analysis (XRD), purity and stability were confirmed by X-ray phase analysis (PXRD), elemental CHN, thermogravimetric analysis (TGA) and IR spectroscopy.

This research was supported by the Russian Science Foundation, Project № 23-43-00017.

CHEMICAL ASSEMBLY OF 1s- AND 1s-3d COORDINATION POLYMERS WITH 3,5-DINITRO-2-PYRIDONATE ANIONS

Nikiforova M.E., Kiskin M.A., Sidorov A.A., Eremenko I.L.

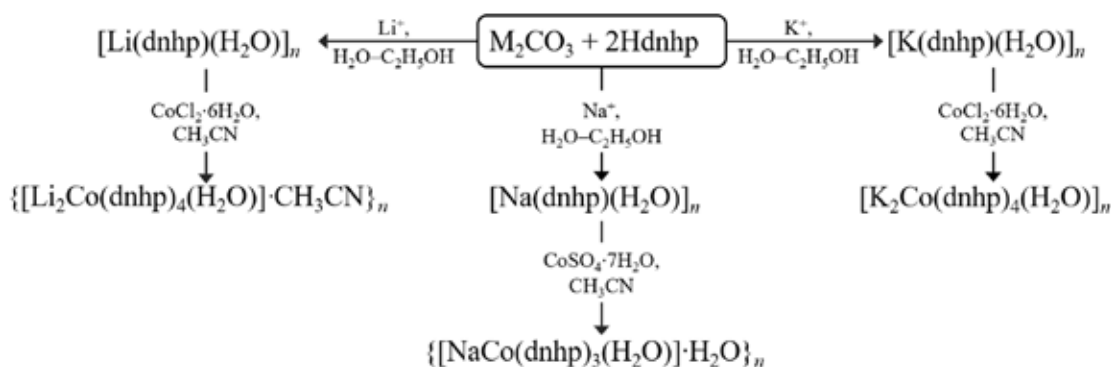
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The study of coordination compounds with organic substances encompasses fundamental issues in organic, inorganic, and coordination chemistry. The primary objective of this scientific field is to synthesize novel complex compounds and develop substances with predetermined properties. An effective way to get these compounds is to use organic molecules that act as bridges. Such a bridging ligand includes 2-hydroxypyridine and its derivatives. Introducing an additional electron-withdrawing nitro group into the pyridine ring of the ligand not only enhances the acidity of the ligand but also opens up new possibilities for coordination, allowing the formation of supramolecular structures.

The work presents the findings of the synthesis and analysis of the crystal structure of novel 1s- and 1s-3d coordination polymers with 3,5-dinitro-2-pyridonate anions.

Coordination polymers were obtained by reacting alkali metal carbonates (Li^+ , Na^+ and K^+) with 3,5-dinitro-2-hydroxypyridin (Hdnhp): $[\text{Li}(\text{dnhp})(\text{H}_2\text{O})]_n$, $[\text{Na}(\text{dnhp})(\text{H}_2\text{O})]_n$ and $[\text{K}(\text{dnhp})(\text{H}_2\text{O})]_n$.

When cobalt(II) chloride is added to $[\text{Li}(\text{dnhp})(\text{H}_2\text{O})]_n$ and $[\text{K}(\text{dnhp})(\text{H}_2\text{O})]_n$, or cobalt(II) sulfate is added to $[\text{Na}(\text{dnhp})(\text{H}_2\text{O})]_n$, 3D-coordination polymers are formed. These polymers are represented by the formulas $[\text{Li}_2\text{Co}(\text{dnhp})_4(\text{H}_2\text{O})]_n$, $[\text{K}_2\text{Co}(\text{dnhp})_4(\text{H}_2\text{O})]_n$ and $[\text{NaCo}(\text{dnhp})_3(\text{H}_2\text{O})]_n$, respectively.



This study was performed within the state assignment for the Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences in the field of fundamental research and programs of the Russian Academy of Sciences.

IRON DOPED HIGH CONDUCTIVE ELECTROLITE $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$ FOR FUEL CELLS: OXYGEN EXCHANGE KINETICS

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Lanthanum gallate-based oxide systems, such as $\text{La}_{1-x}\text{Sr}_x\text{Ga}_{1-y}\text{Mg}_y\text{O}_{3-\delta}$, are considered as electrolyte materials for various electrochemical devices due to their high oxygen-ion conductivity. In order to improve the functional properties of electrolyte materials, various frontier developments have been proposed, including iso- and/or heterovalent doping, the use of sintering aids, the creation of cation deficiency, and so forth. It is known that partial substitution of gallium cations for iron in $\text{La}_{1-x}\text{Sr}_x\text{Ga}_{1-y}\text{Mg}_y\text{O}_{3-\delta}$ has a positive effect on oxygen-ionic conductivity. However, the role of iron to the mechanism and kinetics of heterogeneous oxygen exchange with the gas phase for such materials has not been studied.

The objective of the present study was to elucidate the relationships between iron introduction into the gallium sublattice and the oxygen exchange kinetics of $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8-x}\text{Fe}_x\text{Mg}_{0.2}\text{O}_{3-\delta}$ ($x = 0$ and 0.1) oxides. The oxygen exchange kinetic experiments were conducted using a labeled oxygen atom in a circulation setup employing the oxygen isotope exchange method with gas phase mass spectrometric analysis.

The kinetic characteristic calculations demonstrated that the incorporation of iron into the gallium sublattice enhances the heterogeneous oxygen exchange rate. The identification of individual stages of oxygen exchange enabled the determination of the limiting stage of the process. In the case of $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$, the process determines the introduction of oxygen on the material surface. For the modified composition, the adsorption and oxygen incorporation stages are competitive. It was observed that the introduction of iron resulted in a significant increase in the oxygen diffusion coefficient, on the order of one magnitude.

The research was made possible by a grant from the Russian Science Foundation (grant number 24-19-00040), <https://rscf.ru/project/24-19-00040/>.

CRYSTAL STRUCTURE, LUMINESCENT AND ADSORPTION PROPERTIES OF METAL-ORGANIC COORDINATION POLYMERS BASED ON 1-(AZOLYL)-1,2,3-TRIAZOLE-4-CARBOXYLIC ACIDS

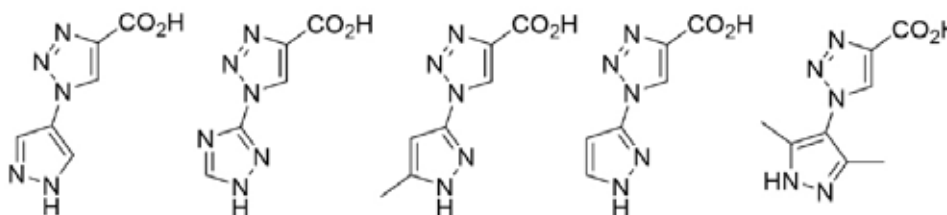
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Due to their porous structure, metal-organic coordination polymers (MOCP) can be used to separate different substances including gases and hydrocarbons. Bidentate ligands should be used in order to synthesize such MOCPs so 1-(azolyl)-1,2,3-triazole-carboxylic acids can be applied.



Scheme 1. Structures of used 1-(azolyl)-1,2,3-triazole-4-carboxylic acid.

Transition metals of the third and fourth periods (Zn, Cd, Cu, Mn) and luminescent rare-earth elements (Eu, Tb) were chosen as metals for the synthesis of MOCPs.

We synthesized several porous polymers using transition metals. Calculated from crystal structures pore sizes for Cd and Zn are 5.7x6.4 Å and 5.9x6.3 Å respectively, calculated specific surface areas are 742 m²/g and 781 m²/g respectively. Their sorption properties and separation ability of gases and aromatic hydrocarbons were studied. Several isostructural linear transition metal polymers were synthesized and their luminescent properties were studied.

Crystal structures of MOCPs were determined by X-ray structure analysis. Phase purity and their chemical composition were confirmed using powder X-ray diffraction and elemental analysis respectively.

This research was supported by the Russian Science Foundation, Project № 23-43-00017.

COORDINATION COMPOUNDS OF Co^{II} AND Fe^{III} WITH PHOTOCHROMIC SPIROPYRANS

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Spiropyran-type photochromic molecules are a large class of compounds that can undergo transformations between closed-ring (SP) and open-ring (MC) forms of merocyanine upon exposure to various external stimuli. The SP isomer is almost transparent in visible light, while the MC isomer has a broad absorption band due to the strong π -conjugation in this form with a nearly planar molecule shape. This provides not only a reversible color change during the transition, but also affects the physical and chemical properties of these compounds.

In this work, we studied the interaction of photochromic 8-methoxy-1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indole] (MNSP) with $\text{Co}^{\text{II}}(\text{hfac})_2$, 1,3,3-trimethylindolino- β -naphthopyrrolospirane (TMI-NPS) and 1,3,3-trimethylindolino-naphthospirooxazine (TMI-NSO) with halides $\text{Fe}^{\text{III}}\text{Cl}_3$, $\text{Fe}^{\text{III}}\text{Br}_3$. Based on the results of the work, crystals were obtained, the crystal structure of the resulting complexes was established (Fig. 1), and the optical and magnetic properties were studied. The compound $\{\text{MNSP} \cdot \text{Co}^{\text{II}}(\text{hfac})_2\}$ exhibits slow magnetic relaxation and is a monomolecular magnet, and as a result of the interaction of TMI-NSO and $\text{Fe}^{\text{III}}\text{Br}_3$ with an auxiliary agent, the product of double oxidation of spiropyran was obtained.

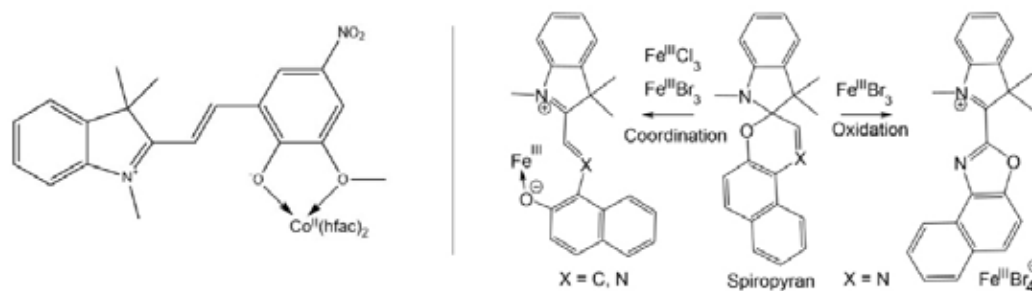


Figure 1. Schematic representation of the $\{\text{MNSP} \cdot \text{Co}^{\text{II}}(\text{hfac})_2\}$ complex (left) and the TMI-NPS, TMI-NSO complexes with Fe^{III} halides (right).

The work was carried out with the financial support of the Russian Science Foundation, project 24-13-00060.

COORDINATION POLYMERS BASED ON 2,1,3-BENZOTHIADIAZOLE DERIVATIVE FOR BENZENE CONTENT DETERMINATION IN CYCLOHEXANE

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Luminescent Coordination Polymers (LCPs) are a new class of luminescent functional materials. Their main applications include fluorimetric detection, bioimaging, and fabrication of luminescent labels for anti-counterfeiting applications. Fluorescent sensors based on LCPs are interesting due to precise tunability of their properties: the size of pores, channels and entrances to the pores, the presence of various substituents, etc., which often allows achieving a selective recognition of one of the substances in a series of compounds with extremely close physicochemical properties.

This work reports the synthesis of LMOF $\{[\text{Zn}_2(\text{im}_2\text{btd})_2(\text{sdc})\text{NO}_3]\cdot 2\text{DMF}\}_n$ and a number of its inclusion compounds with various aromatic molecules. These compounds have demonstrated a luminescent response (intensity increase and shift in the position of luminescence maximum) in the presence of benzene. As a practical application, it was proposed to use these compounds for fluorimetric determination of benzene content in cyclohexane produced in the industry through the hydrogenation of benzene. In addition, the luminescence response of these compounds to o-xylene in a mixture of o-, m-, and p-xylenes was studied.

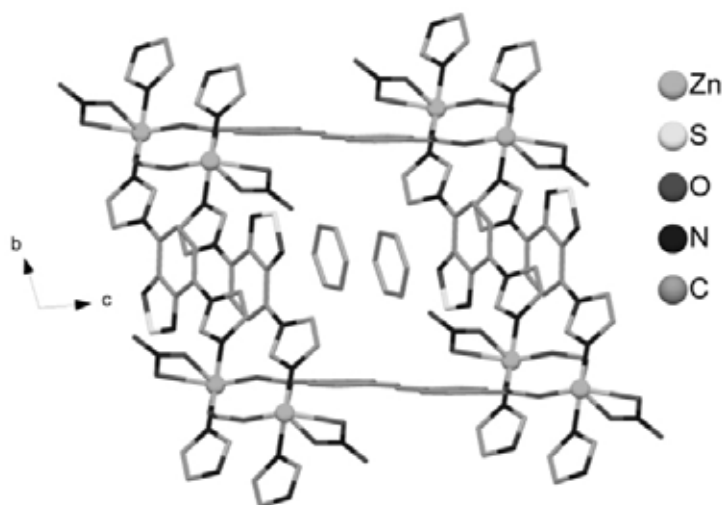


Figure 1. Fragment of the $\{[\text{Zn}_2(\text{im}_2\text{btd})_2(\text{sdc})\text{NO}_3]\cdot 2\text{Bz}\}_n$ crystal structure.

This work was supported by the Russian Science Foundation, project № 23-43-00017.

SYNTHESIS, LUMINESCENT AND COORDINATION PROPERTIES OF NOVEL DI(AZOL-1-YL)2,1,3-BENZOXADIAZOLES

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2,1,3-Benzochalcogenadiazoles attracted enormous interest, especially in materials sciences, which is driven by their potential and real-market applications as highly luminescent dyes, fluorescent sensors for environmental pollutants and as materials for active light-emitting layers in OLEDs. A great number of 2,1,3-benzochalcogenadiazole derivatives with extraordinary photophysical properties have been developed to date. Among 2,1,3-benzochalcogenadiazoles, the bis(azolyl)-substituted derivatives show a great promise as dual-functional materials: highly luminescent compounds and effective bridging ligands for coordination compounds, most importantly metal-organic coordination polymers.



Here, we describe the synthesis of novel bis(azolyl)-2,1,3-benzoxadiazoles, using heteroarylation in superbasic medium and CuI-catalyzed Ulman type reactions. Surprisingly, it was found that these reactions proceed by both ipso- and cine-substitution pathways. In addition, we describe the first examples of Zn(II) and Cd(II) coordination polymers (CPs) based on 4,7- and 4,6-di(1,2,4-triazol-1-yl)-2,1,3-benzoxadiazoles. All obtained compounds were fully characterized and their luminescent properties were studied in details.

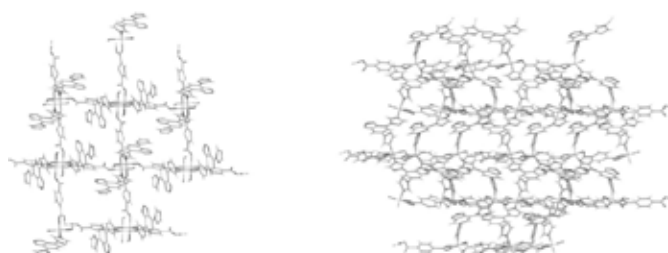


Figure 1. Structures of CPs based on 4,7-di(1,2,4-triazol-1-yl)-2,1,3-benzoxadiazole

This work was supported by the Russian Science Foundation, project 23-43-00017.

SYNTHESIS OF NEW ARYLSUBSTITUTED IMIDAZOLE-*N*-OXIDES USING ARYLDIAZONIUM SALTS

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Nonaromatic 2*H*- and 4*H*-imidazole-*N*-oxides represent the class of cyclic nitrones, the derivatives of which are of significant interest in terms of medicinal chemistry¹. It has previously been shown that direct C(sp²)-H functionalization of such molecules with aromatic moieties appears to be a promising strategy in the targeted design of compounds with pronounced biological activity².

This work demonstrates that 2*H*- and 4*H*-imidazole-*N*-oxides **1** are capable of undergoing direct C–H arylation reactions with various aryldiazonium salts **2** in the presence of diisopropylethylamine to form new C–C bonds. As a result, a series of arylated derivatives **3** have been obtained in good and moderate yields.



The structure of the obtained products **3** was characterized by modern instrumental methods of analysis. Currently, work is underway to determine the pharmacological potential of these compounds using *in silico*, *in vitro*, and *in vivo* experiments.

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THE INFLUENCE OF THE METAL NATURE ON THE STRUCTURE AND DISSOLUTION THERMAL EFFECTS OF LITHIUM DOUBLE CHLORIDES

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In recent years, the search and development of compositions of water-salt mixtures for use as electrolytes for new generation batteries, deep eutectic solvents, components of ionic liquids that improve their performance, has been actively underway [1-3]. The trend towards the use of nature friendly compositions especially attracts the attention of researchers to the salts of alkaline and alkaline earth metals contained in natural water and brines. The study of the solution-solid phase transition plays an important role in the purification of natural water, its desalination and isolation of individual salt components. The thermodynamic description of the dissolution/crystallization processes is the main one for the treatment of natural water, is taken into account in technological developments, allows to control the precipitation/dissolution processes, as well as predict the compositions of precipitating salts.

This paper presents the results of studying the dissolution processes of double chlorides formed in model systems containing lithium, rubidium, caesium and magnesium ions. The compositions of the studied systems and the resulting double salts are as follows: a) $\text{LiCl-MgCl}_2\text{-H}_2\text{O}$ ($\text{LiCl}\cdot\text{MgCl}_2\cdot 7\text{H}_2\text{O}$); b) $\text{LiCl-CsCl-H}_2\text{O}$ ($\text{LiCl}\cdot 3\text{CsCl}\cdot 4\text{H}_2\text{O}$, $4\text{LiCl}\cdot 3\text{CsCl}\cdot 2\text{H}_2\text{O}$); c) $\text{LiCl-RbCl-H}_2\text{O}$ ($\text{LiCl}\cdot 3\text{RbCl}\cdot 2\text{H}_2\text{O}$, $2\text{LiCl}\cdot \text{RbCl}\cdot 4\text{H}_2\text{O}$). The analysis of the obtained thermodynamic data (enthalpy of dissolution, standard enthalpy of salt formation, etc.) reveals the influence of the cations nature on the magnitude of thermal effects. The analysis of the double chlorides structure allows us to conclude about the mechanism of solid phase formation from an aqueous solution.

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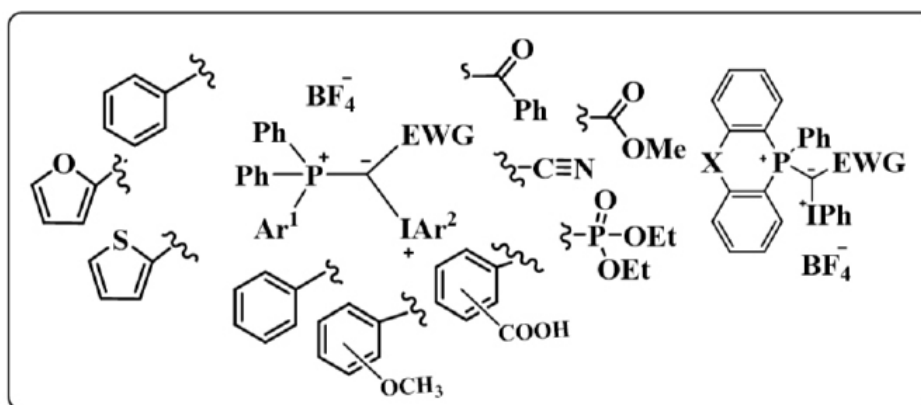
Analysis of the structure of solid phases were carried out in the Research Centre “XRD” of Research Park of St. Petersburg State University.

PHOSPHONIUM-IODONIUM YLIDES: THROUGH THE VARIETY OF FORMS TO THE VARIETY OF PROCESSES

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Interest in studying the properties of ylides has not waned since their creation, as a system with separated charges, due to its structure, is provided with the ability to interact with a wide range of reagents of various nature. Mixed ylides, which contain two “onium” groups with both the same and different heteroatoms at the ylide carbon atom, offer significant advantages. A systematic study of the properties of mixed phosphonium-iodonium ylides, actively conducted at the Faculty of Chemistry, Moscow State University, has identified their unique properties and led to the discovery of new heterocyclization reactions, enabling the creation of previously inaccessible heterocyclic systems.¹⁻³ This communication summarizes the results of our current areas of fundamental research over the past two years, devoted to the creation and active study of new representatives of this class of compounds. Particular attention is paid to identifying the contribution of each of the “onium” components of mixed ylides, as well as their mutual influence. Additionally, the mechanistic concept are substantiated based on physicochemical studies and quantum chemical calculations.



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PHOTOCHEMICAL TRANSFORMATIONS OF RADICAL CATIONS OF ESTERS AND OXIRANES IN FROZEN FREON MATRICES

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Photochemical transformations of radical cations (RCs) of organic oxygen-containing substances (esters of monocarbonic acids, oxiranes) were studied in this work. Freon matrices were used for the stabilization of RCs obtained via indirect ionization of precursors¹.

The nature of RCs and products of their transformations under the action of visible light were determined via quantum chemical approaches as well as EPR spectroscopy and optical spectroscopy.

In the case of methyl formate RC generation, it turned out that when complex formation with matrix molecules (CFCl₃) is possible, it manages to protect the RC against the McLafferty rearrangement. As it turned out, this is not associated with low activation energy for this process, but with excess energy released during indirect ionization instead.

In this case, this allowed us to explore the transformations of these RCs at 77-140 K, to determine their spectral characteristics ($\lambda_{\text{max}} = 490 \text{ nm}$) and investigate the products of their phototransformations (namely, the corresponding distonic RCs).

It was shown that there are different mechanisms of phototransformations of RCs, depending on the structure of the precursor molecule²: reversible cyclization, charge transfer to matrix molecule, intramolecular transfer of hydrogen atom, deprotonation. However, there is no correlation between the structure of the precursor molecule and the phototransformation channels of the corresponding RCs.

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PEROXIDASE-LIKE ACTIVITY OF CeO_2 SOLS STABILISED BY ANTIOXIDANTS

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The International Union of Pure and Applied Chemistry (IUPAC) has identified the directed synthesis of biologically active nanomaterials capable of participating in the regulation of biochemical processes in living systems, due to the manifestation of enzyme-like properties, as one of the most dynamically developing areas of modern materials science. Consequently, the development of reliable approaches to the analysis of bioactivity of nanomaterials with a given structure and chemical composition is an extremely urgent task.

Nanocrystalline CeO_2 was chosen as the object of study as a material demonstrating catalytic activity towards a wide range of substrates, including hydrogen peroxide. Peroxidase activity of enzymes and their mimetics is of great importance in biological processes, since hydrogen peroxide is the most important active form of oxygen that causes oxidative stress in living systems.

The aim of the present work was to analyze the biochemical activity of CeO_2 nanoparticles modified with antioxidants (carnosine, trolox) towards hydrogen peroxide by spectrophotometric and chemiluminescent methods. The sols of nanodispersed CeO_2 were prepared by thermohydrolysis. Surface modification of nanoparticles with antioxidants was carried out in molar ratios of CeO_2 : ligand corresponding to the full coverage of nanoparticles.

The sols of nanodispersed CeO_2 stabilised by trolox and carnosine were obtained. The samples were characterised by, X-ray powder diffraction analysis, scanning electron microscopy, dynamic light scattering, IR and UV spectrometry. The obtained sols exhibit antioxidant properties against hydrogen peroxide.

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COMPLEX COMPOUNDS OF NICKEL(III) AND COBALT(III) WITH ALIPHATIC POLYAMINES

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The complexation of nickel(III) and cobalt(III) cations with the short-range ligand N- and N,O-environment ensures the stability of the highly oxidized states of these metals in a time sufficient for their production, identification and use¹⁻³. We carried out a comparative study of the formation of nickel(III) and cobalt(III) complexes with polynitrogen ligands of the aliphatic amine class (ethylenediamine En, diethylenetriamine Dien and triethylenetetramine Trien) in aqueous solutions. To obtain metal complexes in a highly oxidized state, multicomponent systems were used that provided parallel occurrence of chelation and oxidation of the central atoms. It was established that the use of ammonium peroxodisulfate as an oxidizing reagent in weakly alkaline solutions of polyamines upon heating led to the formation of nickel(III) chelates $[\text{Ni}(\text{En})_3]^{3+}$ ($\log(\beta) = 10.13$), $[\text{Ni}(\text{Dien})_2]^{3+}$ ($\log(\beta) = 13.85$) and $[\text{Ni}(\text{Trien})]^{3+}$ ($\log(\beta) = 12.07$). The oxidation of cobalt(II) cations in solutions of aliphatic polyamines was realized in a wide range of alkaline media when hydrogen peroxide was used as an oxidizing reagent. The absence of electrons in the eg orbitals of cobalt(III) cations in the strong field of polyamine ligands caused significant thermodynamic stability of the chelates $[\text{Co}(\text{En})_3]^{3+}$ ($\log(\beta) = 47.92$), $[\text{Co}(\text{Dien})_2]^{3+}$ ($\log(\beta) = 55.88$) and $[\text{Co}(\text{Trien})]^{3+}$ ($\log(\beta) = 44.01$).

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MUTUAL INFLUENCE OF STRUCTURAL FRAGMENTS IN PHOSPHONIUM-IODONIUM YLIDES AND ALKYNES ON THE CHEMOSELECTIVITY OF THE HETEROCYCLIZATION REACTION

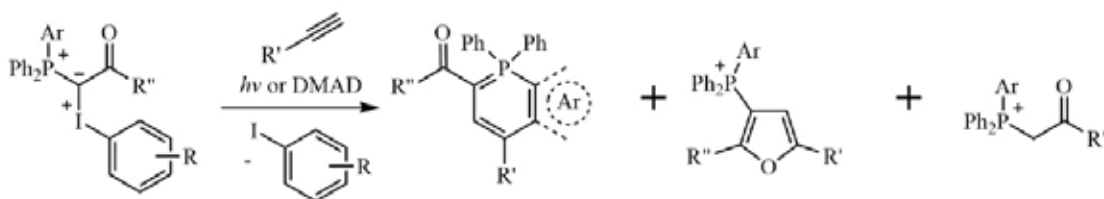
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Promising phosphorus-containing annulated heterocycles – phosphinolines and phosphonium-substituted furans can be obtained by the heterocyclization reaction of mixed phosphonium-iodonium ylides with alkynes^{1,2}. The results of this study open the way to the creation of a concept for the targeted design of phosphinolines and phosphonium-substituted furans based on phosphonium-iodonium ylides.



A series of model and a series of new mixed ylides with various combinations of phosphonium and iodonium moieties and acceptor groups were synthesized, and the influence of key structural units of both the ylide (including the iodonium moiety) and the alkyne on the heterocyclization reaction was studied.

By the means of EPR and NMR, the forming radicals and the influence of structural units on the nature of radical intermediates were analyzed, which made it possible to clarify the mechanism of formation of the target heterocyclic products.

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The work was carried out with financial support from Russian Science Foundation, project № 23-23-00166.

FROM HUMOROUS POST TO DETAILED QUANTUM-CHEMICAL STUDY: ISOCYANATE SYNTHESIS REVISITED

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Isocyanates play an essential role in modern manufacturing processes, especially in polyurethane production. There are numerous synthesis strategies for isocyanates both in industrial and laboratory conditions, which do not prevent searching for alternative highly efficient synthetic protocols.

In this work, we report a detailed theoretical investigation of the mechanism of sulfur dioxide-catalyzed rearrangement of the phenylnitrile oxide into phenyl isocyanate, which was first reported in 1977.¹ The DLPNO-CCSD(T) method and up-to-date DFT protocols were used to perform a highly accurate quantum-chemical study of the rearrangement mechanism. An overview of various organic and inorganic catalysts has revealed other potential catalysts, such as sulfur trioxide and selenium dioxide. Furthermore, the present study elucidated how substituents in phenylnitrile oxide influence reaction kinetics. This study² was performed by a self-organized collaboration of scientists initiated by a humorous post on the VK social network.

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NOVEL TYPES OF RHENIUM CLUSTER COMPLEXES

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Compounds containing covalent metal-to-metal bonds, namely cluster complexes, have a number of promising physical and chemical properties that are attracting the attention of researchers. In particular, octahedral chalcogenide and halide cluster complexes of transition metals can serve as building blocks for materials with properties such as superconductivity, high-efficiency electrical transport, bright red and near-infrared emission when excited by ultraviolet or X-ray radiation, and gas separation. However, the actual task remains the development of methods to obtain new cluster complexes with potentially useful properties.

As a result of this work, a new type of six-nuclear (Fig. 1a), seven-nuclear (Fig. 1b) and eight-nuclear (Fig. 1c) rhenium cluster complexes have been obtained. It should be noted that compounds of this structure have not been previously described not only for rhenium but also for other transition metals. Moreover, the measurement of magnetic susceptibility of the seven-nuclear complexes showed that at room temperature for these compounds the state with two unpaired electrons per formula unit is realized, and with temperature decrease to 1.77 K the complexes transition to diamagnetic state.

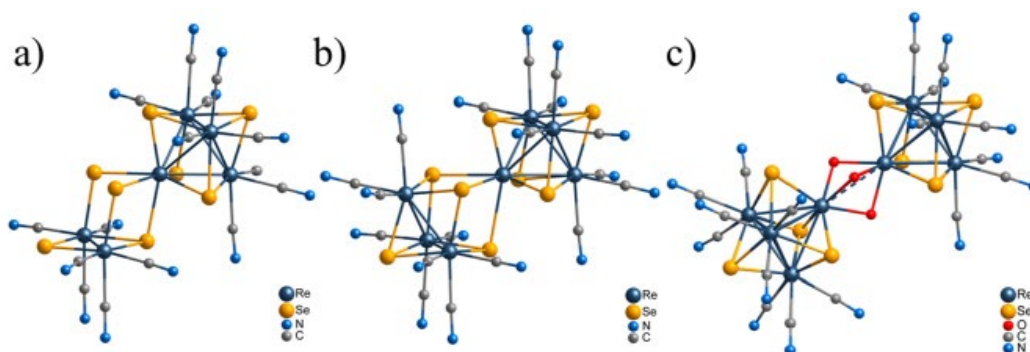


Figure 1. Structure of new cluster anions $[\{\text{Re}_2\text{Se}_4(\text{CN})_6\}\{\text{Re}_4\text{Se}_4\}(\text{CN})_9]^{6-}$ (a), $[\{\text{Re}_3\text{Se}_4(\text{CN})_9\}\{\text{Re}_4\text{Se}_4\}(\text{CN})_9]^{7-}$ (b) and $[\{\text{Re}_8\text{Se}_8(\mu\text{-O})_3\}(\text{CN})_{18}]^{8-}$ (c).

The work was financially supported by RSF, project 23-13-00081.

FORMATION OF NANOCRYSTALS OF COMPLEX OXIDES UNDER “SOFT CHEMISTRY” CONDITIONS

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The morphology, structure, dimensional parameters of complex oxide nanoparticles, and the presence of impurities can significantly affect the functional properties of materials based on them, including magnetic, photocatalytic and other properties, which shows the need for further development of synthesis methods. The work discusses the formation of nanocrystalline particles of orthoferrites and orthophosphates of bismuth and rare earth elements using “soft chemistry” methods^{1,2}.

It is shown that the formation of nanocrystals of complex orthoferrites can be described within the framework of the self-organization mechanism of spatial restrictions on particle growth that arise in Kolmogorov-scale vortices during the coprecipitation of hydroxides in a microreactor. For the formation of nanoparticles with the smallest possible sizes under such spatial restrictions, the necessary conditions are a large contact surface of the reagents and the rapid removal of the resulting products from the reaction zone, which can be accomplished in microreactors of various designs. A scheme has been proposed that makes it possible to optimally combine synthesis methods to obtain nanocrystalline particles of a given composition, structure, shape and size parameters.

It has been shown that in the process of growth of crystallites and particles of complex orthophosphates, the self-organizing spatial limitations of crystal growth are the crystals themselves during their non-oriented fusion into particles. Such accretion blocks the contact of crystallites with the mobile phase - hydrothermal fluid, which ensures a high rate of mass transfer. The resulting solid-phase aggregates of crystallites do not provide any noticeable diffusion mass transfer in the low temperature region, which leads to blocking the growth of crystallites.

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STUDY OF THE INTERACTION OF THE ANION $[B_{10}H_9O(CH_2)_4O]^-$ WITH AMINO ALCOHOLS

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The relevance of this work is in the use of derivatives of $[B_nH_n]^{2-}$ ($n = 10, 12$) anions with biologically active groups in the treatment of oncological diseases, in particular ^{10}B -NCT malignant tumors.

In this study, it was shown that when the 1,4-dioxane derivative of the anion $[B_{10}H_{10}]^{2-}$ interacts with amino alcohols (2-(methylamino)ethanol, 3-(dimethylamino)propanol-1) the cyclic substituent is opened with the addition of a pendant functional group:

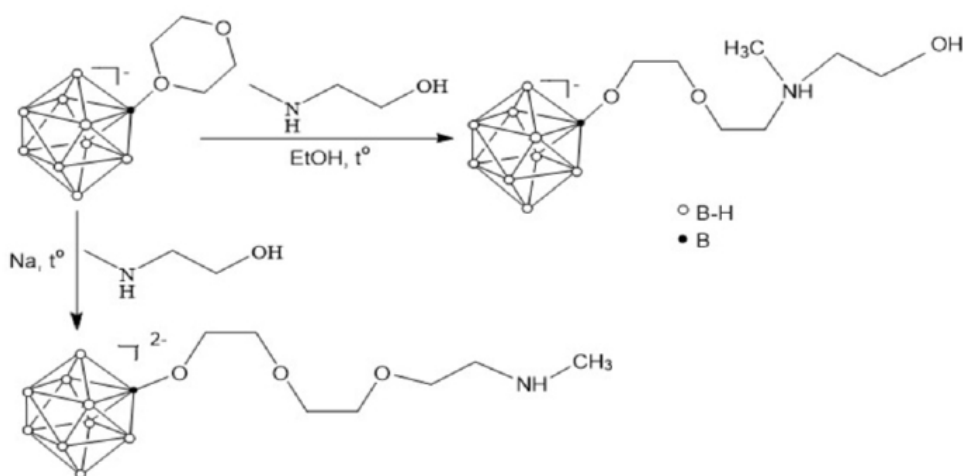


Fig. 1. The scheme of interaction of $[B_{10}H_9O(CH_2)_4O]^-$ with amino alcohols (for example, 2-(methylamino)ethanol).

Various reaction conditions make it possible to regulate the nature of attachment of the pendant group. For example, when carrying out an interaction in pure 2-(methylamino)ethanol behaves like an N-nucleophile, while preliminary ionization of the reagent makes it possible to obtain *closodecaborates* with an attached O-functional group.

In the future, it is planned to develop selective methods for obtaining derivatives of the $[B_{10}H_{10}]^{2-}$ anion with pendant groups of a certain structure using ambifunctional nucleophiles of another type. The obtained *closodecaborates* may be promising for the synthesis of biologically active boron-containing compounds, including for ^{10}B -NCT of malignant neoplasms.

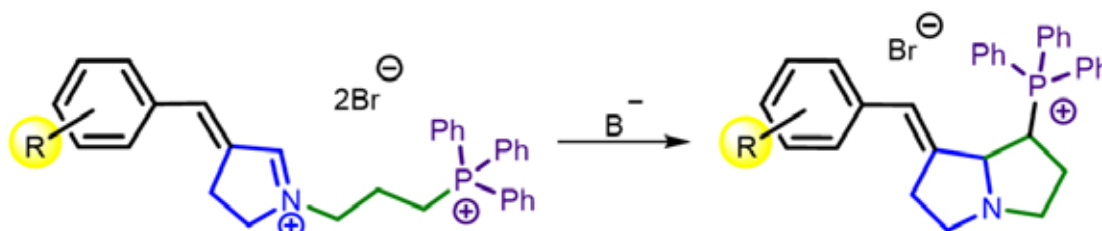
SYNTHESIS OF NEW PHOSPHORYLATED PYRROLIZIDINE DERIVATIVES

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Over the past decades, pyrrolizidine derivatives continue to be the object of close attention of both synthetic chemists and researchers searching for new biologically active substances. This structural fragment is found in many well-known natural and synthetic biologically active compounds, therefore, the development of a convenient method for the synthesis of pyrrolizidine derivatives remains an important and urgent task.¹⁻⁵

We have developed a convenient and simple method of synthesis of pyrrolizidines based on the cyclization of 3-arylidene-1-pyrroline derivatives containing a triphenylalkylphosphonium salt at the nitrogen atom. The advantages of this method include the possibility of wide variation of substituents in the bicyclic system, mild reaction conditions and the absence of the need to use expensive catalysts or reagents.



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The work was supported by Russian Science Foundation No. 23-73-01061, <https://rscf.ru/project/23-73-01061/>

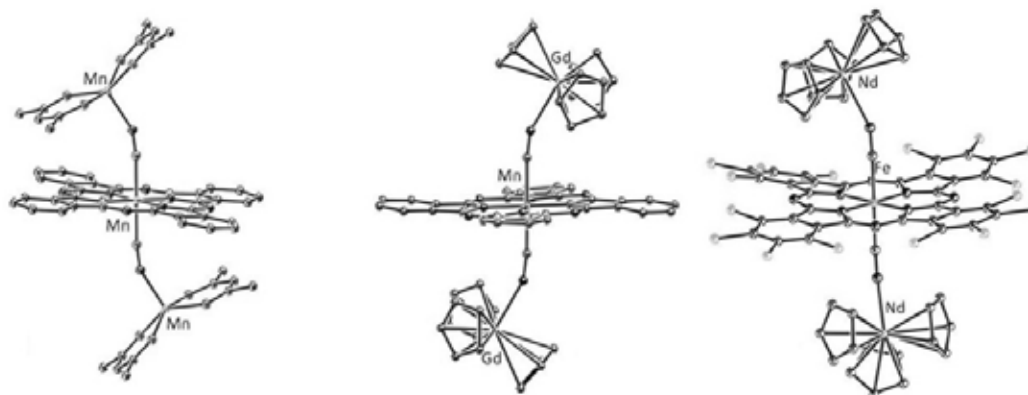
SYNTHESIS AND STUDY OF THE MAGNETIC PROPERTIES OF TRINUCLEAR COMPLEXES BASED ON METAL PHTHALOCYANINES WITH VARIOUS AXIAL LIGANDS

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Metal phthalocyanines (MPc) are macrocyclic compounds that have been known for over a century and are used as industrial dyes. However, having a number of promising properties, these compounds have recently attracted the scientific community as a component for the creation of various functional materials. The properties of MPcs can be tuned by modifying their structure in various ways, for example, by replacing the central metal atom or introducing a variety of axial ligands. In this way, for example, it is possible to obtain multinuclear complexes with promising magnetic properties.

In the course of our work, we obtained cyanidated forms of manganese(II) and iron(II) phthalocyanines, as well as iron(II) hexadecachlorophthalocyanine. Based on these cyanidated macrocycles, a series of trinuclear complexes were obtained by coordinating manganese(II) acetylacetonate, gadolinium(III) tris(cyclopentadienyl) and neodymium (III) (Fig. 1).



All compounds were studied by electron spectroscopy and X-ray diffraction analysis, as well as SQUID magnetometry. It has been established that the $\{\text{Cryptand}(\text{K}^+)\}_2\{\text{Mn}^{\text{II}}(\text{CN})_2\text{Pc} \cdot (\text{Mn}^{\text{II}}(\text{acac})_2)_2\}^{2-} \cdot 5\text{C}_6\text{H}_4\text{Cl}_2$ complex transforms into a high-spin ($S=9/2$) state at low temperature due to the presence of three manganese atoms in different spin states ($S=5/2$ and $S=1/2$) and antiferromagnetic interaction between them.

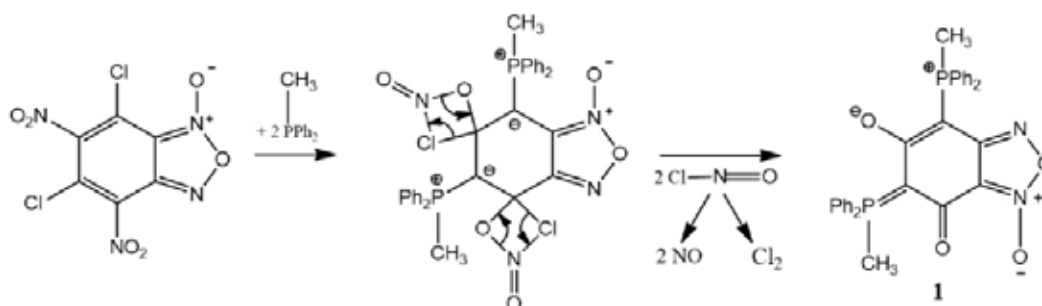
The work was carried out with the financial support of the Russian Science Foundation, project 24-13-00060.

SYNTHESIS AND BIOLOGICAL ACTIVITY OF PHOSPHORYLATED DERIVATIVES OF 5,7-DICHLORO-4,6- DINITROBENZOFUROXANE

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Reactions of tertiary phosphines: methyldiphenylphosphine, 1,2-bis(diphenylphosphino)ethane and 1,3-bis(diphenylphosphino)propane with 5,7-dichloro-4,6-dinitrobenzofuroxane proceed by nucleophilic aromatic substitution of chlorine atoms and nitro groups in the six-membered ring of the latter heterocycle. The structure of phosphorylation products has been proved by EPR, IR, NMR³¹P spectroscopy, elemental analysis (Scheme 1).



Scheme 1.

To confirm the proposed schemes, it was important to record the formation of nitric oxide in these reactions by physical methods. In the process of kinetic studies by the EPR method, the formation of the NO radical from unstable nitrosyl chloride in the processes of phosphorylation of dichlorodinitrobenzofuroxane by various phosphines: methyldiphenyl phosphine, diphosphines: 1,2-bis (diphenylphosphino) was established ethane and 1,3-bis(diphenylphosphino)propane, as shown in Figure 1.

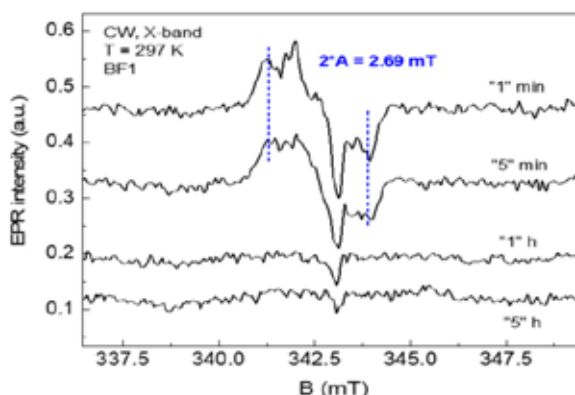


Figure 1. EPR spectral studies of reaction mixture of product 1 for 5 hours, bound NO radical and its parameters (Bruker Elexys E 580)

This paper has been supported by the Kazan Federal University Strategic Academic Leadership Program ('PRIORITY-2030').

RECEIVING AND APPLYING *CLOSO*-BORANE ANIONS AND NATURAL AMINO ACIDS IN BNCT

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¹⁰B-neutron-capture therapy (BNCT) is a promising method for the treatment of malignant tumors. Currently, the only drug authorized for use is para-boronophenylalanine. Its disadvantages are low mass fraction of boron atoms in the molecule, as well as low solubility of the drug in water. In the course of the work we proposed the preparation of alternative candidate structures, selected the conditions for maximizing the yield, solved the problem of conflict of solubility of the reagents, and studied the kinetics of hydrolysis of the ester protecting group.

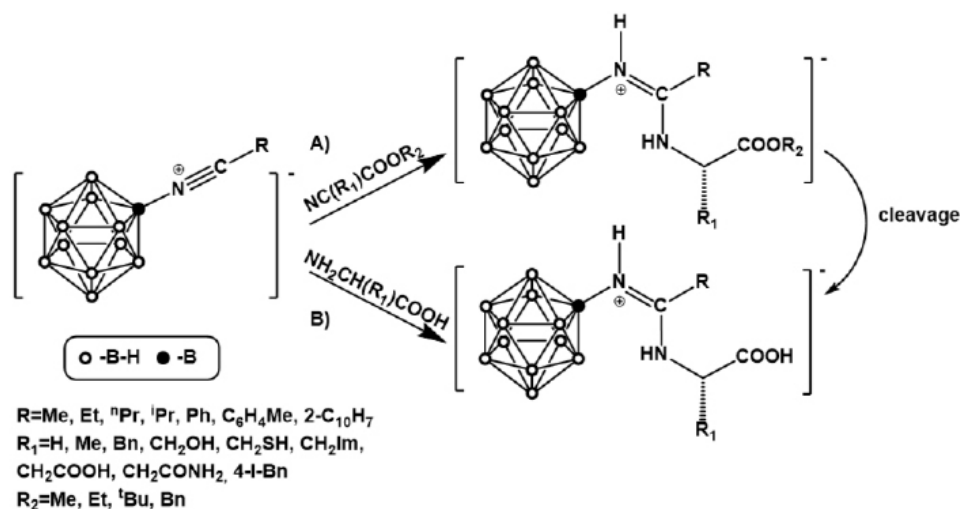


Figure 1: Scheme of preparation of conjugates of *closo*-borate anions and natural amino acids on the example of *closo*-dodecaborate anion.

Thus, conjugates of cluster anions $[\text{B}_{12}\text{H}_{12}]^{2-}$ and $[\text{B}_{10}\text{H}_{10}]^{2-}$, with natural amino acids, as well as their halogen and ester derivatives were synthesized. The obtained substances were characterized by multinuclear NMR, IR spectroscopy, and high-resolution mass spectrometry. The kinetics of hydrolysis of the protecting group was studied for ester derivatives of amino acids, and *in vivo* biodistribution data were obtained for conjugates of *closo*-dodecaborate anion with ethyl ester of glycine and phenylalanine.

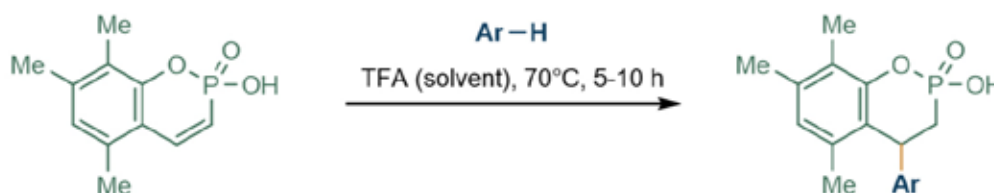
TRIFLUOROACETIC ACID – A UNIVERSAL MEDIUM FOR IMPLEMENTING NEW PHOSPHOLKYLATION REACTIONS OF AROMATIC COMPOUNDS

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2H-1,2-benzoxaphosphinine heterocyclic systems is owed to the fact that these compounds are phosphorus analogs of the known natural compounds coumarin and α -chromene, the derivatives of which were found to have a wide spectrum of biological activity.¹ For this reason, the synthesis of phosphorus-containing coumarin analogs phosphacoumarins and phosphaiso-coumarins are of increased interest. The presence of a reactive double bond in these compounds makes them promising reagents for the preparation of new types of phosphorus-containing heterocyclic systems with useful properties. Previously unknown phosphaneoflavanoids were obtained by phosphoalkylation of aromatic compounds in trifluoroacetic acid in good yields.



Derivatives of 4-substituted resorcinol, 2-naphthol, as well as benzene and its homologues were used as aromatic compounds.

The structure and composition of the obtained compounds were established based on ³¹P, ¹H, ¹³C NMR data, IR spectroscopy, mass spectrometry and X-ray diffraction analysis.

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The work was supported by the Russian Science Foundation and the Cabinet of Ministers of the Republic of Tatarstan within the framework of the scientific project No. 23-23-10020, <https://rscf.ru/en/project/23-23-10020/>

BIOCOMPONENTS PARTITIONING IN MESOSCOPIC FLUIDS CONTAINING CHAIN AMPHIPHILIC MOLECULES OF DIFFERENT STRUCTURE

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Asymmetry in the distribution of biocomponents between various mesoscale structures and their environment is the basis of micellar extraction processes and of applications of polymeric materials for controlled drug delivery. Meanwhile, the molecular mechanisms of partitioning of the target biocomponents are far from being well understood.

In this work, we focus on aqueous and aqueous-salt solutions of amphiphilic substances, namely water-soluble ionic liquids (ILs) or polymerized ILs (polyelectrolytes). Amino acid polymerized ILs based on imidazolium and diallyldimethylammonium polycations were synthesized for the first time. Of particular interest are the results of comparing the extraction capacity of aqueous-salt biphasic systems containing low-molecular-weight and polymerized ILs in relation to model biomolecules (tryptophan, vanillin). Data on phase behavior and partition coefficients of biocomponents between liquid phases for the systems containing ILs of different structure (short-chain alkylimidazolium cation/polycation, halide/amino acid anion) were obtained experimentally and using the ePC-SAFT equation of state (for low-molecular-weight ILs¹) or by the molecular dynamics simulation (for polyelectrolytes).

To describe the effect of the charge distribution of asymmetric ions on the thermodynamic behavior of the solution, a theoretical model based on the variational field theory² was used. The model has been tested both for low-molecular-weight IL³ solutions and for systems containing a linear polyelectrolyte.

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PREPARATION OF TECHNETIUM PENTACARBONYL HYDRIDE

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Technetium pentacarbonyl hydride, $[H^{99}Tc(CO)_5]$, was discovered in 1962¹. Recently, our research group discovered the formation of $[H^{99}Tc(CO)_5]$ as a result of alkaline hydrolysis of $[^{99}Tc(CO)_6]ClO_4$ ². The reaction mechanism is a nucleophilic attack by OH^- on the carbon of the carbonyl group. The reaction products were identified by IR spectroscopy. Neat $[H^{99}Tc(CO)_5]$ immediately condenses to form $[^{99}Tc_3H(CO)_{14}]$, however, in solution it turns out to be much more stable.

In this study a new straightforward synthesis of $[H^{99}Tc(CO)_5]$ by reduction of $[^{99}TcBr(CO)_5]$ with $NaBH_4$ in presence of water and simultaneous extraction of the product in toluene was developed. Yield is 88.2%. IR (ν , cm^{-1} , toluene): 2021.3 (s, $\nu(C\equiv O)$), 682.8 (w, $\delta(Tc-H)$); IR (ν , cm^{-1} , gas phase): 2034.8 (s, $\nu(C\equiv O)$), 688.5 (w, $\delta(Tc-H)$), 601.7 (w, $\delta(Tc-C\equiv O)$), 563.2 (w, $\delta(Tc-C\equiv O)$), 543.9 (w, $\delta(Tc-C\equiv O)$). NMR (toluene- d^8 , δ , ppm): 1H : -5.50 ; ^{99}Tc : -2501.83. EI mass spectrum M^+ , m/z : calculated 239.97 measured 239.9.

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The study was financially supported by the Russian Science Foundation (project no. 22-13-00057).

AN EFFECTIVE SYNTHETIC STRATEGY TO THE PREPARATION OF SUBSTITUTED PYRIDINES BY THE INTERACTION OF PYRAZINES WITH 2,5-NORBORNADIENE

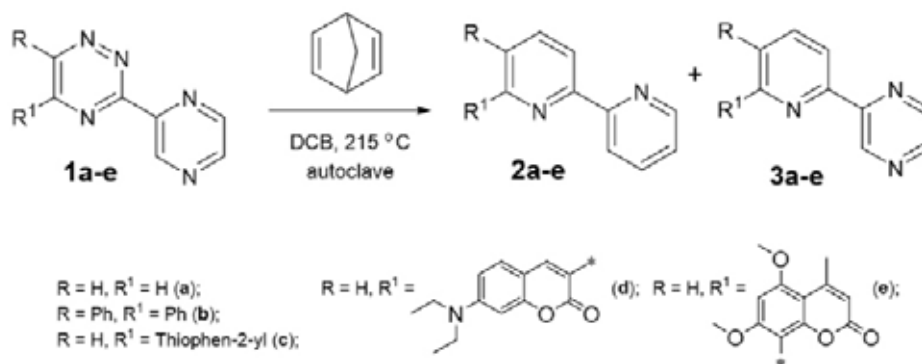
Sayfutdinova Y.M.,^a Kopchuk D.S.,^{a,b} Valieva M.I.,^{a,b} Krinochkin A.P.,^{a,b} Fatykhov R.F.,^a Khalymbadzha I.A.,^a Zyryanov G.V.^{a,b}

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The interactions of azaheterocycles (e.g. 1,2,4-triazines and 1,2,4,5-tetrazines) with dienophiles are of significant interest for the synthesis of various compounds. In this work, we demonstrate the possibility of converting the pyrazinyl fragment into 2-pyridyl one in a reaction with 2,5-norbornadiene under autoclave conditions.

Thus, the reaction of triazines **1a-e** with 2,5-norbornadiene in autoclave (*i.e.* at elevated temperature and pressure^{1,2,3}) resulted in a mixture of the expected product **2a-e** and the corresponding 2,2'-bipyridine **3a-e** (their ratio is close to 1:1), which is easily separated by column chromatography.



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USE OF ROBOTICS IN CHEMICAL SYNTHESIS

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Currently, the use of robotics in scientific research is becoming increasingly common, which is associated with a number of advantages. Firstly, robotization allows a large array of experiments to be carried out automatically, which not only saves the researcher's time, but also minimizes the human factor, which is essential when carrying out a large number of similar experiments. Secondly, robotization makes it possible to minimize the personal presence of the researcher during the process, which is promising in terms of working with harmful and dangerous substances.

This work is devoted to the use of robotic synthesis in a chemical laboratory. The experiments were carried out on a robotic system based on an automated system for PCR tests from the SmartLifeCare company. Analysis of samples after synthesis was carried out using a Knauer Smartline HPLC system. The reactions chosen for study were the formation of oligopeptides from amino acids under the action of sodium trimetaphosphate¹, as well as the reaction of aldol condensation catalyzed by zinc complexes².

On the base of the first reaction, the usage of robotic system to optimize synthesis conditions was considered. The varied parameters were the concentrations (and ratio) of glycine and sodium trimetaphosphate, the amount of added alkali, temperature and time of the process.

On the base of the second reaction, we considered the use of various catalysts (which were zinc complexes with different amino acids), as well as varying the reagents (isomeric nitrobenzaldehydes, bromobenzaldehydes; different ketones: acetone, cyclopentanone, etc.). In addition, the concentration of the catalyst was also varied.

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NEW ALUMINUM AND GALLIUM COMPLEXES AS INITIATORS FOR POLYMERIZATION OF CYCLIC ESTERS

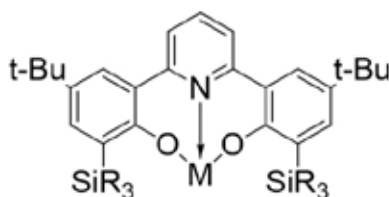
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Biodegradable polymers are an excellent alternative to typical α -olefin polymers derived from petroleum products. The main method for producing biodegradable polymers is ring-opening polymerization (ROP), which requires the presence of an initiator. In industry, this role is played by tin(II) bis-octanoate.¹ The development of new initiators based on less toxic metals is an urgent task in organometallic chemistry.¹

Polymers obtained from aluminum and gallium-containing initiators can be used for medical and food purposes due to the biocompatibility of these metals.²



M = AlMe, GaCl, GaCH₂SiMe₃

R = Me, Ph

The purpose of this work was the synthesis of new aluminum and gallium complexes based on tridentate ligands and the study of their catalytic activity in the polymerization of ϵ -caprolactone, L- and *rac*-lactides, as well as their copolymerization.

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HIGH TEMPERATURE RAPID AND ECOLOGICAL SYNTHESIS OF STABLE DIARYLPYRAZOLES (1,5) FROM (1,3) AS A METHOD FOR PERIPHERAL DIVERSIFICATION OF PYRAZOLE FRAGMENT IN MOLECULES

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The type of molecular editing based on the isomerization of substances allows the expansion of the number of targets to be investigated without the use of new substrates. Thus, the late-stage peripheral diversification of pyrazoles can accelerate the rate of discovery of new drugs and agrochemicals. Therefore, there is a need to develop a methodology for the rapid isomerization of pyrazoles with minimal co-substrates to simplify product isolation.

N-Ar fragments of the structure, are found in pharmacological drugs Celecoxib, CDPPB, Lonazolac, Mepirizole, Rimonabant, Difenamizole, and the isomerization reaction would allow to create new methods of synthesis. The little studied isomerization reaction of pyrazoles with aryl groups is most likely due to the high activation energy (above 50 kcal/mol). The results calculated in this study show high energy barriers of the order of 58 kcal/mol for the pyrazole isomerization reaction; therefore, high temperatures for organic chemistry would be required for the isomerization reaction of two adjacent nitrogen atoms of aryl pyrazoles.

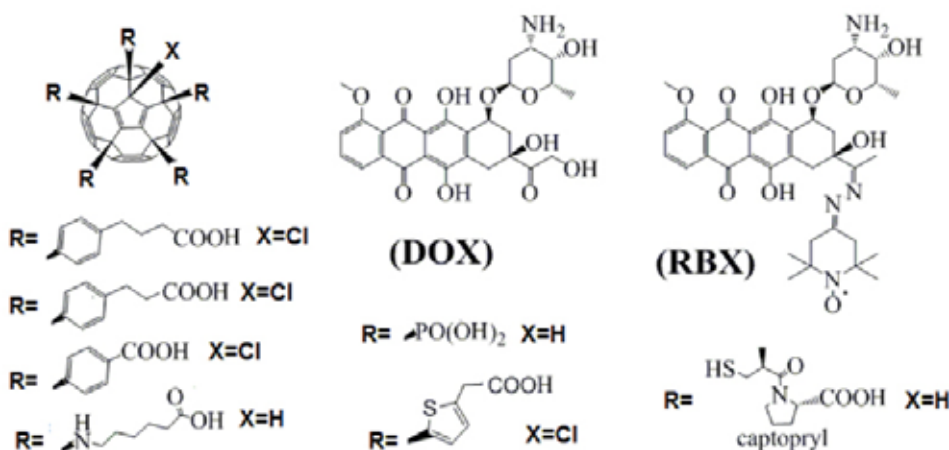
To broaden the scope of this transformation and generalize the conditions, we sought to obtain isomerization products with preparative yields at high temperatures (420-500 °C) using chemical glass capillaries. A correlation between the calculated activation energy and the degree of transformation of pyrazoles was also carried out. It is important to note that such transformations of pyrazoles provide a basis for expanding the synthesis strategy of important pharmaceuticals and materials.

QUANTUM-CHEMICAL MODELING OF THE STRUCTURE AND FORMATION ENERGY OF ADDUCTS OF WATER-SOLUBLE FULLEREN DERIVATIVES WITH THERAPEUTICALLY SIGNIFICANT ANTIOXIDANTS

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The combined use of water-soluble fullerene derivatives together with the antioxidants doxorubicin (DOX) and ruboxil (RBX) makes it possible to reduce their cytotoxicity and, in some cases, increases their therapeutic activity *in vivo*¹. The carried out quantum chemical modeling using the PBE density functional method of the structure of water-soluble fullerene derivatives made it possible to reveal the structure having the maximum binding energy with the antioxidant molecule. In general, this energy does not correlate with the number of intermolecular hydrogen bonds formed in the adduct, since the structural complementarity of the composition is of great importance. The highest binding energy reaches a value of about 35 kcal/mol. At the same time, the dissociation of one of the carboxyl groups does not always lead to increased binding in the adduct due to the accompanying effects of structural distortion.



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The work was supported by the Russian Science Foundation (grant no. 22-43-08005)..

SYNTHESIS AND CYTOTOXIC EVALUATION OF DIHETARYLMETHANES DERIVED FROM 3,3-DIETHOXY-1-PROPANE DERIVATIVES

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 Burilov A.R.,^c Pudovik M.A.^c**

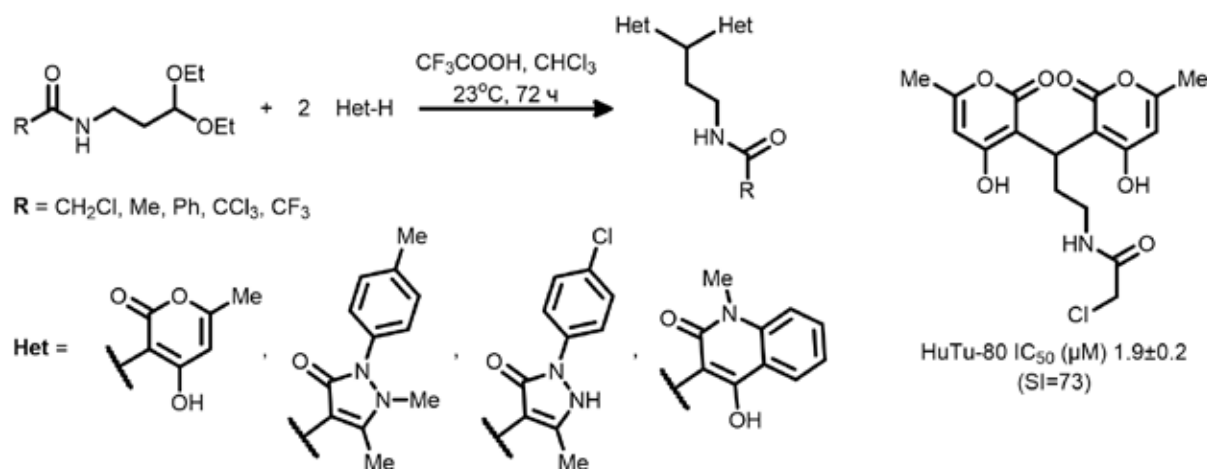
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A serious problem of modern healthcare is the therapy of malignant neoplasms, and therefore the creation of new types of highly effective and selective antitumor agents is one of the priorities of modern organic and medical chemistry.

We have developed an approach to the synthesis of previously unknown derivatives of dihetarylmethane based on the interaction of heterocyclic compounds with N-substituted aminoacetals, obtained a wide range of these compounds and studied their cytotoxicity against tumor and normal cell lines. The leading compounds exhibit cytotoxicity comparable to Doxorubicin against HuTu 80 and M-HeLa cells, while being, unlike Doxorubicin, low-toxic against normal cells.



The work was carried out with the financial support of the Ministry of Education and Science of the Russian Federation at the Kazan Scientific Center (Agreement No. 075-15-2022-1128 dated 30.06.2022).

MULTIFUNCTIONAL SILICA CARRIERS: SYNTHESIS ON HYBRID TEMPLATES, STRUCTURE AND PROPERTIES

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The problems of multidrug resistance of tumor cells and pathogenic microorganisms, as well as the rational use of drugs, are among the most pressing of modern medicine. Substantial progress in solving these problems is not possible without the use of new carriers that can ensure drug delivery and its controlled release, as well as the combination of different therapeutic methods.

The report discusses a new concept of sol-gel encapsulation. It is based on the use of micelles or vesicles of amphiphilic antiseptics containing several different biologically active compounds as templates in the synthesis of mesoporous silica carriers (MSCs). These compounds can be antibacterial drugs (including those that act by mechanisms other than antiseptics), as well as substances with anti-inflammatory, wound healing and other effects. The use of such MSCs and composite materials created on their basis should ensure controlled release of the loaded compounds and their combined action.

The advantages and prospects of this concept will be demonstrated using MSCs synthesized on hybrid templates, which are micelles of quaternary ammonium bases, such as miramistin and its analogues, containing a hydrophobic bioactive solubilize.

It is planned to focus on the analysis of experimental data on the relationship between template composition, conditions of MSC formation (ratio and nature of reaction system components, medium pH, temperature, etc.), structural and morphological characteristics such as silica carriers and the content of encapsulated biologically active compounds.

ON THE STUDY OF VAPOR PRESSURE OVER DILUTE AQUEOUS SOLUTIONS OF SOME VOLATILE COMPOUNDS

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The study of the properties of binary and multicomponent aqueous solutions is important for the correct assessment of the reactivity of substances in various media, the development of analytical methods for determining the composition and content of components in real objects with complex composition, and the design of technological lines. However, at present, the properties of many aqueous solutions of substances and limitedly soluble liquids have been studied over a wide range of concentrations. To estimate the parameters of highly dilute solutions of substances, the ideal solution approximation is mainly used, although in practice it is often not fulfilled. Therefore, assessing the properties of dilute solutions is important and relevant, for example, for the development of analysis techniques where the analytes are gases and vapors of volatile compounds. It is convenient and practical to use new instrumental approaches that make it possible to evaluate changes in properties in the system using indirect parameters.

In this regard, the goal of the work was to estimate the vapor pressure over dilute aqueous solutions of volatile compounds (alcohols, ketones, carboxylic acids) using the piezoquartz microweighing method.

Aqueous solutions (or mixtures with water) of volatile C_2 - C_5 compounds (alcohols, ketones, carboxylic acids) in the concentration range of 0-1 wt. % were studied in 0.01% increments, in the range of 1-10 wt. % in 1% increments. Boiling temperatures are determined for each mixture and solution. The vapor pressure over solutions (or mixtures) was estimated indirectly from the signals of piezoelectric quartz resonators with hydrophilic coatings based on deep eutectic solvents.

It has been established that for all studied substances there is a maximum boiling point and vapor pressure in the range of 0.01-0.1 mass. %, which may indicate the formation of azeotropic mixtures, or different degrees of structurization of solutions.

The work was carried out with the financial support of the Russian Science Foundation, project 22-76-10048.

SYNTHESIS OF NOVEL [1,2,5]OXADIAZOLO[3,4-*d*][1,2,3]TRIAZINONES

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1,2,5-Oxadiazoles (furazans) and their *N*-oxides (furoxans) are of significant interest for the preparation of potential therapeutic agents or components of high-energetic materials. However, it is worth noting that the target preparation of bi- and polycondensed structures based on 1,2,5-oxadiazole core has not been studied well enough. In this work, we have developed a new method for the synthesis of heterocyclic structures containing a triazine fragment annelated to the heterocyclic core of furoxan and furazan.

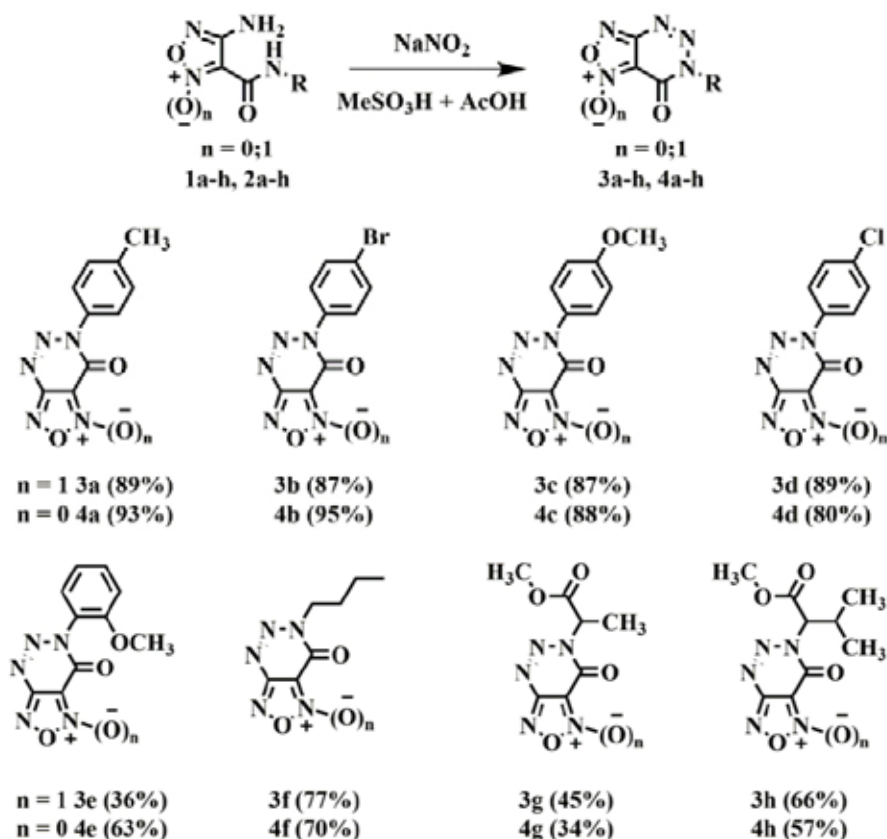


Image 1. Synthesis of novel triazinones.

The structure of all obtained substances was confirmed using modern physico-chemical methods. For furoxan derivatives, their NO-donor activity was evaluated.

The work was performed with the financial support of the RSF, project 23-43-00090.

THE CATALYTIC OXIDATION OF TRIPHENYLPHOSPHINE BY MOLYBDENUM- AND TUNGSTEN-CONTAINING COMPLEXES

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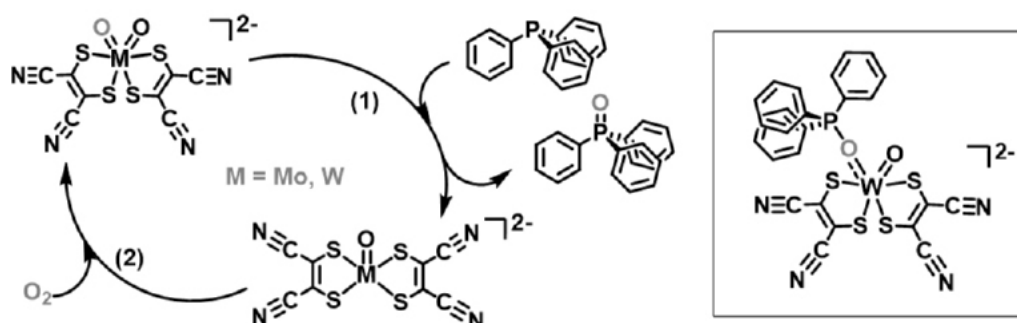
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Model complexes of tungsten and molybdenum with various dithiolene ligands are widely used for studying the natural enzymes of these metals¹. It is generally assumed that most processes involving these enzymes are oxo transfer, i.e. the transfer of an oxygen atom from a substrate to another molecule². Early studies conducted using enzyme models have shown that oxotransfer processes are second-order reactions. However, there are increasing reports of the detection of catalytic processes involving models³.

In this study, the interaction between $[\text{Bu}_4\text{N}]_2[\text{MO}_2(\text{mnt})_2]$ complexes (where $\text{M} = \text{Mo}$ or W , $\text{mnt}^{2-} = [\text{C}_2\text{S}_2(\text{CN})_2]^{2-}$) and PPh_3 was investigated. It was found that these reactions lead to the catalytic oxidation of the phosphine to produce phosphine oxide. Using ^{31}P NMR spectroscopy, the formation of the adduct $[(\text{mnt})_2\text{WO OPPh}_3]^{2-}$ was detected only in the case of the tungsten complex.



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The authors express their gratitude to the St. Petersburg State University Science Park. The work was performed using the equipment of the RC "CAMR", "XRD", "CMR".

CHALCOGENIC BONDS WITH ISOCYANIDES

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Chalcogenic bonds are intensively studied class of non-covalent bonds¹.

As a result of cocrystallization of mono- and diisocyanides with chalcogenic bond donors – bis(perfluoropyridin-4-yl)telluride and bis(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)telluride we could prepare three co-crystals having Te...C contacts, with length substantially less than sum of van der Waals radii. Such interaction with participation of isocyanogroup was explored in crystal state for the first time. The most relevant example of related interaction is halogen bond formation between halogen bond donors and isocyano group that has been described earlier². In the report we will discuss strength and nature of the identified non-covalent interactions with using X-Ray, spectral methods and theoretical calculations.

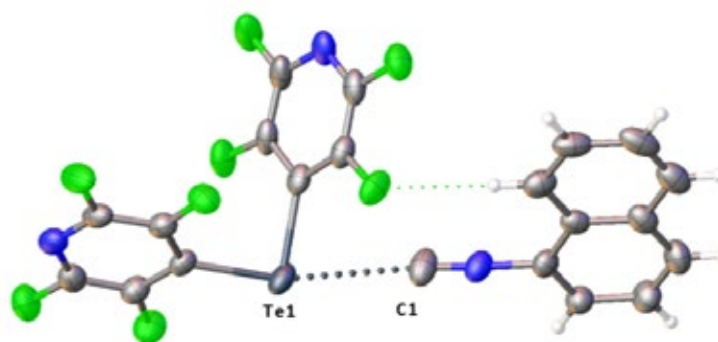


Image 1. Dimer, formed via ChB bond in the cocrystal of bis(perfluoropyridin-4-yl)telluride

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THE RELATIONSHIP BETWEEN ENTHALPY AND VOLUME CHANGES ON MELTING OF ORGANIC NON-ELECTROLYTES

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The thermochemistry of the melting of organic non-electrolytes has been studied for many decades. Information on the melting enthalpies of organic compounds is necessary for solving both fundamental and applied problems. The shortcomings of existing experimental methods for determining these quantities raise the problem of developing predictive approaches. However, despite the long history of the issue, there are no theoretical concepts or empirical schemes that allow predicting the melting enthalpies of organic compounds from physicochemical or structural parameters with sufficient accuracy.

The present work examines the relationship between enthalpies and volume changes during melting. It was found that at the melting point, the fusion enthalpy of non-self-associated aliphatic and aromatic compounds is proportional to the difference between the molar volumes of the liquid and crystalline phases¹. The proportionality coefficient depends on the shape of the molecule and increases when moving from spherical particles to long-chain compounds. In order to describe this dependence quantitatively, the sphericity parameter was introduced, which is defined as the ratio of the thickness of the molecule to its length (*sp*). The correlation between the ratio of the melting enthalpy to the volume change during melting and the sphericity parameter is described by the following equation:

$$\Delta H_m / \Delta V_m = 1.08 \cdot (1 - sp) + 0.35$$

The relations between enthalpy and volume changes accompanying phase transitions in liquid and plastic crystals were also considered.

The relationships found are of interest from the point of view of further investigation of the melting mechanism. In addition, the established relationships can be used for the construction of phase diagrams and the selection of phase change materials.

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The work was financially supported by the Russian Science Foundation, project 22-43-04412.

SYNTHESIS OF 5-[4-(ARYLSULFANYL)PHENYL]-2,2'-BIPYRIDINES USING ARYNE INTERMEDIATES

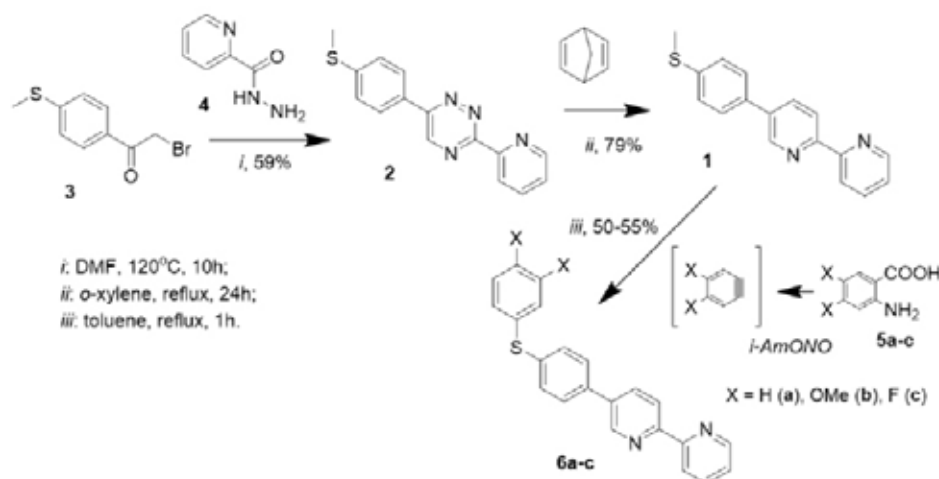
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A convenient method for the preparation of 5-aryl-2,2'-bipyridines with para-arylsulfanyl group in an aromatic substituent was proposed. The synthesis was performed using in situ generated aryne intermediates without the use of complex experimental procedures and expensive reagents/catalysts. The structure of one product was confirmed by XRD data. This approach is a new variant for the preparation of 5-aryl-2,2'-bipyridines with an extended conjugation system.



The structure of the target products was confirmed by ¹H, ¹⁹F, and ¹³C NMR spectroscopy, mass spectrometry, and elemental analysis. In addition, the structure of product 6a was additionally confirmed by X-ray diffraction data.

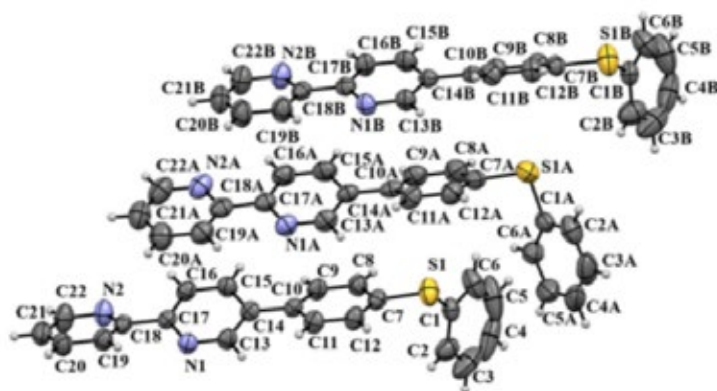


Fig. 1. General view of molecule of compound 6a in crystal.

The study was carried out with the financial support of the grant No. 075-15-2022-118

THE INFLUENCE OF THE CENTRAL ATOM ON THE PHYSICO-CHEMICAL PROPERTIES OF HETEROPOLY COMPOUNDS (HPC)

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Acidic petnahydrates of hexamolybdochromate(III)- (**HPC 1**) and hexamolybdocobaltate(III) (**HPC 2**) nicotinic acid with composition: $(\text{H}_3\text{O})_3[\text{Cr}(\text{Co})\text{Mo}_6(\text{OH})_6\text{O}_{18}]\cdot(\text{C}_6\text{H}_5\text{NO}_2)2\cdot5\text{H}_2\text{O}$ have been synthesized and studied by such methods as X-ray, TGA, IR and NMR spectroscopy. A comparative analysis of the dependence of the physicochemical properties of substances on the central atom was carried out based on the experimental and literary data¹.

Table1. A dependence of the physicochemical properties of HPC on the central atom.

central atom	Ionic radius, Å	(z^2/r)	length of the Met–O links, (Å)	Thermal stability	Solubility, (g/ml)	f (mdin/Å)
$\text{Cr}^{3+}(\text{K.Ч.}=6)$	0,615 [3]	14,63	1,968 [2]	245 °C	0,042	2,09
$\text{Co}^{3+}(\text{K.Ч.}=6)$	0,545 [3]	16,51	1,912	265 °C	0,055	2,67

The increase in the thermal stability of **HPC 2** is obviously associated with an increase in the polarizing effect (z^2/r) of the central atom Co^{3+} , which leads to an increase in 'f' and a decrease in the interatomic bond distance of Co –O (table 1). The weakening of the hydrogen bonds of organic fragments with heteropoly anion from 1,57 Å in **HPC 1**² to 1,67 Å in **HPC 2** due to the inductive effect leads to an increase in the solubility of **HPC 2** (0,055 g/ml) compared with **HPC 1** (0,042 g/ml). Similar patterns for GPS confirming the principle of trans-influence were described in the works of M.A. Porai-Koshits and L.O. Atovmyan⁴.

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COPPER(I) COMPLEXES WITH CYCLIC AMINOMETHYLPHOSPHINES – A PATH TO RATIOMETRIC LUMINESCENT THERMOMETRY

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The synthesis and study of transition metal complexes exhibiting dual-band luminescence is a current challenge, the solution of which could lead to the creation of new materials for measuring the temperature of submicron objects. In our research, we have synthesized a series of polynuclear copper(I) complexes with six- and eight-membered cyclic aminomethylphosphines (Figure 1).

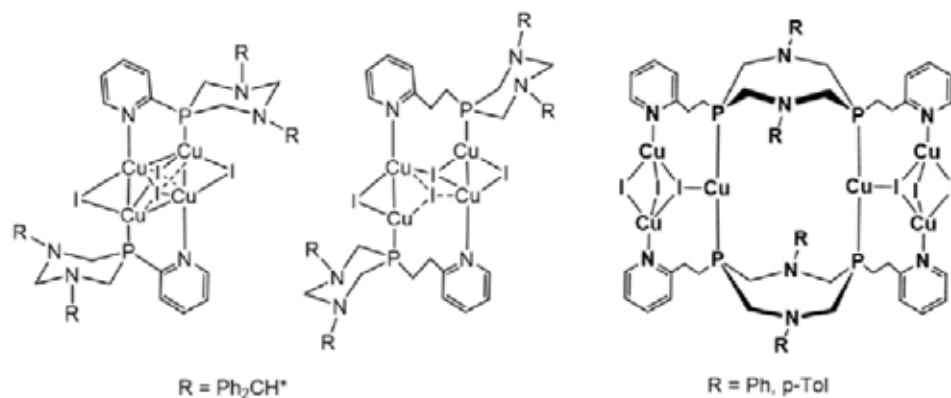


Figure 1. Structures of the luminescent copper(I) complexes with cyclic aminomethylphosphines

The photophysical parameters of these complexes were investigated, demonstrating their dual-band luminescence. Based on tetranuclear copper(I) complexes, composite materials have been developed, which are of interest as luminescent ratiometric thermometers operating over a temperature range from 77 to 373 K.

The work was supported by the Russian Science Foundation, project 22-13-00147.

THE SYNTHESIS OF 4-PYRONE-3-CARBOXYLIC ACIDS AND THEIR ENAMINODIONES-BASED DERIVATIVES

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4-pyrone-3-carboxylic acids and their derivatives are the important heterocyclic compounds that are of interest for the production of bioactive molecules, including the substances with antiviral activity. Wherein the acids themselves remain poorly studied and poorly available substrates.

In the present study a convenient method of synthesis of 4-pyrone-3-carboxylic acids and their *tert*-butyl esters was found, which is based on the transformation of enaminodiones **1**. As the result of the Claisen condensation of the substrates **1** in dioxane in presence of sodium hydride, the stable chelate complexes **2** are formed and precipitated. The processing of the compounds **2** by the saturated potassium hydrosulphate solution leads to its cyclisation with the formation of the esters of 4-pyrone-3-carboxylic acids **3**. The stirring of the chelate complexes **2** with the excess of trifluoroacetic acid in dichloromethane is accompanied by the removal of the *tert*-butyl group and gives the target 4-pyrone-3-carboxylic acids **4**.

The 4-pyrone-3-carboxylic acids and their esters obtained in the study are of the future interest as polyfunctional molecules for the construction of new heterocyclic and polycarbonyl structures.

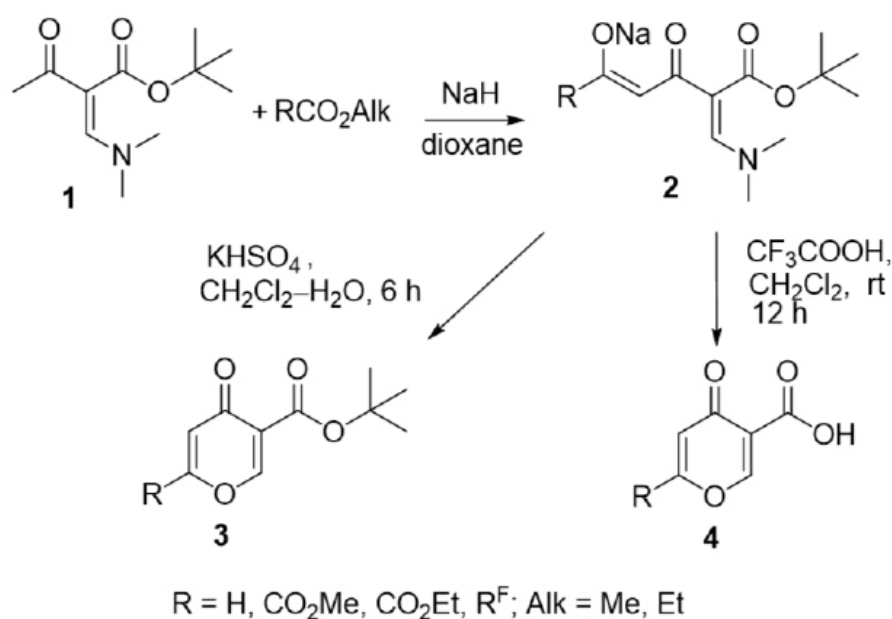


Figure 1. The scheme of production of 4-pyrone-3-carboxylic acids and their derivatives

This work was funded by the RSF grant No 22-73-10236.

PREPARATION AND PROPERTIES OF 5-ALKYL-SULFONYL- AND 5-ALKYL-SULFINYL-1H-TETRAZOLES

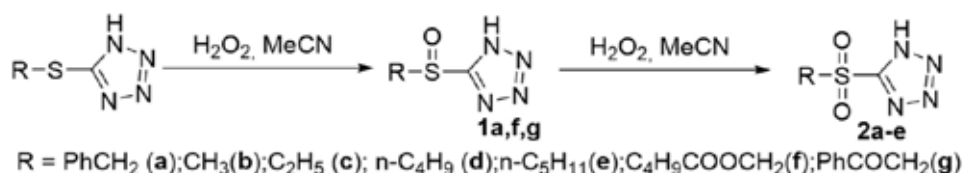
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5-R-sulfonyl- and 5-R-sulfinyl-1H-tetrazoles are promising but poorly studied compounds. These compounds due to the easily leaving sulfonyl or sulfinyl group, can be used to obtain variously substituted tetrazoles, as well as for the synthesis of other compounds^{1,2,3}. At the same time, the synthesis of sulfones and sulfoxides which do not contain substituents at the nitrogen atoms of the heterocycle has practically not been studied.

We have proposed a method for the synthesis of 5-alkyl-sulfonyl- and 5-alkyl-sulfonyl-1H-tetrazoles based on the interaction of the corresponding

5-alkylsulfonyl-1H-tetrazole with 60% H₂O₂ solution in acetonitrile.



We found that, depending on the conditions, can be obtained 5-alkylsulfonyl- and 5-alkyl-sulfonyl-1H-tetrazoles. Using quantum chemical calculations, it is shown that the energy barrier of sulfonyl and sulfinyl tetrazoles oxidation is sufficient to isolate the products of complete and partial oxidation.

Also, the reactivity of corresponding of 5-alkyl-sulfonyl- and 5-alkyl-sulfonyl-1H-tetrazoles was studied using the example of alkylation and nucleophilic substitution reactions.

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DESIGNING LUMINESCENT GROUP 11 METAL COMPLEXES WITH PYRAZOLE OR PYRAZOLATE LIGANDS

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Pyrazole-based ligands are extensively employed in transition metal chemistry, as they can function as bridge ligands and counter ions.¹ Pyrazoles in their NH form coordinate to group 11 metal ions through the lone pair of electrons on the imine-like nitrogen atom.² Deprotonated pyrazolate ligands allow formation of neutral polymeric or cyclic complexes, while bis-pyrazole molecules lead to the formation of metal-organic frameworks (MOFs).

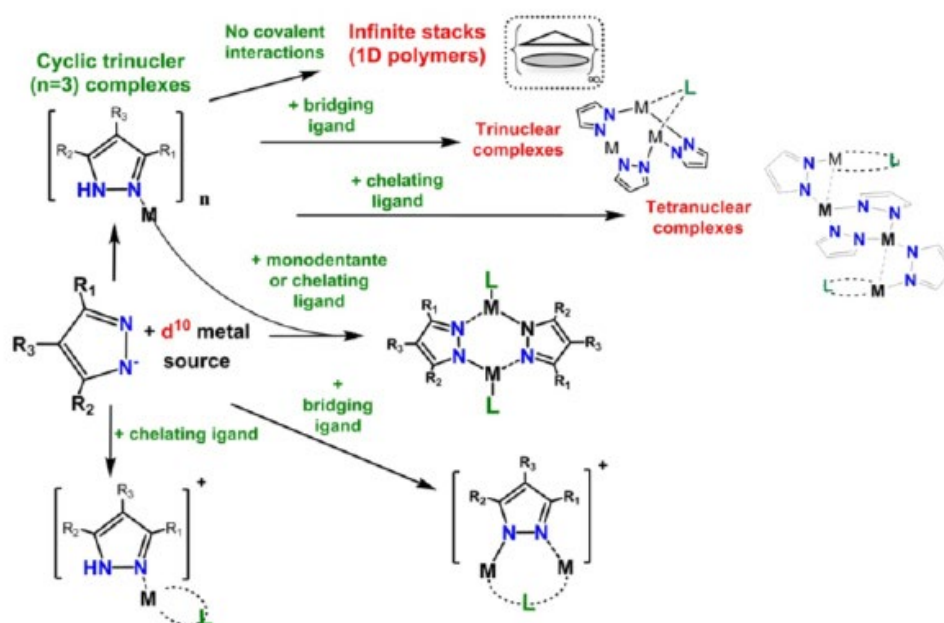


Figure 1. Different paths of group 11 metal pyrazolates formation.

The control of the photophysical properties of these complexes can be achieved by modifying the pyrazolate ligand³, by introducing auxiliary N-,P-ligands, or by forming new covalent or non-covalent complexes⁴ with organic phosphors.

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SYNTHESIS OF CHIRAL α -AMINO ACIDS AND THEIR DEUTERATED ANALOGUES USING THE MICHAEL REACTION

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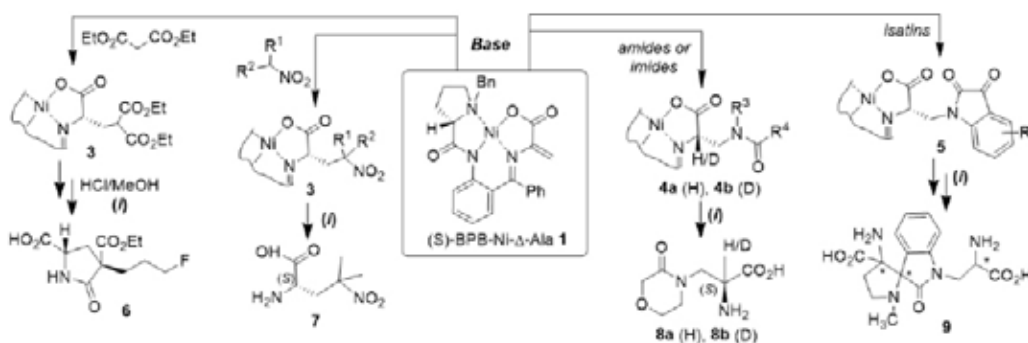
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Chiral unnatural α -amino acids and their deuterated analogues are widely used in various fields of biochemistry, such as pharmaceuticals and catalysis, as well as in the study of metabolic processes in living organisms.^{1,2}

The Michael reaction is one of the most popular and fundamental methods used to form C-C and C-N bonds. Due to its high efficiency and easy availability of reagents, this reaction is considered a main method for obtaining derivatives of α - and β -amino acids.³

In this work, we studied the addition of various compounds, including amides, imides, isatin, nitroalkanes, and CH acids, to the activated double bond of a chiral complex (S)-BPB-Ni- Δ -Ala **1** (Scheme).



In all cases, the reactions were conducted in the presence of bases, and the products **2-5** were obtained with high diastereoselectivity ($dr > 20:1$) and yields ranging from 55% to 96%. The decomposition of complexes **3**, **4a** and **4b** resulted in the corresponding α -amino acids **7**, **8a** and **8b** with yields between 85% and 95%. Further modification of products **2** and **5**, followed by hydrolysis in acidic conditions, yielded the corresponding chiral α -amino acids **6** and **9**.

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NOVEL «2+1» TRICARBONYL COMPLEXES OF TECHNETIUM-99,99M AND RHENIUM WITH FATTY ACIDS

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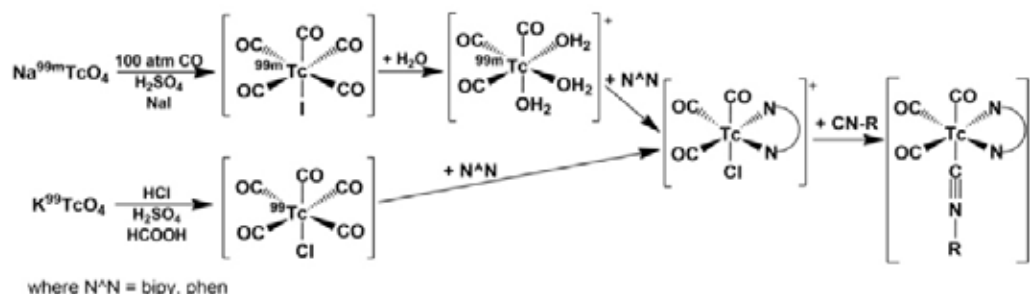
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$[M(CO)_3(H_2O)_3]^+$ cations ($M = Tc$ or Re) are convenient precursors for tethering $^{99m}Tc(CO)_3$ or $^{186,188}Re(CO)_3$ fragments to biomolecules. Introduction of $M(CO)_3$ core into a biomolecule requires substitution of three labile water ligands with bulky tridentate chelators or a combination of mono- and bidentate coordination units. In this study we used the latter approach to label fatty acids with technetium-99m. Previously we found that technetium and rhenium tricarbonyl cores formed strong complexes with combination of monodentate isocyanide ligand $CNCH_2COOEt$ and bidentate 1,10-phenanthroline and 2,2'-bipyridine ligands¹.

The aim of this work was to develop a procedure for preparing similar «2+1» tricarbonyl complexes of technetium-99,99m and rhenium with isocyanides of long chain fatty acids $(CN(CH_2)_4CH(COOEt)SC_{10}H_{21})$, $CN(CH_2)_{10}COOEt$. The procedure is presented on the following scheme:



The complexed we isolated and characterized by IR and NMR spectroscopy. The IR spectrum of the complexes contains three bands characteristic of the tricarbonyl fragment. The coordination of the isocyanide group is confirmed by the 1H NMR data. The lipophilicity of the technetium-99m complexes was measured.

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THERMODYNAMIC STABILITY, LABILITY AND STRUCTURE OF HOMO- AND HETEROLIGAND COMPLEXES OF OXOVANADIUM(IV) WITH AROMATIC N-DONORS AND AMINO ACIDS

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Oxovanadium(IV) complexes are very perspective for the treatment of various diseases. In the literature, compounds of this metal have been described with proven *in vitro* biological activity against tumor cells¹, and also as effective compounds in the treatment of type II diabetes².

Heteroligand complex compounds of oxovanadium(IV) are considered to be of particular interest for solving these problems. In the present work, the equilibria proceeding in the systems of oxovanadium(IV) – aromatic N-donors – amino acids at 25.0°C on the background of 1.0 M KNO₃ were studied by spectrophotometry, NMR-relaxation and EPR methods. By using a modelled and 3D-printed attachment for the NMR ampoule, the lability parameters of a number of studied coordination compounds were determined. The experimental results were analyzed using the STALABS^{3,4} program, which allowed us to determine the compositions and stability constants of all complex forms present in these systems. The structures of reagents, intermediates and final products of reactions were optimized using the ORCA⁵ program by DFT at the B3LYP/def2-TZVPP level, taking into account the effects of the environment in the continuum solvent model C-PCM.

The results derived from the present study are essential for the development of new drugs based on oxovanadium(IV) compounds.

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DETERMINATION OF THE PHYSICO-CHEMICAL EFFECTS ON AN INCREASE IN THE RATE OF RADICAL FORMATION IN OXYGEN-FREE AQUEOUS-ORGANIC SYSTEMS CONTAINING METAL OXIDE NANOPARTICLES UNDER THE ACTION OF X-RAY IRRADIATION

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Nowadays, metal and metal oxide nanoparticles (NPs) containing elements with a high atomic number are considered as perspective nanoradiosensitizers for various applications in medicine (for example, therapy and theranostics) and material chemistry (in particular for material modification). The effect of increasing sensitivity to ionizing radiation is generally based on the peculiarities of energy absorption and subsequent reactions of radicals in organized systems.

Previously we demonstrated that the increase of the number of radicals in the presence of metal gold and HfO_2 NPs in oxygen-free water-alcohol systems irradiated with X-rays (20–45 keV) is mainly attributed to a physical phenomenon – the photoelectric effect^{1,2}.

In this work, we report the first experimental evidence of a specific increase in the rate of radicals formation trapped by the PBN spin trap with subsequent EPR detection in model systems containing NPs WO_3 and SnO_2 , and compare the effect of the composition and size of the NPs on the physico-chemical mechanism of radiosensitization.

The obtained results give an evidence of the size effect for NPs WO_3 , as well as radiation-chemical processes involving the transformation of $\text{W(VI)} \rightarrow \text{W(V)}$. Similar-type behavior was found for SnO_2 NPs: the nonlinear dependence of the rate of radical formation on the concentration of SnO_2 NPs indicates a complex physico-chemical mechanism of radiosensitization.

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This work was supported by the RSF, project 22-73-00054.

C-H FUNCTIONALIZATION STRATEGY IN THE SYNTHESIS OF PHARMACOLOGICALLY ACTIVE COMPOUNDS AND FUNCTIONAL MATERIALS

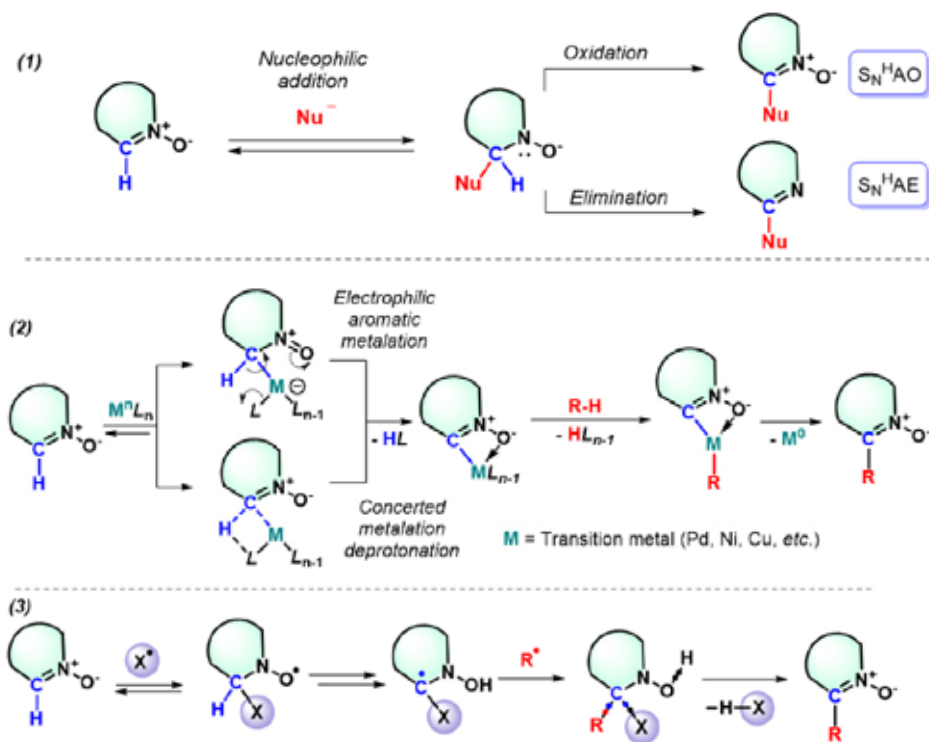
Varaksin M.V.,^{a,b} Moseev T.D.,^a Akulov A.A.,^a Nikiforov E.A.,^a Lavrinchenko I.A.,^a Idrisov T.A.,^a Nelyubina A.A.,^a Charushin V.N.,^{a,b} Chupakhin O.N.^{a,b}

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The C-H functionalization strategy is known to be a convenient tool in the synthesis of azaheterocyclic compounds. This method provides various efficient strategies to prepare target organic molecules of various architectures of interest in medicinal chemistry and materials science. Particularly, these synthetic schemes have currently been applied to functionalize both aromatic and *non*-aromatic azaheterocycles using by metal-free nucleophilic substitution of hydrogen S_N^H (1), transition metal-mediated cross-dehydrogenative coupling (CDC) reactions (2), as well as radical-mediated cross-dehydrogenative coupling (CDC) reactions (3).



(1): Nucleophilic substitution of hydrogen reactions according to «Addition-Oxidation» $S_N^H(AO)$ and «Addition-Elimination» $S_N^H(AE)$ protocols

(2): Transition metal-mediated cross-dehydrogenative coupling (CDC) reactions

(3): Metal-free radical-mediated cross-dehydrogenative coupling (CDC) reactions

The work was financially supported by the Ministry of Science and Higher Education of the Russian Federation (Agreement No. 075-15-2022-1118).

LUMINESCENT PROPERTIES OF THE PH-SENSITIVE FAMILY OF $\{\text{Mo}_6\text{I}_8\}$ COMPLEXES WITH H_2O AND OH-LIGANDS

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Octahedral molybdenum iodide cluster complexes $[\{\text{Mo}_6\text{I}_8\}\text{L}_6]^n$ (L is an apical ligand of organic/inorganic nature) exhibit pronounced luminescence in the red and near-IR regions, however the exact mechanism of this process remains unclear. Literature notes that both the ligands in a cluster complex and the distances between cluster cores can affect luminescence, but the influence of these factors has only been studied on relatively small groups of compounds. Cluster complexes $[\{\text{Mo}_6\text{I}_8\}(\text{H}_2\text{O})_x(\text{OH})_{6-x}]^{x-2}$ ($x = 2, 4, 6$) are suitable for studying the influence of these parameters on luminescence, as they exhibit different intercluster distances, and their ligands can be varied by altering the pH of the environment.

In this work, complexes of the composition $[\{\text{Mo}_6\text{I}_8\}(\text{H}_2\text{O})_4(\text{OH})_2](\text{An})_2 \cdot n\text{H}_2\text{O}$ ($\text{An} = \text{NO}_3^-$, $n = 3$; $\text{An} = \text{OTs}^-$, $n = 2$), $[\{\text{Mo}_6\text{I}_8\}(\text{H}_2\text{O})_4(\text{OH})_2](\text{PhO})_2\text{PO}_2]2 \cdot 6\text{H}_2\text{O} \cdot 2\text{EtOH} \cdot 2(\text{PhO})_2\text{PO}_2\text{H}$; $[\{\text{Mo}_6\text{I}_8\}(\text{H}_2\text{O})_2(\text{OH})_4] \cdot 12\text{H}_2\text{O}$; $[\{\text{Mo}_6\text{I}_8\}(\text{H}_2\text{O})_6](\text{An})_4 \cdot n\text{H}_2\text{O}$ ($\text{An} = \text{NO}_3^-$, ClO_4^- , SO_3CF_3^- , $n = 2$; $\text{An} = \text{OTs}^-$, $n = 0$) were obtained. Analysis of the electronic absorption spectra of aqueous solutions established that a decrease in pH value leads to the protonation of apical ligands and the formation the $[\{\text{Mo}_6\text{I}_8\}(\text{H}_2\text{O})_6]_4^+$ cation. Such protonation results in an increase in luminescence intensity, accompanied by a hypsochromic shift of the emission maximum. Furthermore, decomposition of the obtained spectra into their components using the Gaussian function showed that as the pH decreases, the contribution of higher-energy components increases.

For all compounds obtained in solids, the temperature dependence of luminescence was studied. At room temperature, a decrease in the crystal packing density leads to an increase in the quantum yield and luminescence lifetime, as well as the contribution of two high-energy components of the spectrum. A decrease in temperature, in turn, leads to a redistribution of the intensities of the Gaussian components and, accordingly, a hypsochromic shift of the emission maxima.

The work was carried out with the financial support of the Russian Science Foundation, project 19-73-20109.

ESTIMATION OF THE CONTRIBUTION OF MOLECULAR VIBRATIONS TO THE FREE ENERGY OF A CHEMICAL SYSTEM

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The vibrational free energy model in quantum chemistry is sensitive to the values of low frequencies, which in turn are very sensitive to both the level of theory (how interactions between frequencies are described) and to the non-covalent interactions of the molecule with surrounding particles, which, as a rule, are solvent molecules.

We studied models for calculating the contributions of low frequencies to the free energy of a molecule and searched for a model that would use reliable information about low frequencies from quantum chemical calculations (number, reality) and was not sensitive to their unreliable characteristics, such as vibrational frequencies. We showed that low frequencies (up to $\sim 300\text{ cm}^{-1}$) cannot be accurately calculated using existing approaches and proposed an improved model based on the quasi-harmonic approximation of D. Troular¹, which is robust to errors in the description of low frequencies.

The approach we propose allows us to extract as much information as possible from obviously incorrect low frequencies of vibrations and reduce their influence on the relative energy of molecules without compromising their accuracy and calculation time, thereby solving the problem of sensitivity of low frequencies.

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The research was carried out with the financial support of the Russian Science Foundation (grant 22-73-10124).

CONFORMATIONAL ANALYSIS OF α - AND β -AMINOPHOSPHINE OXIDES IN SOLUTION. EXPERIMENT AND THEORY

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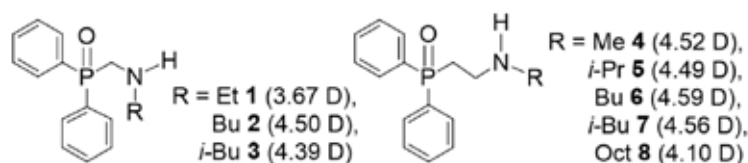
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Secondary amines containing a phosphoryl group are used as building blocks for the synthesis of modified carbamoylmethylphosphine oxides – extractants of rare earth elements and actinides,¹ as well as transition metal complexes.²

Experimental and theoretical conformational analysis of α - and β -aminophosphine oxides **1-8** was carried out using the methods of dipole moments, IR spectroscopy and quantum chemistry in the gas phase and in benzene solution (DFT B3PW91/6-311++G(df,p)+CPCM). The experimental dipole moments of *N*-(diphenylphosphinylmethyl)-*N*-alkylamines **1-3** and *N*-(diphenylphosphinyethyl)-*N*-alkylamines **4-8** were determined in benzene (μ_{expt} , D).



A comparison of experimental data (dipole moments, IR spectra) and theoretical results indicates that in solution α - and β -aminophosphine oxides **1-8** exist as conformational equilibrium of several forms, in which the phosphorus atoms are pyramidal, phenyl substituents on the P atoms are pre-dominantly *cis*-oriented, and the methylene or ethylene bridges are *gauche*-oriented with respect to the P=O bond. In some conformers, intramolecular bonds arise between the hydrogen atom of the amine fragment and the oxy-gen atom of the phosphoryl group.

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INTERACTION OF 2-METHYLBENZO-1,3,2-DIOXAPHOSPHORIN-4-ONE WITH HEXAFLUOROACETONIMINE: DFT STUDY

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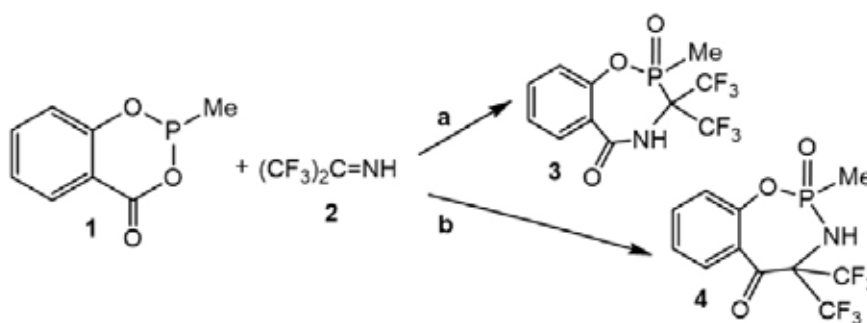
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It is known that the interaction of 2-R-4-oxo-5,6-benzo-1,3,2-dioxaphosphorinanes with hexafluoroacetone imine leads to the formation of derivatives 2-R-5-oxobenzo[e]-1,3,2- and 2-R-5-oxo benzo[e]-1,4,2-oxazaphosphepines depending on the nature of the substituent R.^{1,2}

Quantum chemical study of the reaction mechanism of 2-methylbenzo[e]-1,3,2-dioxaphosphorin-4-one **1** with hexafluoroacetone imine **2**, leading to the formation of amidophosphate **4** (scheme 1b), showed that the reaction proceeds in three steps. At the first step, which limits the entire process, through a transition state with ΔE 22.0 kcal/mol, intermediate-1 with a pen-ta-coordinated phosphorus atom is formed, which at the second step rear-ranges into intermediate-2 with a different orientation of the fragment $\text{HN}=\text{C}(\text{CF}_3)_2$, and at the third step, intermediate-2 through a transition state with ΔE 14.6 kcal/mol is transformed into the reaction product. The reaction is exothermic ($\Delta E = -21.3$ kcal/mol). Interaction along route (1a) (scheme 1) – the formation of 2-methyl-3,3-bis(trifluoromethyl)-2,5-dioxobenzo[f]-1,4,2-oxazaphosphepine **3** proceeds in one step ($\Delta E = 25.7$ kcal/mol),³ i.e. there is some gain in energy.



Scheme 1.

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INVESTIGATION OF THE EQUILIBRIUM OF CRYSTAL VIOLET LACTONE

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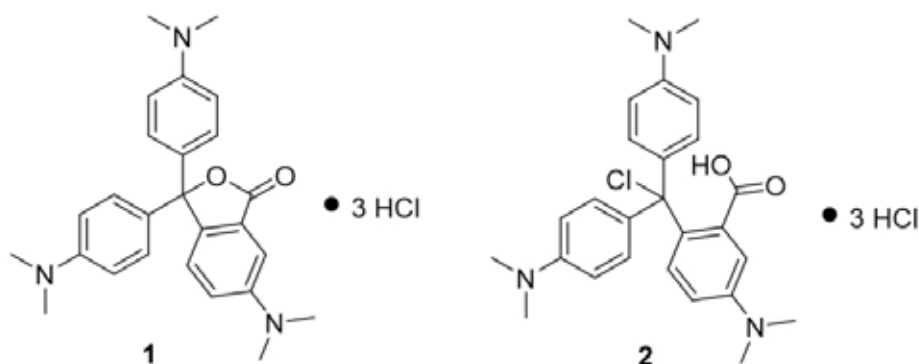
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Crystal violet lactone (CVL) belongs to the class of triphenylmethane dyes, absorbs strongly in the visible part of the spectrum. It's applied as a component in organic thermochromic compositions, a marker for fuel and for producing "smart" coatings.

The presence of a lactone cycle in a dye molecule contributes to the transition from a colorless form to a colored one due to formation of a conjugated p-system with an open ring. Until now a detailed research of an equilibria in CVL solutions have not been conducted.

Thus, CVL salts **1**, **2** by passing gaseous HCl through a dye solution in acetone have been obtained. Their composition have been investigated and confirmed by elemental analysis and argentometric titration. XRD has allowed to establish that 3 HCl molecules form salt **1** by amino groups of the dye.



Obtaining a CVL salt with an accurately known composition have made possible studying the equilibria, as well as receiving the constants between colored and colorless forms¹.

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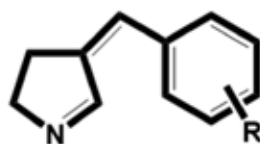
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NEW 3-ARYLDENE-1-PYRROLINIUM COORDINATION COMPOUNDS: SYNTHESIS AND STRUCTURAL FEATURES

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The use of new coordination compounds is one of the most accessible ways to obtain substances with desired properties. Using metals and ligands that have certain sets of properties, it is possible to obtain complexes whose properties represent both a superposition of the properties of their components, and substances that have completely new characteristics inherent exclusively to them.



This work presents a study of the interaction of a number of 3-arylidene-1-pyrrolinium derivatives with metal salts. This class of organic compounds was chosen as having a specific type of biological activity - the ability to inhibit the formation of bacterial biofilms of the ESKAPE group of pathogens, characterized by increased resistance to antibiotics.

In the process of work, coordination compounds of substituted 3-arylidene-1-pyrrolines with a number of existential metals were obtained. Using copper complexes as an example we have shown the influence of the nature of the counterion and the substituent in the arylidene fragment on the structure of the resulting complex. Thus, if in trifluoroacetate complexes the main factor determining the structure is the nature of the substituent in the N-donor ligand, then in nitrate complexes the structure is entirely determined by the nature of the nitrate anion. It is interesting to note that no similar dependencies were found for zinc complexes and their structure is determined only by the configuration of the metal ion. Silver complexes turned out to be very interesting from the point of view of structural analysis. The main factor in them, which influences the structure of the complexes is non-covalent interactions formed with the participation of metal ions. Thus, in the resulting compounds Ag...Ag, Ag...O, Ag... π and a number of other interactions are realized.

The work was carried out with financial support from the Russian Science Foundation (project No. 23-13-00374).

NEW METHODS FOR STUDYING THE PHOTOCHEMICAL AND BIOLOGICAL PROPERTIES OF RUTHENIUM NITRO-NITROSOCOMPLEXES

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Ruthenium nitrosocomplexes are promising compounds for the development of new photoactivated chemotherapy agents, in which the selective delivery of a photosensitive agent to cancer cells and their subsequent activation by light offers an interesting opportunity to address problems associated with traditional antitumor chemotherapy.

In addition to the synthesis of novel complex compounds with promising ligand environments, an important aspect of research involves the reliable determination of photochemical properties under various conditions with the goal of subsequent testing for photoactivated anticancer activity.

As a result of the studies conducted, cytotoxicity in relation to the MCF-7 cancer line was examined on $[\text{RuNO}(\text{L})_2(\text{NO}_2)_2\text{OH}]$, where L represents methyl nicotinate, methyl isonicotinate, ethyl nicotinate, ethyl isonicotinate, 1.10-phenanthroline. The significant dependence of cytotoxicity on the lipophilicity of these compounds was demonstrated.

A flow-through system was developed to record IR optical spectra, which allowed for the determination of the quantum yields of the reactions and the study of photolysis processes. Using the ESI-MS method, the major complex forms present in solution, both before and after the photolysis process, were identified.

The work was carried out with the financial support of the Russian Science Foundation, project 22-43-09001.

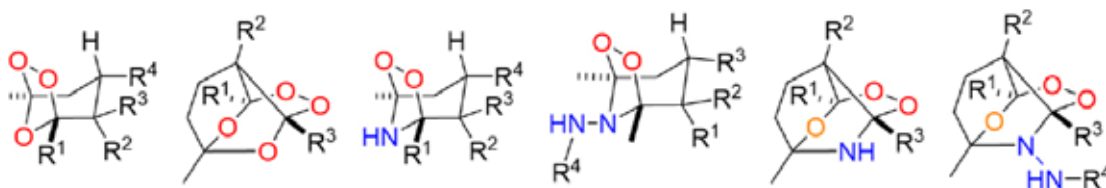
THE MYSTERIOUS WORLD OF ORGANIC PEROXIDES

**Yaremenko I.A., Fomenkov D.I., Budekhin R.A., Demina A.A., Belyakova Yu.Yu.,
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Organic peroxides are widely used in the polymer industry as radical polymerization initiators and crosslinking agents. In modern medical practice, the natural peroxide artemisinin, its derivatives and synthetic analogs are important antimalarial drugs. Active research is underway to develop synthetic peroxides with antiparasitic, anticancer, fungicidal and antiviral activity, including against SARS-CoV-2.

In our studies, we have developed approaches¹⁻³ for the synthesis of stable peroxides from carbonyl compounds, H_2O_2 , and a source of NH-group in the case of aminoperoxide synthesis. Aminoperoxides are remarkable in that they contain both an oxidizing and a reducing agent in their composition. The crucial role of stereoelectronic effects in intermediate oxycarbenium and peroxy-carbenium cations and transition states in the selectivity of peroxide synthesis is shown. The synthesized peroxides exhibit antimalarial activity, cytotoxicity and selectivity towards cancer cells. Nontrivial transformations of the peroxides have been discovered.⁴



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SENSOR PROPERTIES OF LUMINESCENT COORDINATION POLYMERS BASED ON FLEXIBLE POLYCARBOXYLIC ACIDS

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Due to their unique properties, lanthanide-based metal-organic framework materials (Ln-MOFs) have achieved some excellent results in the field of luminescent detection. In this work, Ln-MOFs based on various flexible ligands, polycarboxylic acids, were considered, their structures and luminescent properties were studied, and their ability to detect harmful substances and anti-counterfeiting applications were investigated (Figs. 1, 2). The results showed that these Ln-MOFs could detect iron(III) ions in water¹; the phytotoxin gossypol in water and cottonseed oil²; and ofloxacin in water and meat³. In addition, three new anti-counterfeiting strategies with different modes have been developed.

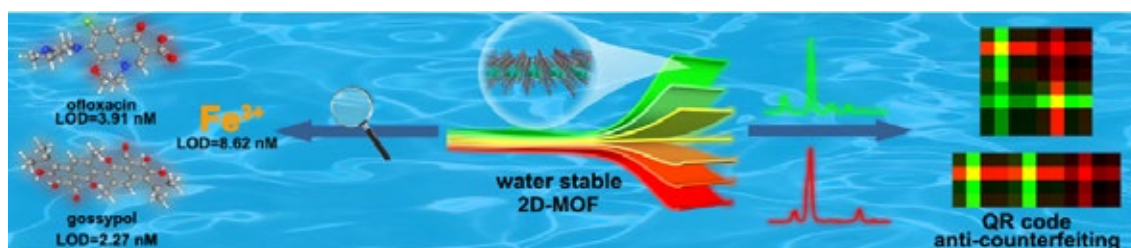


Figure 1. Sensor properties and anti-counterfeiting protection based on NIIC-1-Ln

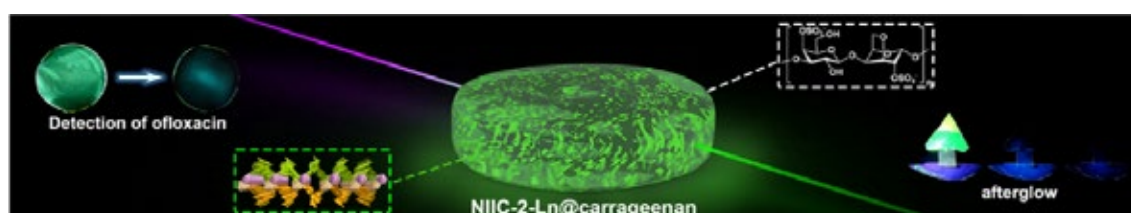


Figure 2. Sensor properties and anti-counterfeiting protection based on NIIC-2-Ln

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SYNTHESIS OF NEW HYDRAZONES BASED ON PHOSPHANEOFLAVONOIDS AND FUNCTIONALLY SUBSTITUTED CAG PHOSPHONATES OF UNSYMMETRICAL TYPE

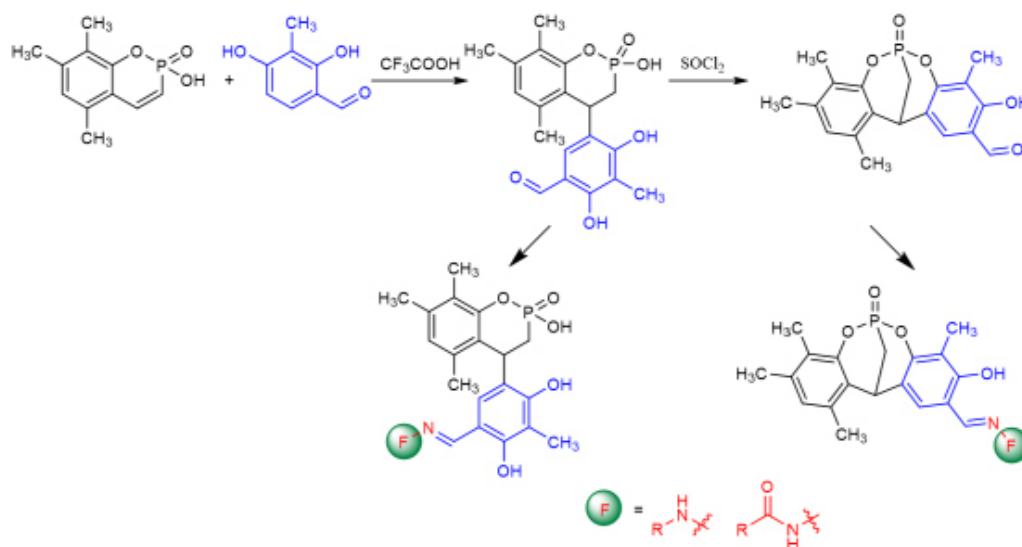
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The development of methods for the synthesis of new types of phosphorus-containing polycyclic structures does not lose its relevance today.

In continuation of our previous works^{1,2}, we have realized the synthesis of new neophosphaflavonoids and functionally substituted cag phosphonates of unsymmetrical type, containing a terminal carbonyl group. Modification of the resulting compounds led to new, previously undescribed hydrazones with potential antimicrobial activity and cytotoxicity.



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SYNTHESIS OF BIS(AZA-18-CROWN-6) DIENONE OF CYCLOPENTANONE SERIES, SUPRAMOLECULAR COMPLEXES BASED ON IT

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Supramolecular systems based on crown esters are proposed to be used for chemical and environmental analysis. Of particular interest are crown-containing dyes combining chromophore and ionophore fragments in their structure. In order to study the possibility of using bis(azacrown)-containing dienones as chemosensors, bis(aza-18-crown-6) containing dienone **1** was synthesized. The starting dienone of the cyclopentanone series **1** was synthesized by the condensation reaction of cyclopentanone and the formyl derivative N-phenylase-18-crown-6-ether in the presence of KOH. The structure of the obtained dienone **1** was established using NMR, IR, and electron spectroscopy and confirmed by elemental analysis data.

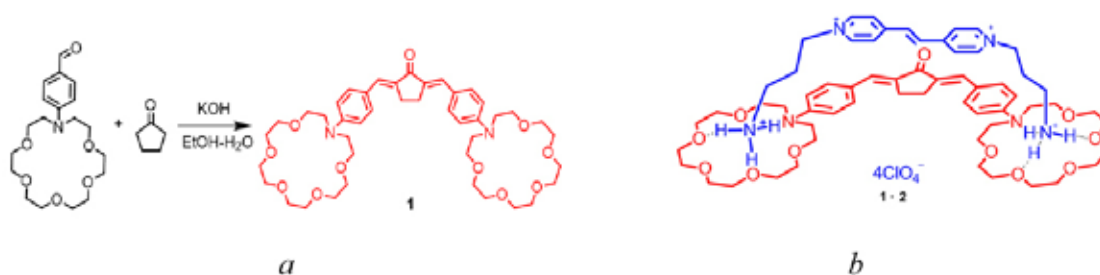


Figure 1. Synthesis, structure of dienone **1** (a) and its complex with diammoniopyridyl derivative of dipyrildylethylene (b)

A supramolecular donor-acceptor complex formed by bis(aza-18-crown-6)-containing dienone **1** with bis(ammonio)pyridyl dipyrildylethylene derivative **2** through hydrogen bonds was studied using absorption, luminescence and NMR spectroscopy. It was shown that dienone **1** with dipyrildylethylene derivative **2** in MeCN form a supramolecular complex of a pseudocyclic structure with intermolecular charge transfer (ICT). The formation of complex **1·2** leads to quenching of the fluorescence of dienone **1**. When Ca²⁺ cations are added to the solution of complex **1·2**, an increase in the fluorescence of **1** is observed. The research results show that the charge-transfer complex between **1** and **2** is an example of a supramolecular system capable of causing a strong fluorescent response when interacting with Ca²⁺ ions.

The work was carried out with the financial support of the Russian Science Foundation (project №22-13-00064).

STUDY OF THE INFLUENCE OF SUBSTITUENTS ON THE STRUCTURE AND THERMAL PROPERTIES OF VOLATILE Cu^{2+} COMPLEXES

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Cu-based films and nanoparticles are used as conductors in microelectronics, as catalysts, and as components of optoelectronics. The method of chemical vapour deposition (MOCVD) is convenient for their preparation. $\text{Cu}(\text{L})_n$ complexes, $\text{L} = \text{R}^1\text{C}(\text{O})\text{CHC}(\text{X})\text{CR}^2$ β -diketonates ($\text{X} = \text{O}$) and their derivatives - β -iminoketonates ($\text{X} = \text{NR}^3$) are often used as precursors. Usually, increasing the carbon skeleton of the ligand in such complexes makes them more low-melting, which is more convenient for practical use.

Therefore, this work extends the library of above volatile copper compounds and is devoted to the study of the influence of substituents in L on their structure and thermal properties. In a series of non-fluorinated complexes, symmetric derivatives (hd or i-hd, $\text{R}^1 = \text{R}^2 = \text{Et}$, $\text{X} = \text{O}$ or NH) are chosen as the objects of study. Due to the peculiarities of synthesis, the influence of isomerism of the NR^3 -group position is considered on the example of fluorinated derivatives ($\text{R}^3 = \text{H}$: $\text{R}^1 = \text{nC}_3\text{F}_7$, $\text{R}^2 = \text{Me}$ (L_1) or vice versa (L_2)).

The complexes were prepared by reaction of freshly precipitated $\text{Cu}(\text{OH})_2$ with HL, purified by recrystallisation / sublimation, and characterised by CHN(F)-analysis, IR spectroscopy and powder XRD.

According to PCA data, β -diketonate $\text{Cu}(\text{hd})_2$, unlike its analogues, exhibits two structural transformations in the range from 150 to 255 K, which are due to a change in the conformation (ordering) of Et substituents. During these transitions, the unit cell volume decreases discontinuously. β -Iminoketonate $\text{Cu}(\text{L}_1)_2$ exists as a *cis-trans* isomer, whereas $\text{Cu}(\text{L}_2)_2$ forms a *trans*-isomer (like the analogue with a smaller skeleton $\text{Cu}(\text{kft})_2$, $\text{X} = \text{NH}$, $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{CF}_3$).

Thermal properties were investigated by thermogravimetry and differential scanning calorimetry (DSC). On the basis of DSC, the temperatures and $\Delta_{\text{pt}}H$ and $\Delta_{\text{pt}}S$ of phase transitions were found. It is shown that an increase in the carbon skeleton L leads to a decrease in T_{mp} (in both cases, $\sim 80^\circ\text{C}$ relative to analogues with a five-membered skeleton).

MONOISOTOPIC BIOPOLYMERS EXHIBIT FASTER CHEMISTRY

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Inorganic materials, e.g. semiconductors, being depleted of heavy stable isotopes are known to deviate strongly in some physicochemical properties from their isotopically natural counterparts. For instance, silicon ^{28}Si (99.87%) has a 60% higher thermal conductivity at 80K than silicon with natural ($\approx 92\%$ ^{28}Si) isotopic composition. Qualitatively similar results have been obtained for monoisotopic diamond (99.8% ^{12}C) and gallium arsenide.

Here we explored for the first time the effect of simultaneous depletion of the heavy carbon, hydrogen, oxygen and nitrogen isotopes on the bacterium *E. coli* and the enzymes expressed in it. Bacteria showed significantly faster growth, with most proteins exhibiting higher thermal stability, while for recombinant enzymes expressed in depleted media, faster kinetics was discovered. At room temperature, the almost monoisotopic luciferase, thioredoxin and dihydrofolate reductase as well as Pfu DNA polymerase showed up to a 250% increase in activity compared to the native counterparts, with an additional $\sim 50\%$ increase at 10°C [1]. Diminished conformational and vibrational entropy is hypothesized to be the cause of the accelerated kinetics. Ultralight enzymes may find an application where extreme reaction rates are required.

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An abstract visualization of a complex molecular or material structure. It features a dense, interconnected network of small, colored spheres (primarily blue, green, and yellow) forming a large, irregular, and porous shape. The structure is set against a dark, almost black background, which makes the vibrant colors of the spheres stand out. The overall appearance is reminiscent of a microscopic view of a material or a complex chemical molecule.

SECTION 2

CHEMISTRY AND TECHNOLOGY OF MATERIALS

STRATEGIES TOWARDS OBTAINING NOVEL GROUP 10 METAL-BASED INTERMETALLICS WITH COMPLEX ARCHITECTURES

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Intermetallic compounds (IMC) and their derivatives are extremely important objects in terms of both fundamental point of view and potential for their applications. Their study is associated with interdisciplinary research at the cross-point between inorganic chemistry, solid state chemistry, condensed matter physics and materials science. IMC not only form a wide variety of structures and are characterized by non-classical chemical bonding schemes, but also exhibit a whole range of non-trivial physicochemical properties, which determine the potential for their functionalization.

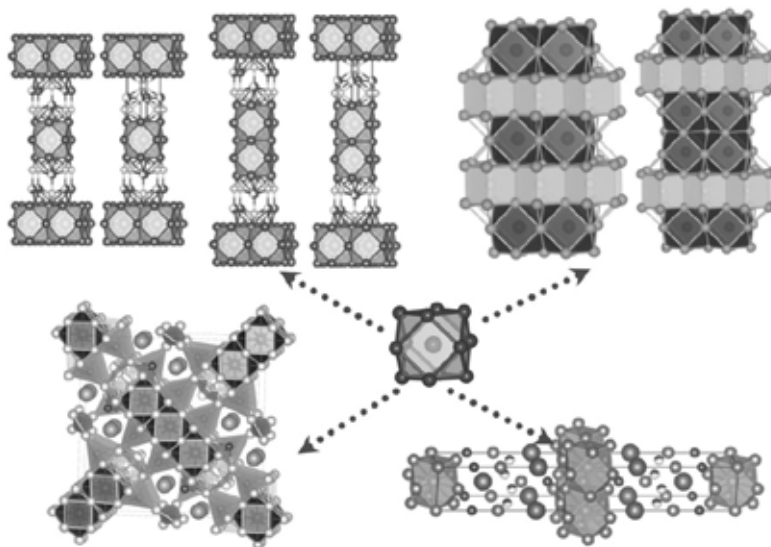


Figure 1. Examples of complex architectures based on the AuCu_3 -type fragments.

Based on the research of the authors, this report showcases the problems of design and targeted synthesis of complex architectures based on stable intermetallic fragments, such as AuCu_3 (see Fig. 1), NiAs , Ni_2In , provides the description of crystal and electronic structures, emphasizes the structure-property relationship for these compounds, and discusses the subject of designing and creating compounds built as intrinsic heterostructures with a given order of alternation/packing of fragments, as well as the influence of structure on functional properties.

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Functional high-entropy materials

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High entropy materials are of interest from scientific and practical point of view. Thus, this review describes several methods of synthesis of high entropy materials, their disordered atomic structure and novel functional properties.

Development and preparation of materials with prescribed properties is one of the task of modern material science. Traditional method of solving such a task for metallic materials consist of selection of base chemical element and post doping of this element by others elements in low amounts. Nevertheless about 20 years ago the development of materials made of five or more elements with nearly equivalent amount is began. As a result, almost simultaneously by few independent groups of researches a new type of materials were developed and named as high-entropy materials. High-entropy materials are groups of constrictive and functional materials based on multicomponent alloys [1]. Given review is devoted to synthesis, structure and functional properties of such high-entropy materials, theirs carbides, nitrides, oxides and boride [2-6].

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Work is done according to state task of IMET UB RAS with the usage of CCU “URAL-M” equipment.

DEVELOPMENT OF ENVIRONMENTALLY FRIENDLY THERMOELECTRIC MATERIALS BASED ON COMPLEX COPPER SULFIDES

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Thermoelectric materials for generating electricity out of waste heat are in demand by the automotive industry. Such materials are capable of transferring up to 40% of the lost energy in the form of waste heat into the vehicle's on-board electrical system, significantly reducing fuel costs. Strict requirements are imposed on such materials. They should demonstrate thermoelectric efficiency of the order $ZT = 1$ ($ZT = S^2 T \sigma / \kappa$, where S is the Seebeck coefficient, T is the absolute temperature, σ is the specific electrical conductivity, and κ is the thermal conductivity) and must be environmentally friendly and do not contain expensive chemical elements.

In recent years, there has been an interest in thermoelectric materials based on complex copper sulfides, which are often analogs of natural minerals. They have many features in common. In particular, they have highly symmetrical crystal structures built by sharing CuS_4 and MS_4 tetrahedra, where M is a transition or post-transition metal, they display the coexistence of Cu^+ and Cu^{2+} cations; finally, they demonstrate properties of narrow-band or even degenerate semiconductors.¹

We have recently proposed new approaches to the development of thermoelectric materials based on complex copper sulfides. They consist in creating, by heterovalent substitutions, conditions for the realization of valence fluctuations for the implementation of fast hopping conductivity, which increases the efficiency of transport of charge carriers, as well as clustering and local disordering to effectively reduce heat transport. In this paper, we will demonstrate the results of studies of synthetic analogs of three families of compounds related to copper-sulfide minerals – colusites, tetrahedrites, and owensites, described by the simplest formulas $\text{Cu}_{26}\text{V}_2\text{Sn}_6\text{S}_{32}$, $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$, and $\text{Ba}_6\text{Cu}_{12}\text{Fe}_{13}\text{S}_{27}$.

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OXIDE SYSTEMS AND MATERIALS AT HIGH TEMPERATURES: THERMODYNAMICS, VAPORIZATION, MODELING

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Modern scientific and technological solutions during synthesis and operation of advanced materials at high temperatures dictate the necessity of the availability of information on vaporization processes and thermodynamic properties of oxide systems as well as glasses, ceramics, and coatings based on them. It is these data that were systematized during research into vaporization of oxide systems based on SiO_2 , ZrO_2 , HfO_2 , B_2O_3 , GeO_2 , P_2O_5 , containing also oxide-modifiers from first till fifth groups of the D.I. Mendeleev Periodic Table. Advantages of application of the acid-base concept for the prediction of the composition of vapor over oxide systems as well as semi-empirical and statistical thermodynamic approaches for the calculation of their thermodynamic properties up to the temperature 3000 K were illustrated. The main results and regularities of the high temperature description of oxide systems were obtained using the data found by high temperature mass spectrometry.¹⁻⁹ First potential capacity of this approach are considered during synthesis of new materials based on high-entropy oxides formed in the $\text{SrO-La}_2\text{O}_3\text{-TiO}_2\text{-ZrO}_2\text{-Fe}_2\text{O}_3$ system.

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LOW TEMPERATURE CHEMISTRY OF REFRACTORY OXIDES

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In the work, based on the concepts of melting of surface and intergranular formations in polycrystalline systems - non-autonomous phases, the processes are divided into low-temperature – $T < T_{m2D}$, and high-temperature – $T \geq T_{m2D}$ (T_{m2D} is the melting temperature of the non-autonomous phase). It is shown that the main features of the chemistry of low-temperature processes are the kinetic inhibition of solid-phase interaction due to the absence of fast mass transfer paths through non-autonomous phases and the lack of expression of the effects of entropic stabilization of phases, since the influence of entropy on the value of the Gibbs energy decreases with decreasing temperature.

Using the example of obtaining nanocrystalline particles based on $ZrO_2-M_2O_3$ ($M=REE$), Al_2O_3 , ZrO_2-SiO_2 , TiO_2 , etc., the features of the processes of formation of nanocrystals of refractory oxides, as well as the features of equilibrium and metastable states at low temperatures. At low temperatures, phase formation occurs either over extremely long periods of time¹ or in the presence of a mobile medium in the reaction system². At $T < T_{m2D}$, liquid, gas, or supercritical fluid can act as such a medium, providing rapid mass transfer of reagents. The formation of a new phase in this case occurs due to dissolution-crystallization and the aggregation-accommodation process.

Using the example of the synthesis of nanoparticles of simple and complex oxides, the influence of the structure of prenucleation clusters, limitations of mass transfer processes, the size of critical nuclei, and barrier-free nucleation on the mechanism of formation of nanocrystals, their structure, and particle size distribution during low-temperature synthesis is analyzed. The reasons for the stabilization of a substance with a nonequilibrium structure are analyzed. The mechanism of phase formation by aggregation of clusters with their accommodative restructuring within the aggregate is considered.

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CURRENT PROBLEMS OF MODERN CHEMISTRY OF HIGH-PURITY SUBSTANCES

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The development of materials with a low content of impurities is one of the scientific areas being developed at the Institute of Chemistry of High-Purity Substances of the Russian Academy of Sciences. The scientific and methodological basis for this direction was work on the theory of processes for separating mixtures of substances, on the development of methods for high purification and analysis of substances. Currently, in the context of unprecedented sanctions, in accordance with the strategy of achieving scientific and technological sovereignty, import substitution of a number of high-purity substances and materials is relevant.

It is of interest to obtain multicomponent mixtures of highly pure substances. These include glass-forming compounds formed by chalcogens in combination with elements of groups 4 and 5 of the Periodic Table. Effective methods have been developed for producing chalcogenide glasses with high transparency in the mid-IR range.

A significant change in the properties of a material is achieved by alloying it. A technique has been developed for manufacturing active laser media by diffusion doping of ZnSe and ZnS with chromium and iron ions. For fiber optics based on quartz light guides, methods have been developed for producing glasses doped with rare earth elements and bismuth. Fiber lasers and optical amplifiers with high technical characteristics were manufactured using fiber light guides.

An important area of fundamental and materials science research has emerged - the production and study of the properties of monoisotopic simple (Si, Ge, B, Mo) substances and their compounds (hydrides, fluorides, chlorides) with high chemical and isotopic purity. Plasma-chemical and chemical (hydride) methods have been developed for obtaining high-purity monoisotopic varieties of silicon and germanium. An isotope effect has been revealed in the optical and thermophysical properties of isotopically enriched silicon and germanium. The ongoing development of solid-state functional materials based on high-purity substances has significantly stimulated the development of highly sensitive methods for determining impurities, the creation of equipment and methodology for high purification of substances.

COMPOSITE COATINGS FORMED ON MAGNESIUM ALLOYS BY IMPREGNATION OF THE PEO-LAYERS WITH FLUOROORGANIC COMPOUNDS

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This study presents the ways of the composite coating formation using fluoroorganic compounds, such as fluoroparaffins and solutions of tetrafluoroethylene (TFE) telomers. Possessing a high plasticity, low melting temperature, and low melt fluidity, fluoroparaffins, for instance, are the prospective materials, which do not require the high temperatures after impregnation in the outer porous part of similar to ceramic layers formed by plasma electrolytic oxidation (PEO). Composite coatings formed using fluoroparaffins and TFE-base materials provide along with a high corrosion resistance the hydrophobicity due to multimodal roughness. The application of materials to the surface and into the pores of the coating was performed using dip-coating method and centrifugation. Analysis of SEM images and EDS maps of elements distribution along the examined surface showed that maximum fluoroparaffin concentration was on the surface and in pores of the coating. According to the data obtained, the composite coating possesses the best protective properties. The corrosion current density for this coating decreased by two orders of magnitude in comparison with the base PEO-layer.

The surface treatment of the PEO-layer with TFE telomers and fluoroparaffins does not only increase the impedance modulus, measured at the low frequency, $|Z|_{f \rightarrow 0 \text{ Hz}}$, from $1.3 \cdot 10^5 \Omega \cdot \text{cm}^2$ up to $2.5 \cdot 10^6 \Omega \cdot \text{cm}^2$ and $5.8 \cdot 10^7 \Omega \cdot \text{cm}^2$, respectively, but also provides the electrode/electrolyte interface with more capacitive character. Even after 24 hours of exposure to seawater, all the studied samples show the higher protective properties as compared to the base PEO-layer ($|Z|_{f \rightarrow 0 \text{ Hz}}$ is by more than three times higher).

The scratch test data analysis confirms the positive effect of the fluoroparaffins in the composite coating on its mechanical properties. The fluoroparaffin layer works as a dry lubricant, reducing the wear of the base PEO-sublayer. The presence of the fluoroparaffin layer on the PEO-coating enables one to supply the hydrophobic properties to the surface, as indicated by the contact angle increases from 37° up to $122\text{--}137^\circ$, depending on the used material. The coating obtained using a telomeric solution has the lowest wettability. For such coating, the value of the contact angle attains to 142° .

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DEVELOPMENT OF TECHNOLOGY AND CREATION OF MATERIALS TO COMBAT THE SPREAD OF BACTERIAL INFECTIONS AND THEIR TESTING IN A HOSPITAL CONDITION

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The discovery of antibacterial drugs (ABDs) was one of the most significant events in medicine of the twentieth century. ABDs seemed to be a universal tool for combating bacterial infections, but time and practice have shown these expectations to be wrong. Numerous mechanisms of antibiotic resistance (AR) allowed bacteria to evade the effects of antibiotics, and by the end of the twentieth century, the rate of development of AR began to significantly exceed the rate of introduction of new drugs to the market. The World Health Organization recognizes AR as one of the most significant threats to humanity. Therefore, the search for non-drug methods to counteract the spread of infections is one of the most important tasks of modern science. One way to solve this problem consists in developing materials with antibacterial properties.

This development, based on the interdisciplinary collaboration of physicists, chemists, materials scientists, microbiologists and pharmacologists, makes it possible to create materials that can prevent the spread of bacterial infections through touch surfaces. Today, one of the most promising areas of combating the spread of infections in medical institutions is the creation of metal materials with extreme wettability.¹ The report will present technologies for creating such materials, developed in our laboratory in recent years. Then we will focus on analyzing the results of tests of the materials we created, in hospitals in Moscow. We will also discuss the prospects for the wider use of such bactericidal materials not only in medical institutions, but also in shopping centers, educational institutions, in transport and other places characterized by increased risks of contact transmission of infections. This will minimize human losses during the spread of future bacterial pandemics.

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MODERN MOLYBDENUM-BASED ALLOYS AND NEW PRODUCTION TECHNOLOGIES

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Molybdenum, as a metal with a melting point of 2622°C, is potentially the basis for structural heat-resistant materials that can withstand significant loads at temperatures above 1200°C. However, the implementation of this ability is associated with significant technological difficulties, which are based on the strong dependence of the mechanical properties of molybdenum on the content of harmful impurities in it. The main one is oxygen. Its solubility in the molybdenum lattice is vanishingly small and at room temperature is 1-2 ppm. At higher oxygen concentrations, it forms thin deposits of MoO₂ oxide on the intergranular surface of polycrystalline molybdenum, which leads to a decrease in the plasticity of the material. For this reason, all technologies for the production of molybdenum products necessarily pursue the goal of either reducing the oxygen content in the material due to its deep purification (annealing in hydrogen, vacuum annealing, vacuum melting), or binding it into oxides by doping with elements that have a higher affinity for oxygen. This report is devoted to molybdenum alloys, the production of which is carried out using smelting technologies. These technologies are used to produce more complex and critical products from molybdenum: these are molybdenum-based alloys alloyed with various elements that strengthen the solid solution, elements that form carbides, nitrides and other refractory compounds. To produce these alloys, a duplex ingot smelting process developed at the Institute of Physics and Technology of the Russian Academy of Sciences is used, which includes sequential vacuum arc and vacuum electron beam melting. The use of this process has made it possible to significantly improve the quality of products from the currently most popular molybdenum alloys of Soviet design and has made it possible to develop new molybdenum alloys that are significantly superior in their strength characteristics to existing ones. New technologies for the production of granules from molybdenum alloys have been developed, and the possibility of their use in additive technologies based on laser 3D printing has been shown. A new direction in the materials science of molybdenum has been created - highly alloyed alloys.

The work was carried out within the framework of the State assignment of the ISSP RAS

ADVANCED TECHNOLOGIES OF HARDENING AND REPAIR OF METAL SURFACES FOR ENSURING TECHNOLOGICAL SOVEREIGNTY OF THE RUSSIAN FEDERATION IN METALLURGY AND MACHINE BUILDING

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The study presents a technology of creating ceramic superhard and low friction coatings and alloyed layers with the basis on new scientific principles and ensuring a breakthrough result as multiple improvements of material properties. The coatings based on boron carbides/nitrides, zirconium nitrides/borides and bismuth-alloyed surface layers of steel, formed by high-energy short-pulse laser treatment, have microhardness up to 43 GPa, heat resistance up to 1050 °C, excellent wear resistance and ultra-low friction coefficient (up to 0.03) in a wide range of loads at high sliding speeds (32 m/s) and dry friction condition¹⁻².

To ensure technological sovereignty in metallurgy, presented are Russian innovative technologies for the production and repair of mold copper plates of continuous casting machines with wear-resistant composite coatings and thickness recovering technology of the chromium-zirconium copper plate by multipass friction stir lap welding². As a result, the share of Russian slab molds with a coating at Russian Iron and Steel works raised from 3% in 2012 up to 60% by the end of 2023, with total economic impact of the implementation over 2019-2023 exceeded 34 billion rubles.

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CHEMICAL NANOTECHNOLOGY OF MOLECULAR LAYERING: FROM BIRTH TO WIDE INDUSTRIAL IMPLEMENTATION

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The molecular layering method (ML), the principles of which were formulated and experimentally substantiated in the works of V.B. Aleskovsky and S.I. Koltsov in the middle of the last century, from the end of the 20th century to the present day it has been actively developing in many industrialized countries¹. The main areas of development are related to the creation of functional thin-film structures for use in micro-, nano-electronics and other fields². Depending on the intended purpose, a wide range of objects of different geometric shapes and sizes are used as substrates: wafers made of monocrystalline silicon, different brands of glass, dispersed materials, including porous materials, various types of fibers (carbon, glass, polymer), as well as finished products requiring the application of functional nanocoatings^{1,2}.

The report presents the results of developments on the creation of industrial production of flow-vacuum type ML installations, carried out by the First All-Russian Engineering Center for Molecular Layering Technology together with Botlikh Radio Plant LLC and Engineering Center for Molecular Layering LLC (St. Petersburg). Design and technological documentation for putting products into production have been developed (GOST R 15.301 - 2016), prototypes of flow-vacuum type installations have been manufactured and tested, four technological processes of ML oxide nanocoatings of titanium and aluminum on the surface of silicon and glass plates have been developed, on the inner surface of glass housings of X-ray tubes and on polyethylene films to give them electret properties.

Since 2024, industrial production of ML units has begun.

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MODERN MATERIALS AND TECHNOLOGIES IN SHIPBUILDING AND NUCLEAR POWER ENGINEERING

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Construction of modern advanced marine vehicles and facilities that equally feature high performance, technical and operational characteristics calls for new requirements to the materials used in these structures. Modern materials must have a combination of high properties that are sometimes difficult to achieve concurrently.

A number of extensive tests and research performed in several fields of the Institute’s activity enabled us to develop industrial technologies for manufacturing of the Arc-index steels with the quality to obtain special requirements for cold and crack resistance characteristics at temperatures down to minus 60 ÷ minus 70 °C.

Likewise, the most important challenge to unify the chemical compositions of shipbuilding steels was solved on the basis of precision methods of thermal and mechanical processing of steels. The capability to control the structural state of steels enabled us to move on to the issues of developing the combination of “strength” – “thickness of rolled metal” – “cold resistance” by varying of technology methods of steel plates manufacturing based on five grades of steels.

Extensive and detailed research on creation of a new titanium alloy showed that the required strength values can be obtained only for pseudo- β -alloys of titanium in a thermally strengthened state. Alloys of such class being under optimal heat treatment, obtain increased set of physical and mechanical properties, including a higher fracture toughness as compared to ($\alpha+\beta$)-class alloys.

Another groundbreaking research activity is also the development of gas isostatic isothermal pressing (GIP) technology for the manufacturing of bulky parts for shipbuilding and nuclear power engineering. By now, the fundamental technologies have been created for complex shape products made of titanium alloys of various classes. The influence of comprehensive factors in creation of bulky structures has also been investigated.

NANOCRYSTALLINE OXIDE MATERIALS FOR SEMICONDUCTOR GAS SENSORS FOR DETECTING BIOMARKERS IN EXHALED AIR

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The interest in the problem of detecting low concentrations (ppt-ppb-ppm) of vapors of volatile organic compounds (VOCs) including short-chain fatty acids and nitrogen-containing compounds in exhaled air is due to the need for non-invasive determination of biomarkers reflecting the state of the gastrointestinal tract, liver, lungs, heart and other organs. Taking into account the uniqueness of the metabolomic profile of each person, a quick and accessible analysis of exhaled air biomarkers in the clinic will allow both the development of personalized treatments for many diseases and monitoring the effectiveness of their treatment. The creation of new sensors and affordable devices is also extremely important for the development of personalized recommendations for a healthy lifestyle, a healthy, balanced diet, which is the basis for the prevention of major non-infectious diseases.

Artificial olfaction systems based on semiconductor sensors make it possible to detect VOCs in the air in real time. However, their use for medical diagnostics is limited by an insufficiently low detection limit. A promising approach to increase the sensitivity of semiconductor sensors is, on the one hand, directed modification of the type and concentration of active centers on the surface of the sensitive material and, on the other hand, the use of pulsating heating. The design of the composition and the development of synthesis techniques that ensure reproducible production of highly dispersed semiconductor oxides with microstructure parameters preserved under conditions of pulsating heating made it possible to obtain new materials for semiconductor sensors capable to detect short-chain fatty acids at the level of 10-20 ppb.

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PHYSICOCHEMISTRY OF CELLULOSE-BASED NANOSTRUCTURES

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Against the backdrop of constant discussions about climate change on our planet, as well as a possible resources depletion, the revival of scientists interest to the study of natural polymers, in particular - cellulose and cellulose - based materials, is relevant and comply with the principles of green chemistry task. Plants, whose cell walls are its main source, grow thanks to sunlight, water and soil nutrients, binding carbon dioxide from the atmosphere. Cellulose is the most abundant polymer on Earth, whose reproduction can be estimated from 1.5×10^{12} tons of total annual biomass growth. The macromolecule consists of D-glucose units, adopting a predominantly elongated rod conformation, estimated at 2 - 20 nm, and combining regions of order and disorder in their structure. Due to this, it is possible to isolate cellulose in the form of fibers, smaller fibrils, as well as micro and nanocrystalline modifications. This is determined by the nature of the raw material, conditions of synthesis and subsequent processing, including acid hydrolysis, fermentation, chemical modification and mechanical treatment. The development of modern approaches to the production of such materials contributes to technologies for production of other commercial products - lignin, biofuel, conductive soot.

The physicochemistry of cellulose derivatives is extremely diverse: they allow surface modification, combination with already known polymer and carbon matrices, can form hydrogel and aerogel structures. The report highlights the latest developments in the field of methods for producing cellulose and its derivatives, combinations with carbon nanostructures and biologically active substances, as well as the possibility of self-organization, which ensures the creation of materials with unique properties. Their use is possible in the building and constructional materials industry, food and petrochemical industries, flexible electronics, catalysis, biochemistry and medicine. The report also focuses on the use of modern instrumental methods to control the structure and chemical composition of such materials and characterization of the properties of composites.

PROMISING ULTRAHIGH-TEMPERATURE CERAMIC MATERIALS

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Ceramic materials based on superfluid compounds, primarily on the basis of zirconium and hafnium diborides and carbides, are attracting increasing attention in various fields of science, including for use in the most thermally stressed components of promising descent vehicles, due to the ability of such ceramics to stand up to high temperatures, good mechanical properties, high thermal conductivity and high resistance to oxidation. In order to reduce the consolidation temperatures of these promising materials, methods of their reactive hot pressing and spark plasma sintering have been developed, the positive influence of sintering additives, including MAX-phases (Ti_2AlC and Ti_3AlC_2) has been shown.

Taking into account the significant difference in the composition of the atmospheres of celestial bodies such as Mars, Venus or Titan, a satellite of Saturn, the behaviour of ultrahigh-temperature ceramics based on $\text{ZrB}_2(\text{HfB}_2)\text{-SiC}$ and TaC-HfC-SiC systems has been studied under the influence of high-speed gas flows of nitrogen and carbon dioxide, which are the basis of the atmospheres of these planets^{1,2}; the peculiarities of the degradation processes of these materials have been established.

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ANODE MATERIALS BASED ON COPPER-DOPED SODIUM TRITITANATE WITH A HIERARCHICAL STRUCTURE FOR SODIUM-ION BATTERIES

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Sodium trititanate ($\text{Na}_2\text{Ti}_3\text{O}_7$) has attracted attention as a promising anode material for sodium-ion batteries due to its specific capacity, suitable potential values and, as a result, the possibility of operation under increased current loads. However, this material has low electrical conductivity, which is due to its wide band gap. In addition, research is conducted aimed at facilitating the transport of Na^+ ions in $\text{Na}_2\text{Ti}_3\text{O}_7$. Within the scope of this work, a method for the synthesis of copper-doped sodium titanate with a hierarchical two-level (micro/nano) architecture has been developed in order to create new materials for negative electrodes of sodium-ion batteries with improved functional characteristics.

The obtained materials consist of “microflowers” structures formed by nanotubes and nanosheets. It was found that as a result of copper doping, the band gap of $\text{Na}_2\text{Ti}_3\text{O}_7$ decreases by ~ 1.2 eV, and the electronic conductivity increases by almost 2.5 times. The modification of $\text{Na}_2\text{Ti}_3\text{O}_7$ with copper is accompanied by a distortion of the lattice, and an increase in the volume of the unit cell by $\sim 9.5\%$. It was established that doping is accompanied by enhanced transport of charge carriers and an increase in the diffusion coefficient of Na^+ ions as a result of electrochemical (de-)sodiation of sodium trititanate. Copper doping leads to a decrease in polarization of the electrode from $\text{Na}_2\text{Ti}_3\text{O}_7$. It was found that the specific capacity of sodium trititanate with an admixture of copper at high current densities of 3C and 4C is noticeably higher than that of undoped $\text{Na}_2\text{Ti}_3\text{O}_7$ (almost 2.0–2.5 times). At the same time, at low current densities of 0.1C and 0.5C, the materials have similar capacitance values.

LAYER-BY-LAYER CHEMICAL ASSEMBLY OF NANOMATERIALS INVOLVING REAGENT SOLUTIONS: FROM THE FIRST EXPERIMENTS TO PRACTICAL APPLICATION

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As it is known [1-4], Layer-by-Layer (LbL) chemical assembly involving solutions of reagents by successive ionic, ionic-colloidal and colloidal layers deposition provides an opportunity to create new hybrid nanomaterials with a unique set of properties and some of them cannot be obtained using other methodological approaches. An analysis of publication activity in this field confirms a high potential for its development, as indicated, for example, by the annual publication of about 80-100 patents and 40-50 reviews during the last 5-7 years. At the same time, most of the works are devoted to various aspects of LbL application in biomedicine, electrochemical power engineering, and the creation of new high-performance membranes.

The report gives a brief historical review of the development of LbL methodology and notes priority Russian works in which LbL conditions for a wide range of inorganic compounds were proposed and justified. On the example of the synthesis of multilayers of Mn(III,IV)- and Ce(III,IV)-containing oxyhydroxides, it is shown that coatings with controlled thickness from such compounds can be deposited on the surface of substrates with any complex shape and practically at room temperature. The design features of automated laboratory and semi-industrial facilities for LbL assembly are presented in the report, and the main problems of such synthesis are considered, referring to the relatively low “growth rate” of thin-layer structures, the need to choose the conditions of irreversibility of processes on the surface, etc. Prospects for the development of LbL assembly are analyzed, related to the improvement of experimental facilities for synthesis and the creation of new routes for the synthesis of multilayers of hybrid compounds, including those with hierarchically organized morphology. The material summarized allows us to attribute the outlined synthesis approaches to “key” routes of nanotechnology.

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NEW GENERATION OF MONOATOMIC CLATHROCHELATE CATALYSTS AND HYBRID ORGANO-INORGANIC CATALYTIC MATERIALS BASED ON THEM FOR HIGH-PURITY HYDROGEN AND SYNGAS PRODUCTION

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Metal clathrochelates and functional organo-inorganic materials based on them are known¹ to be promising catalysts for high-purity hydrogen and syngas production. The designed polyaromatic-terminated d-metal clathrochelates, physisorbed on carbon materials, were found²⁻⁶ to be efficient electrocatalysts of the hydrogen evolution reaction $\text{HER } 2\text{H}^+/\text{H}_2$, including those in semi-industrial water electrolyzers. Their performances are encouraging being similar to those for the best molecular and non-platinum solid-state catalysts. Electrocatalytic activity of these clathrochelate electrocatalysts was found to be affected by the number of the terminal polyaromatic group(s) per a molecule. The use of suitable carbon materials of a high surface area, as the substrates for their efficient immobilization, allowed to substantially increase an electrocatalytic activity of thus obtained hybrid cathode materials. In the case of the reaction of dry reforming of methane (DRM) into syngas of a stoichiometry CO/H_2 1:1,^{7,8} the designed metal clathrochelates with terminal polar groups are only the single-atom precatalysts, where each of their catalytically active single sites is encapsulated by a macrobicyclic ligand. Choice of their designed ligands allowed an efficient immobilization of these macrobicyclic complexes on the surface of a given highly porous ceramic material as a substrate and caused increase in a surface concentration of the catalytically active metallocenters (and, therefore, that in a the catalytic activity of hybrid organo-inorganic clathrochelate-based materials). These new “single-atom catalysts”, being the derivatives of abundant 3d-biometals and low-toxic α - dioximes, are in good accordance with basic principles of “green chemistry” and “economy of atoms”.

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PREPARATION OF HIGH-PURITY ISOTOPICALLY ENRICHED MONOSILANES AND MONOGERMANES AND STUDY OF THEIR IMPURITY COMPOSITION

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Isotopically enriched silicon and germanium are of great interest for studying the influence of isotopic composition on the properties of substances¹, and are also promising for the fabrication of quantum computing devices² and neutrinoless double β -decay detectors³. The purest silicon and germanium single crystals are obtained by hydride method by deep purification of monosilane or monogermane and subsequent thermal decomposition⁴.

The results of works on obtaining high-purity monosilanes $^{28}\text{SiH}_4$, $^{29}\text{SiH}_4$ and $^{30}\text{SiH}_4$ with the basic isotope enrichment of 99.9 - 99.99 at. %, as well as monogermanes $^{70}\text{GeH}_4$, $^{72}\text{GeH}_4$, $^{73}\text{GeH}_4$, $^{74}\text{GeH}_4$ and $^{76}\text{GeH}_4$ with the content of the main isotope at the level of 99.9 at. % (except $^{76}\text{GeH}_4$). Deep purification was carried out by cryofiltration and low-temperature rectification methods. The yield of the rectified product was 70-75 %.

The impurity composition of the samples was investigated by gas chromatography and chromatography-mass spectrometry with detection limits of 10^{-4} - 10^{-7} mol. %.

The content of molecular impurities in rectified $^{28}\text{SiH}_4$, $^{29}\text{SiH}_4$ and $^{30}\text{SiH}_4$, as well as $^{70}\text{GeH}_4$, $^{72}\text{GeH}_4$, $^{73}\text{GeH}_4$, $^{74}\text{GeH}_4$ and $^{76}\text{GeH}_4$ is at the level of $n \cdot 10^{-4} \div 1 \cdot 10^{-7}$ mol %. No isotopic dilution of hydrides within $1 \cdot 10^{-2}$ at. % occurs during purification.

Single-crystal samples of silicon and germanium of high purity were obtained from rectifiers of isotopically enriched hydrides.

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NANOPARTICULATE CONTRAST AGENTS BASED ON Mn(II) AND HEXARENIIUM CLUSTERS: EFFECT OF MORPHOLOGY OF PARTICLES AND THEIR COATING ON CONTRASTING ORGANS AND TISSUE

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The present work introduce nanoparticulate contrast agents based on Mn(II) and hexarhenium clusters $[\text{Re}_6\text{Q}_8(\text{CN})_x(\text{OH})_{6-x}]^{4-}$ ($\text{Q}=\text{S}^{2-}, \text{Se}^{2-}$, $x=6, 2$). It has been shown that the interaction of Mn(II) with the heteroligand cluster $[\text{Re}_6\text{S}_8(\text{CN})_2(\text{OH})_4]^{4-}$ leads to the formation of nanoparticles with lamellar morphology¹, while $[\text{Re}_6\text{Se}_8(\text{CN})_6]^{4-}$ form spherical nanoparticles².

Manganese containing nanoparticles based on $[\text{Re}_6\text{S}_8(\text{CN})_2(\text{OH})_4]^{4-}$ exhibited pH-induced release of Mn(II) ions and aggregation of NPs, which was caused by protonation of the apical hydroxyl ligands of the $[\text{Re}_6\text{S}_8(\text{CN})_2(\text{OH})_4]^{4-}$ cluster in acidic media.

MR scanning of mice with intravenously injected NPs indicates a preferential accumulation of lamellar NPs in the intestine¹, rather than in the liver and kidneys. In turn, spherical nanoparticles based on $[\text{Re}_6\text{Se}_8(\text{CN})_6]^{4-}$ showed contrast in almost the entire abdominal region².

Both types of NPs showed low cytotoxicity, lack of hemolytic and hemagglutinating activity.

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HYBRID POWDER MATERIALS AgI-SiO_2 : PROMISING REAGENTS FOR ARTIFICIAL PRECIPITATION TECHNOLOGIES

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Hybrid powder (HPs) reagents can have great potential in artificial precipitation technologies, because they are operating in the intertemperature range. This happens various physicochemical and mechanical patterns, which are realized in the processes of nucleation, condensation and the formation of downward flows^{1,2}.

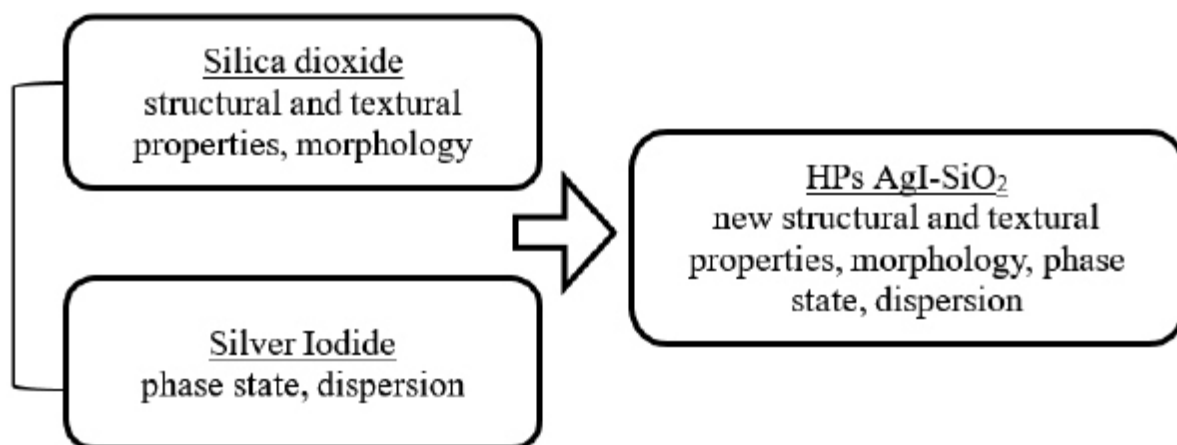


Figure 1. Properties of the initial components of the hybrid and characteristic features of the synthesized hybrid

HPs AgI-SiO_2 exhibit several mechanisms of action on atmospheric moisture: silver iodide is active in the region of negative temperatures (nucleation), and silicon dioxide binds free air moisture in the region of positive temperatures. In the course of research, it was found that when creating a hybrid without the formation of a chemical bond between the components, additivity and synergism appear in the formation of characteristic features.

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ANISOTROPIC LUMINESCENT MEDIA IN MICROFLUIDIC CHANNELS: CONTROL OF ORIENTATION AND OPTICAL BEHAVIOR

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Integration of microfluidic devices with liquid crystals (LC) is a promising research area that offers new solutions for molecular electronics and biomedicine^{1,2}. In this work, we summarize the research in orientation and optical behavior of thermotropic and lyotropic liquid crystals and their composites with nanoscale quantum dots and carbon C-dots in microfluidic channels. Fig. 1 shows the examples of respective textures in polarized and UV light.

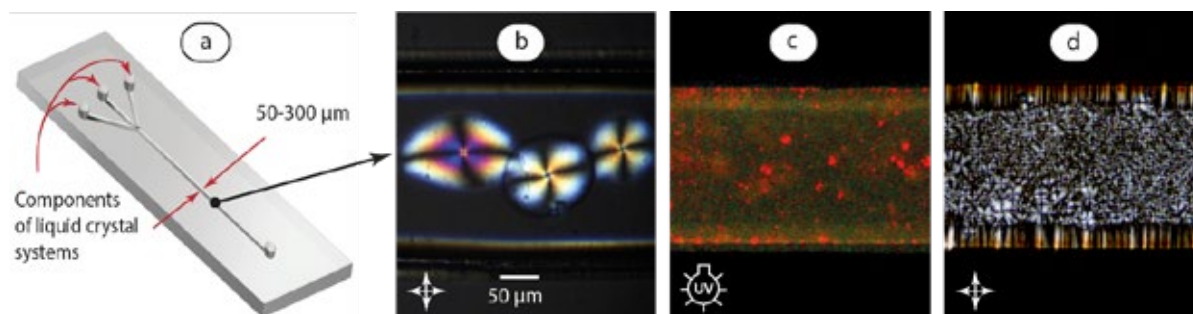


Figure 1. Microfluidic channels with integrated LC matrix: a – microfluidic chip, b – aqueous LC dispersion, c – LC with quantum dots, and d – LC with carbon C-dots.

A behavior of such systems in microfluidic channels was characterized with respect to a broad set of factors such as flow velocity, impact of microchannel walls and geometry, temperature, magnetic field, and the presence of colloids. It was shown that microfluidic confinement favors formation of new orientation states of mesophases and broadens the resulting options for control of optical and luminescent properties of the composites.

The revealed effects provide new options for development of microtechnological devices with integrated polarized luminescent materials for quantitative in-flow monitoring of temperature, flow velocity, and various molecular agents.

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GEOMETRICAL-TOPOLOGICAL APPROACHES TO MODELING CRYSTALLINE SUBSTANCES WITH SPECIFIED PROPERTIES

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Modern methods and computer tools for geometrical-topological description of crystal structures and their physical properties are considered. The main problem of modern materials science is the difficulty of predicting the required properties of new materials. To solve this problem, a wide range of machine modeling methods are used, such as density functional theory, molecular dynamics, and Monte Carlo methods, the distinctive feature of which is high requirement for computing resources. In addition, the configuration space of any chemical system contains an infinite number of possible geometric realizations, and it is impossible to study all of them. Therefore, it is necessary to find routes to efficiently search for stable geometric configurations without sequential scanning of the entire configuration space.

The methods we are developing belong precisely to such solution options. These methods are based on the representation of crystal space in the form of a geometrical model of partition into atomic or molecular domains (Voronoi polyhedra) or a topological model of a periodic atomic network. The methods are implemented in the ToposPro software package (<https://topospro.com>) and enable one to automatically analyze large sets of theoretical and experimental data on the crystal structure of chemical compounds of any nature and complexity using universal algorithms. As a result of this analysis, we have created a system of databases and Internet services, TopCryst (<https://topcryst.com>), containing the values of unique structural descriptors for all currently studied crystalline substances. Examples are given of using ToposPro and TopCryst resources for modeling known and predicting new crystalline inorganic substances and materials of various classes: intermetallic compounds, ionic and covalent compounds with high hardness. Correlations between geometrical-topological structural descriptors and mechanical properties of solids are considered.

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FLOURPOLYMER MATERIALS AND DEVICES FOR RECONSTRUCTIVE SURGERY

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High biocompatibility of fluoropolymers determines their wide application for the development of implants for regenerative surgery. For that moment, fluoropolymers are used for the development of artificial blood and bile vessels; artificial heart valves; implants for plastic surgery; membranes for dentistry; implants for traumatology and orthopedics¹. The materials with ferroelectric and piezoelectric properties are of great interest in the field of “smart” implants, which stimulate the tissue regeneration process by intrinsic electrical activity, without any batteries or electrodes.

Herein, we present the results on the applicability of domestic electroactive polymer material, vinylidene fluoride-tetrafluoroethylene (VDF-TeFE) copolymer, as a biologically active material for the development of membranes for oral mucosa regeneration, membranes for septic wounds treatment, 3D-printed implants for solid tissues regeneration in head and neck region, intramedullary implants for the treatment of congenital anomalies of locomotor apparatus of children and artificial vessels. For the comparison, the results of physicochemical and biomedical studies of ferroelectric polymer membranes fabricated using electrospinning and solution-blowing techniques are presented. The assessment of physicochemical characteristics and clinical efficiency of ferroelectric and paraelectric semipermeable fluoropolymer membranes was performed. The results on surface modification of VDF-TeFE membranes for the enhanced biocompatibility are presented.

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FABRICATION OF COMPOSITE MATERIALS WITH METAL OXIDE NANOPARTICLES SYNTHESIZED IN PLASMA DISCHARGE UNDER ULTRASONIC ACTION

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The purpose of this work is to develop approaches to create composite materials based on synthesized nanoparticles of metal oxides (zinc, tin, iron, aluminum, etc.) using an organic polymer matrix, study the principles of their formation and properties, including using ultrasonic cavitation, as well as the creation of composite materials with specific characteristics.

Metal oxide nanoparticles were synthesized in a plasma discharge under the influence of ultrasonic cavitation. A copolymer of ethylene and vinyl acetate was used as a polymer matrix. Using solution technology and then melt compounding technology, samples of polymer composite materials with a homogeneous distribution of nanoparticles were obtained. In images of composite material films obtained on a scanning electron microscope, nanoparticles and agglomerates of metal oxide nanoparticles are visible. According to X-ray phase and X-ray fluorescence analysis, it was possible to qualitatively confirm the presence of nanoparticles inside the polymer film: peaks related to metals are visible in the spectra. The results of studies of fractures of films obtained at liquid nitrogen temperature using scanning electron microscopy show that the structure of the material is quite integral, there are no visible large defects or cavities.

Physical and mechanical tests of films made of composite material with different contents of nanoparticles were carried out, data on the values of the elastic modulus, Poisson's ratio, proportionality limit, shear modulus, yield strength, ultimate strength and ultimate deformation were obtained. The results of mechanical tests show that ultrasonic treatment of nanoparticles before their introduction into the polymer matrix has a positive effect on the physical and mechanical properties of films made from the studied composite material.

The work was carried out with the financial support of the RSF, project No. 23-19-00540.

PHASE EQUILIBRIA IN THE Li-Mn-Eu-O SYSTEM: THE CONCENTRATIONAL TETRAHEDRON

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Using the method of topological modelling and based on fragmentary experimental data¹, an isothermal concentrational tetrahedron of the Li–Mn–Eu–O system was plotted for the first time², describing possible solid-phase transformations in the system that occur at a constant temperature with a change in partial pressure of oxygen P_{O_2} with no consideration of polymorphism, solid solutions formation as well as metastable states formation. The tetrahedron is being divided into 36 trigonal bipyramids. Rising up from the base (Li–Mn–Eu triangle, Fig. 1) to the top vertex (O) corresponds to a change in phase equilibria in the Li–Mn–Eu–O system with increasing partial oxygen pressure. At a fixed Li : Mn : Eu ratio, isoconcentration lines successively pass through different triangular pyramids of the Li–Mn–Eu–O isothermal tetrahedron, Fig. 1, and the phase composition of the composites changes with P_{O_2} varying. The diagram ($T < 267$ K) covers the P_{O_2} range of 10^{-10} – 10^{15} Pa, if being assessed by the calculated (P – T) diagrams of Mn–O system.

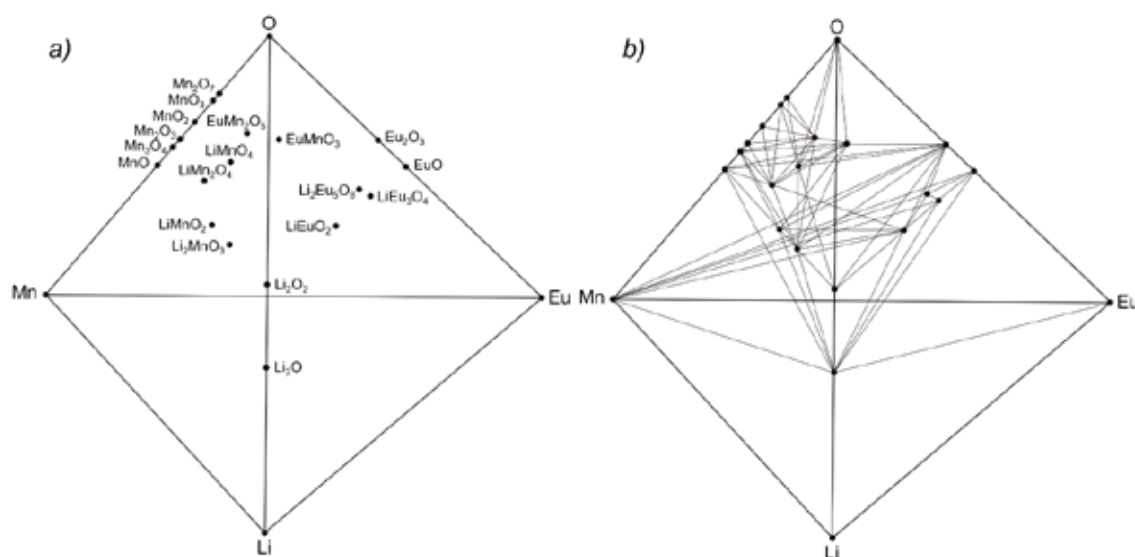


Fig. 1. Isothermal concentrational diagram of subsolidus phase equilibria in the Li-Mn-Eu-O system: figurative points (a) and tetrangulation therein (b).

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THE THERMOPHYSICAL PROPERTIES OF CoCrFeNi HIGH-ENTROPY ALLOY: THE IMPACT OF CHEMICAL SHORT-RANGE ORDER

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The coefficient of thermal expansion (CTE), density and thermal conductivity as a function of temperature are important for the study of phase transformations, design of materials, in the processes of heat transfer and thermal expansion of materials, i.e. they are fundamental parameters in the field of materials science and chemistry of new materials. Despite numerous studies of the mechanical properties and structural state of the CoCrFeNi¹ system, the key thermophysical characteristics of CoCrFeNi alloys at high temperatures and their relationship with the structure have not been sufficiently studied.

In our work, we systematically investigated the thermophysical properties of as-cast and homogenized CoCrFeNi alloys. Measurements of the coefficient of thermal expansion, specific heat capacity, and thermal diffusivity of high-entropy CoCrFeNi alloys revealed reversible anomalies in the temperature range 750–1050 K. The anomalies are explained by the diffusion process of local chemical ordering during heating and cooling cycles.

Based on the results of high-temperature studies of the thermophysical properties of CoCrFeNi alloys, it can be concluded that the effects of temperature homogenization have a noticeable effect on the behavior of the temperature curves of CTE, heat capacity and thermal conductivity. Thus, homogenization of cast samples is necessary if they are to be used at high temperatures. At the same time, after heat treatment, CoCrFeNi alloys also show a significant deviation from monotonic behavior, caused by local chemical ordering, in the temperature range of interest for most heat transfer applications i.e. approximately in the range 873–1120 K.

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STRUCTURES OF BIMETALLIC LANTHANIDE(III)-CHROMIUM(III) COMPLEXES WITH THERMOCHROMIC PROPERTIES

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Bimetallic multiligand inorganic-organic complex compounds with a variety of structural topologies and physico-chemical properties appear promising as precursors for the creation of a variety of functional materials and composites. Thermochromic substances are of a specific interest as they change color upon exposure to temperatures especially reversible action substances which include bimetallic lanthanide(III)-chromium(III) complexes with N, O, S-donor ligands such as ϵ -caprolactam, DMSO, DMFA and nicotinic acid.

The compounds crystallize in one of three related structural types, the mutual packing of ions in the structure of which topologically corresponds to that in the NaCl structure. The structures of all compounds belong to the island type and include complex lanthanide cations and complex chromium anions which are bound together by coulomb forces and hydrogen bonds [1, 2].

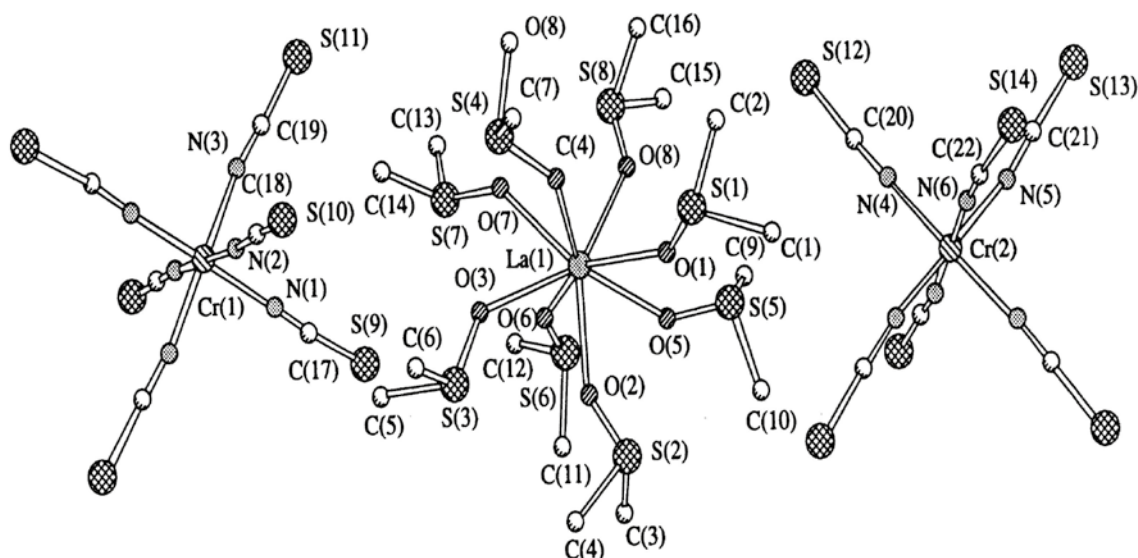


Figure 1. Crystal structure of lanthanum complex with DMSO.

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GRAPHENE-LIKE MATERIALS VIA ULTRASONIC TREATMENT OF NATURAL GRAPHITE SUSPENSIONS

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Direct ultrasonic exfoliation, as suggested in many studies¹, is an effective technique to manufacture highly concentrated suspensions of few-layered graphene nanoplatelets (FLGP) that are widely used as basis for conductive inks and thin films with excellent optical properties in the recent years. Main focus in the literature is to obtain suspensions with narrow layer distribution, whereas systematic studies of the influence of process parameters on suspension concentration, electrical conductivity as well as FLGP particle size distributions is still lacking.

In the present study, we report the main results of the complex study of the influence of process temperature, medium nature, graphite concentration on electrical conductivity, particle size distributions and layer distribution for FLGP suspensions. It is shown that reducing exfoliation temperature and ultrasonic horn relative surface area increases suspensions' quality (mean particle size decreases, suspension electrical conductivity and graphene yield increase).

Calculations of process thermodynamic parameters suggest² that polyols, mainly ethylene glycol are very prospective in stabilization of the newly formed graphene surface. Influence of medium dielectric constant was studied. It is shown that there is no simple dependence of suspension electrical conductivity on dispersion medium dielectric constant.

The results of the current study suggest that suitable conditions for manufacturing FLGP suspensions with predefined properties can be effectively chosen in case of direct ultrasonic exfoliation.

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CdZnSeS QUANTUM DOTS: REPRODUCIBLE FABRICATION AND CONTROL OF THE OPTICAL PROPERTIES

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Semiconductor colloidal quantum dots (QDs) are photoluminescent nanoparticles possessing a unique combination of optical properties that make their application in various fields of science and technology attractive. At present, clear requirements to the target properties of QDs as a material have been formed. First, they are high quantum yield (QY) and the ability to precisely control the photoluminescence (PL) wavelength for the application of QDs in photonics¹, as well as colloidal stability in aqueous media and the presence of functional groups on the surface for the application of QDs in the development of chemical and medical sensors and test methods². The key limitation hindering the transition from single prototypes to mass application of QDs is the complexity and often low reproducibility of their fabrication and modification procedures. Thus, it is necessary to focus on a combination of single-step and reproducible protocols for synthesis and modification of QDs. The example of such systems is CdZnSeS QDs stabilized by functional thiols derivatives.

The series of CdZnSeS QDs with the PL maximum wavelength in the range 530-620 nm has been obtained. The dependences of optical and size properties of QDs on the reaction mixture composition and synthesis conditions are presented. A set of simple methods for QDs hydrophilization by molecules of functional thiols has been developed using thioglycolic, 3-mercaptopropionic, dihydrolipoic acids and 2-mercaptoethanol. A non-typical effect of QY increase after QDs hydrophilization (up to 65%) was found and its explanation was proposed. The colloidal stability of the obtained QDs in aqueous medium for 6 months was considered. High reproducibility of the proposed approaches of nanoparticles synthesis and surface modification was shown.

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STRUCTURE FEATURES OF CAST Ni_3Al BASED INTERMETALLIC ALLOYS.

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Cast economically alloyed $\gamma'\text{Ni}_3\text{Al}$ -based alloys have a lower density, higher melting point and oxidation resistance, and a higher operating temperature ceiling than modern high-temperature nickel-type alloys^{1,2}. The work examines the features of the crystallization of domestic (VKNA/VIN type) and the most advanced foreign ($\gamma'+\gamma$) low-alloy alloys (IC type) based on $\gamma'\text{Ni}_3\text{Al}$, provides experimental data on the nature of the structures formed during the directional crystallization of alloys with different types of alloying (with additives Re, Ru, Co or without them), on the nature of the distribution of components in the $\gamma'\text{Ni}_3\text{Al}$ and γNi phases and structural components. Data are presented on the study of the influence of heat treatment (HT) in a wide range of temperature-time parameters on the microstructure, distribution of alloying elements and phase composition (scanning and transmission electron microscopy) and mechanical properties of VKNA-type alloys. A comparative analysis of the influence of temperature and the duration and rate of cooling after HT on the heat resistance of the alloys showed that, unlike other alloys based on Ni_3Al , for single crystals from economically alloyed alloys of the VKNA type and parts made from them, short-term HT (1150°C/ 1h) to relieve casting stress. The alloys demonstrate high heat resistance at 1100-1200°C and the ability to briefly withstand temperature surges up to 1250-1300°C (in case of emergency situations).

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MULTISCALE MODELING OF THE STRUCTURE AND PROPERTIES OF LAYERS AND INTERFACES IN OLED

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Organic molecules used in OLED devices (1st fluorescent, 2nd phosphorescent or 3rd TADF generations) consist of a large number of atoms, are flexible and, as a result, their properties are highly dependent on the environment. On the other hand, explicit quantum mechanical treatment of the environment of the active center is prohibitively expensive. Also, the available polarizable continuum models (PCMs) do not provide any reliable description of inhomogeneous environment. However, the multiscale approach allows high accuracy calculations of various properties for these compounds without requiring huge computational resources.

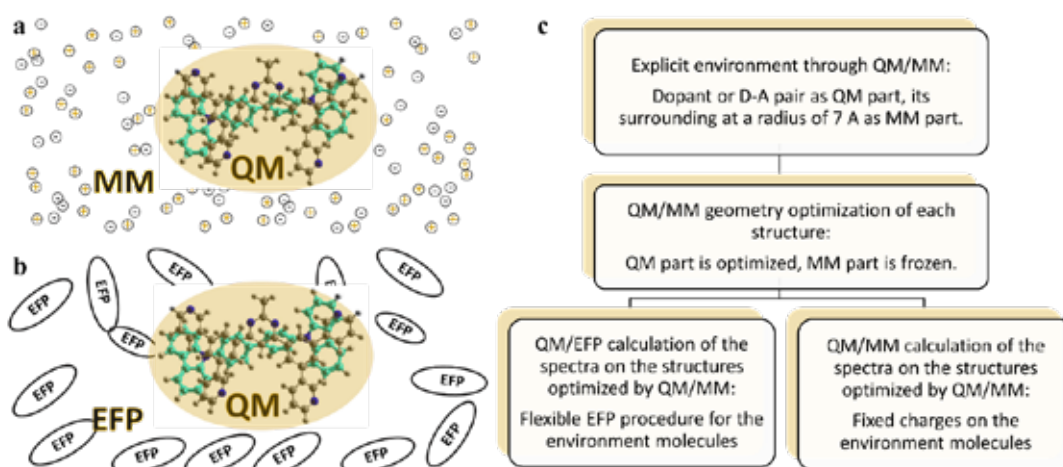


Figure 1. Hybrid treatment of the environment within the (a) QM/MM, (b) QM/EFP scheme and (c) flowchart of multiscale modeling.

In this work, the structures of the dopants with host or exciplexes, formed at interfaces, with its environment were generated using molecular dynamics. The spectra of the dopants or exciplexes were calculated using TD-DFT method. The environment of the chromophores was modelled as a QM/MM approach (Fig. 1a), and as effective fragment potentials (EFP) method (Fig. 2a). It was found that EFP provides the best description of the environment, making it possible to include both structural effects and molecular polarizability.

This work was supported by RSF (project № 24-49-02038 (in part of QM calculations and MD simulation) and № 23-23-00429 (in part of QM/MM and QM/EFP calculations)).

COMPOSITE MATERIALS BASED ON HYBRID CARBON NANOSTRUCTURES

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The essential feature of hybrid materials based on carbon nanostructures of different dimensions (0D, 1D, 2D) are synergistic effects due to changes in texture, molecular, crystalline or electronic structure, surface and porosity development, and formation of a certain type of morphology.

The paper presents the results of the study of the regularities of hybrid structures formation when combining carbon nanotubes (CNTs) and graphene into a single composite, including in the presence of a polymer matrix. Model calculations by quantum chemistry methods (Orca, XTB) have been applied to evaluate the mechanisms of interaction between individual components. It is shown that more thermodynamically stable systems are formed when cylindrical CNTs are used (as compared to conical nanotubes); an increase in the degree of functionalization of the graphene component also contributes to the stability of the hybrid material.

On the basis of model calculations the types, ratios and methods of functionalization of initial components for obtaining stable composites with given characteristics have been selected. Complex physical and chemical diagnostics of experimental samples by methods of electron microscopy, FTIR and Raman spectroscopy, XRD, TG/DSC analysis was carried out.

On the example of epoxy composites the influence of hybrid modifiers on the failure mechanism under bending and tensile loading has been shown. Functionalized forms of carbon nanostructures close to model objects were used to obtain a material demonstrating strength gain under different types of mechanical loading. As a result, the composites were obtained showing an increase in Young's modulus by 25% and tensile strength by 78%. At the same time, the elastic modulus and flexural strength increased by 34 and 41%, respectively, while maintaining the material deformation parameters.

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FABRICATION OF EXTREME WETTABILITY COATINGS FOR CORONA DISCHARGE LOSSES REDUCTION

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Energy transportation by overhead power lines faces economic and environmental challenges related to durability, corona discharges, and leakage currents.

A solution to these problems can be the use of modern functional coatings on wires, provided that the coatings are durable in conditions of an open atmosphere and prolonged exposure to corona discharge. In this work, using laser processing and chemical modification of the surface, new types of coatings were created and studied, including superhydrophobic, superhydrophilic and impregnated coatings, to reduce the corona discharge current. The results show that in rainy conditions, superhydrophobic and superhydrophilic coatings effectively reduce corona currents, while impregnated coatings increase them. In addition, superhydrophilic coatings have been found to demonstrate improved performance when operated in rainy conditions and after prolonged exposure to corona discharge. In particular, it has been shown that although storage in dry conditions may slightly reduce the anti-corona efficiency of the coating due to surface contamination, exposure to a corona discharge and precipitation helps restoring the anti-corona characteristics of the superhydrophilic samples.

The research results confirm the high operational resistance of the resulting anti-corona coatings, which can significantly reduce corona losses under various conditions, which opens up new prospects for increasing the efficiency and reliability of electricity transportation via overhead power lines.

The study was carried out with financial support of RSF grant 23-73-30004.

PERSONALISED HETEROGENEOUS-STRUCTURED OSTEOINDUCTIVE BIO-CERAMIC BONE-GRAFTS OF COMPLEX CHEMICAL COMPOSITION AND ARCHITECTURE BASED ON HEAVILY-DOPED STABILIZED GLASERITE-LIKE PHASES

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Current approaches to the regeneration of bone defects barely address the aspects of the complex nature of bone tissue structure and its multimodal interface with the surrounding tissues. The complex nature and complexity of each organ leads to different rates and mechanisms of their regeneration, which may eventually lead to the dominance of restoration of one tissue type over others. In this respect, the design of the scaffold should take into account the complexity of the structure and surroundings of the reconstructed bone and, as a result, should be a combination of different types of materials with individual macrostructure, chemical composition, and a set of mechanical properties.

The complex chemical composition of the scaffold is the key characteristic that endows the material with a complex of biological properties and defines the resorption behavior of such scaffold in the body. Traditional bioceramics with simple chemical composition based on basic biogenic elements (calcium, phosphorus, oxygen) has limited possibilities to improve its functional characteristics, unlike, for example, modern structural alloys, which often have a very complex chemical composition and the resulting new properties. It seems that the complication of the chemical composition of the inorganic matrix is in the line of development of the regenerative medicine approach - to stimulate the organism to produce the substances necessary for therapy (the organism as a drug factory).

This talk will focus on the design of personalized heterogeneous-structured scaffolds based on a new generation ceramic materials with complex chemical composition and architecture, to stimulate and provide osteoinductivity and other phenomena that are inaccessible to modern bioceramics and which accompany bone formation, growth and remodeling.

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NANOSIZED PARTICLES ENGINEERED FROM Cu(I) COMPLEXES WITH CYCLIC P,N-LIGANDS FOR INTRACELLULAR ROS GENERATION

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The work presents luminescent nanoparticles based on a series of new Cu(I) complexes with cyclic P,N-ligands. Substituents variation at the P and N atoms of ligands allows to optimize the structure of Cu(I) complexes for the formation of luminescent nanoparticles with high chemical stability in aqueous solutions and solutions simulating biological media. The colloidal stability of the resulting nanostructures ensured by the formation of the triblock copolymer F-127 hydrophilic shell. The cytotoxic activity of nanoparticles towards cancer and normal cells is comparatively lower than that of the corresponding molecular complexes, which correlates with the chemical stability of the nanoparticles. Anticancer specificity towards certain cell lines and the apoptotic cell death pathway correlate with intracellular ROS generation and localization in specific cell organelles^{1,2}.

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LAVES PHASES IN THE FCC-COBALT ALLOYS DISPERSIVELY HARDENED BY Co_3Nb AND Co_3Ta PARTICLES

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Developing new heat-resistant alloys based on cobalt is an urgent task, but it is associated with several difficulties. The main challenge is the lack of stable phases in cobalt systems with transition metals that are suitable for use as hardening phases¹. This requires the identification of new stable phases that can be used for hardening purposes. Previously, we proposed the intermetallic compounds Co_3Nb and Co_3Ta , which have the Mg_3Cd -type of the crystal structure. These compounds form nanoscale plates during the decomposition of the supersaturated *fcc*-cobalt solid solution through the formation of the Guinier-Preston zones and with the participation of the Suzuki atmospheres (in rhenium-containing alloys)². Although rhenium helps to preserve the reticulated microstructure of the nanoscale plates of the Co_3Nb and Co_3Ta phases, its inclusion in the alloy composition causes these phases to become metastable. The nuclei of stable Laves phases are initially formed at the grain boundaries, but during secondary recrystallization, they end up in the grain body where they grow and absorb niobium or tantalum, resulting in the dissolution of the Co_3Nb and Co_3Ta particles.

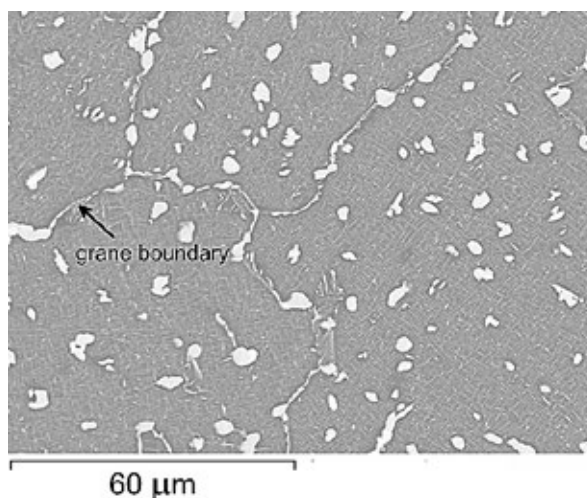


Figure 1. Laves phase particles at the boundaries and in the body of matrix grains.

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SYNTHESIS OF MOLYBDENUM, TUNGSTEN, AND VANADIUM POLYOXOMETALLATE DISPERSIONS FOR CATALYTIC APPLICATION

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Compounds of molybdenum, tungsten and vanadium (oxides, nitrides and carbides) are effective catalysts for a large number of chemical reactions. The necessity to create import-substituting technologies, as well as the synthesis of new types of supported catalysts (honeycomb, membrane) leads to the search for new effective synthesis methods, characterized by flexibility, scalability and simplicity of hardware design. These requirements are met by the sol-gel method, which is based on the use of sols—stable dispersions of nanoparticles.

This work is devoted to the development of methods for the synthesis of sols of molybdenum, tungsten and vanadium polyoxometalates, and catalysts based on them.

The synthesis of dispersions of molybdenum, molybdenum-vanadium and molybdenum-tungsten polyoxometalates (blue) was carried out by the reduction of inorganic salts of the corresponding metals or their mixtures in an acidic medium. The influence of synthesis conditions (type and content of reducing agent, pH value of the dispersion medium, concentration of initial salts) on the conditions and rate of formation of dispersed phase particles was investigated.

It was found that in the pH range from 1.0 to 2.5, when using organic reducing agents (glucose, ascorbic acid, hydroquinone), stable molybdenum blue dispersions are formed, the particles of which are represented by torus-shaped clusters of the Mo_{154} family. The highest rate of particle formation is observed when ascorbic acid is used as a reducing agent.

If carrying out syntheses using mixtures of salts under certain conditions, the formation of molybdenum-tungsten and molybdenum-vanadium blue dispersions occurs, which in their colloidal chemical properties (aggregative stability, stability with respect to indifferent electrolytes, sign and value of zeta potential) are close to dispersions molybdenum blue. The developed methods for the synthesis of dispersions were used in sol-gel processes for the production of powdered, supported and membrane catalysts.

The research was carried out within the state assignment of Ministry of Science and Higher Education of the Russian Federation (FSSM-2023-0004).

MESOPOROUS HYDROXYAPATITE POWDERS

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Hydroxyapatite (HA, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) is one of the least water-soluble calcium phosphates, widely studied and used in the world as a material for replacing bone defects, coating implants and a precursor for obtaining biocompatible composite materials. At the same time, HA, due to its low solubility, thermomechanical stability, the possibility of obtaining mesoporous powders was regarded as a material suitable for applications beyond biomedical ones. Its use as a sorbent or as support for catalysts and several others [11] are being evaluated. In this regard, the importance of controlling its dispersion, morphology, mesoporosity, and pore volume of the resulting materials, is increasing. Porosity and pore size are two of the main characteristics of materials and have a decisive influence on such phenomena as biological behavior (interaction with cells and wettability by biological fluids), on sorption of various pollutants, and on adhesive properties (support–catalyst interaction). The different approaches, including ripening in mother solution, polymer template and organic solvent application were applied and powders with mesoporous structure were obtained. The developed HA powders were characterized by specific surface area (SSA) up to $196 \text{ m}^2/\text{g}$, total pore volume (TPV) up to $0.71 \text{ cm}^3/\text{g}$. Doping of HA by the Fe^{3+} and Mg^{2+} ions led to SSA of 194.5 and $86.91 \text{ m}^2/\text{g}$, correspondingly. Thus, we developed different methods to synthesize the mesoporous HA for different applications.

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NANOARCHITECTONICS OF LAYERED SILICATES AS A BASIS FOR THE CREATION OF NEW FUNCTIONAL MATERIALS

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Under the conditions of directed hydrothermal synthesis, a number of porous aluminosilicates were obtained - analogues of natural minerals, qualitatively different from them in a set of certain specified characteristics (morphology and particle sizes, porous-texture characteristics, chemical composition, surface properties), control over which was carried out by selecting appropriate conditions for the synthesis of such compounds, based on knowledge of the mechanism of their crystallization, mutual transformation and self-organization.

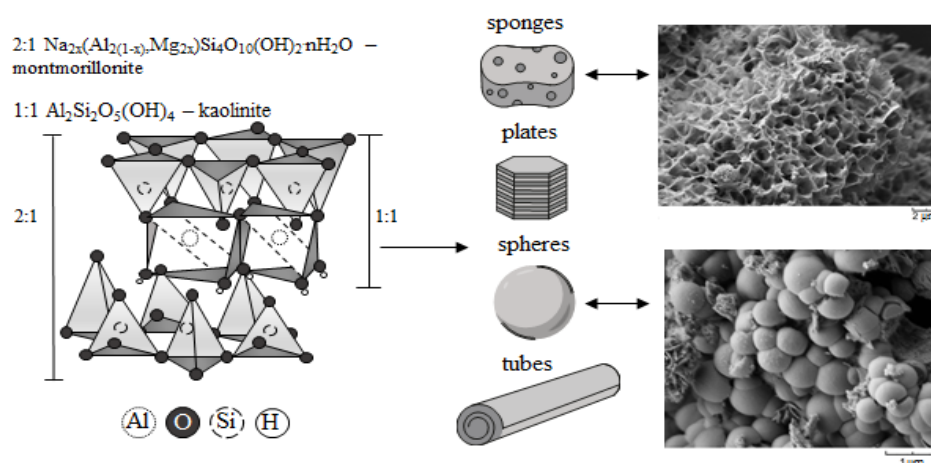


Figure 1. Structure and morphology of particles of the studied layered silicates.

The production of synthetic porous aluminosilicates with a given set of characteristics opens up wide opportunities for the development of new functional materials with improved properties, in particular, effective hemo- and enterosorbents, catalysts, drug carriers, which may have all the requirements necessary for such materials - high chemical and phase purity, have high porosity and sorption capacity, adjustable catalytic activity, selectivity, non-toxicity and hemocompatibility.

SYNTHESIS AND RESEARCH OF FUNCTIONAL MATERIALS BASED ON PALLADIUM NANOPARTICLES

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Functional materials based on Pd nanoparticles can have a wide range of technical applications as functional elements of various photovoltaic devices, sensors, catalysts and fuel cells. The composition, physical and chemical properties of such materials depend on the methods of their preparation and synthesis conditions. This paper presents the results of the development of various approaches for the synthesis of Pd nanoparticles and the study of the properties of materials based on them.

The first series of materials are thin silica films (~30-45 nm thick) doped with Pd and PtPd nanoparticles (4-8 nm in size) obtained by spin-coating¹ from sols. Semiconductor structures of n-InP/SiO₂@Pd, with a Pd crystallite size of 8 nm² were obtained². The measurement of the current-voltage characteristics of the InP/Pd thin-film structures showed a decrease in the cut-off voltage in the presence of H₂. It was observed that by illuminating the structure with an LED and exposing it to an impulse of H₂ caused changes in the photovoltage and photocurrent changed. This suggests that SiO₂@Pd films have the potential for use in hydrogen sensors.

The second series of materials are composites with Pd nanoparticles and bimetallic (Cu)Pd and (Ag)Pd nanoparticles obtained by reduction from salt solutions using various reducing agents. The catalytic activity of electrode materials based on Pd, (Cu)Pd and (Ag)Pd nanoparticles was found to be high and comparable to that of commercial materials.

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CARBOSILICOTHERMAL SYNTHESIS OF SILICON-CONTAINING MAX PHASES

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MAX phases provide a unique combination of important performance characteristics that neither ceramics nor metals offer. In terms of the complex of properties, the MAX phase (primarily the silicon-containing MAX Ti_3SiC_2 and Ti_4SiC_3 phases) is better suited than other materials for working in harsh conditions associated with the combined action of high temperatures, aggressive environments, shock mechanical and thermal influences. It is expected that replacing titanium atoms in the structure of the Ti_3SiC_2 and Ti_4SiC_3 MAX phases with transition metals of groups 4–6 (Zr, Hf, Ta, etc.) will significantly increase the refractoriness of the resulting materials and, accordingly, improve their thermal stability.

This work presents the results of the synthesis of MAX phases in Zr-Ti-Si-C systems; Ta-Ti-Si-S; Hf-Ti-Si-C. The synthesis was carried out by carbo-silicothermic reduction in vacuum of the oxides of the corresponding metals using silicon carbide as the main reducing agent and elemental silicon as an auxiliary reducing agent. Quaternary MAX phases with high zirconium content $\text{Zr}_2\text{TiSiC}_2$ and $\text{Zr}_3\text{TiSiC}_3$ have been obtained for the first time. It has been established that the MAX phase $\text{Zr}_2\text{TiSiC}_2$ is a compound of variable composition $\text{Zr}_{2-\delta}\text{Ti}_{1+\delta}\text{SiC}_2$ ($\delta \approx 0 \div 0.35$). It has been shown that the MAX phases Ti_3SiC_2 and $\text{Zr}_2\text{TiSiC}_2$ are extreme representatives of a series of $(\text{Ti}_{1-x}\text{Zr}_x)_3\text{SiC}_2$ solid solutions having an immiscibility range in the range $0.22 < x < 0.55$. The crystal structure of the obtained compounds was studied.

A ceramic material based on a solid solution of $(\text{Ti}_{0.85}\text{Zr}_{0.15})_3\text{SiC}_2$ was obtained by hot pressing of carbo-silicothermic synthesis products. High-temperature strength tests were carried out, which confirmed a significant increase in the heat resistance of the resulting ceramics compared to hot-pressed ceramics based on the Ti_3SiC_2 MAX phase.

This work was carried out in accordance with the state assignment of the Institute of Chemistry FRC Komi SC UB RAS No. 122040100040-0 and using the equipment of the Center for Shared Use of Scientific Equipment “Khimiya” of the Institute of Chemistry FRC Komi SC UB RAS.

DIFFUSION AND SURFACE EXCHANGE OF OXYGEN AND WATER IN PEROVSKITE-LIKE COMPLEX OXIDES

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Perovskite-like, partially substituted barium zirconates, $\text{BaZr}_{1-x}(\text{Ce}-\text{Y}-\text{Yb}-\text{Me})_x\text{O}_{3-d}$, have oxygen-ionic, hole and proton conductivity. They are promising for use as an electrolyte in medium-temperature fuel cells.

The purpose of this work was to measure the total electrical conductivity and Seebeck coefficient of zirconates in atmospheres with different humidity ($\log(\text{pH}_2\text{O}) = -4 - -1.7$) depending on the partial pressure of oxygen ($\log(\text{pO}_2) = -20 - -0.68$) and temperature using the 4-contact method at direct current on a measuring setup based on Zirconia - 318 and calculation of charge carrier transfer numbers. Using the method of relaxation of the total electrical conductivity depending on temperature (600 – 1000 °C), we obtained data on the total electrical conductivity when switching the atmosphere with different humidity ($\log(\text{pH}_2\text{O}) = -4 - -1.7$) at a constant partial pressure of oxygen and with different partial pressure of oxygen ($\log(\text{pO}_2) = -4 - -0.68$) at constant humidity. The parameters of diffusion and surface exchange of charge carriers were calculated.

The samples were synthesized using the solid-phase method. The phase composition of the samples was analyzed by X-ray diffraction (K α -radiation of copper). X-ray studies were carried out in a wide range of temperatures, partial pressure of oxygen and partial pressure of water vapor on a Shimadzu XRD - 7000 diffractometer with a high-temperature chamber, a unit for setting and controlling the partial pressure of oxygen (Zirconia - 318) and a unit for setting and controlling the humidity of the atmosphere above the sample. The unit cell parameters of zirconates were refined using full-profile Rietveld analysis.

The work was carried out with the financial support of the Russian Science Foundation, project 24-23-00524.

SYNTHESIS OF NEW COMPOSITE NANOMATERIALS BY IMMOBILIZING Au NANOPARTICLES ON THE SURFACE OF SYNTHETIC VALLERIITES AND STUDYING THEIR PHOTOCATALYTIC PROPERTIES

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Layered 2D materials, whose properties are radically different from those of their 3D counterparts, are of great importance for a wide range of applications. Recently, using a simple autoclave synthesis method, we prepared a 2D material, an analogue of the natural mineral valleriite¹. The electronic structure features of such materials make them promising for use in (electro)photocatalysis, the manufacture of solar cell elements, etc.

In this work, nanocomposite materials were obtained by immobilizing gold nanoparticles (GNPs) on the surface of synthetic valleriite from intermediate and final aqueous solutions of citrate reduction of HAuCl_4 and their photocatalytic activity was studied.

According to XPS, TEM, EDX, SAED data, gold immobilized from the final citrate hydrosols on the surface of valleriite nanoflakes is presented in the form of isolated spherical metal GNPs with $d \sim 11$ nm. When using intermediate products of citrate reduction of HAuCl_4 , in addition to spherical ones, a large number of anisotropic GNPs are formed and the portion of gold fixed on the surface increases by an order of magnitude, up to 2-3 at.%, compared to immobilization from final GNP sols (0.2 at.%).

A study of the photocatalytic activity of the obtained materials in the reduction reaction of indigo carmine by citrate-ion showed that the process is limited by the photogeneration of electron-hole pairs and their recombination. In the case of nanocomposites, a synergistic effect was not detected, probably due to the discrepancy between the energy of the localized surface plasmon resonance and the band gap of valleriite.

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CHEMICAL-PHYSICAL PRINCIPLES OF WEAR ELIMINATION DURING SLIDING FRICTION WITHOUT LUBRICATION

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Wear-free sliding friction due to lack of lubrication remains one of the main research objectives, since wear significantly reduces the service life of mechanical components. Although wear-free friction is achievable under sliding friction with proper hydrodynamic lubrication or under microscale normal loads, overcoming wear under high normal loads, high sliding speeds and under boundary lubrication remains a major challenge. The report presents a new approach to significantly reduce the wear of plain bearings operating in dry conditions at high normal forces and sliding speeds. Sleeve bearings are made of steel shafts tested on various materials. The surfaces of the steel shafts were alloyed with bismuth oxide using a new high-energy short-pulse laser treatment [1]. To introduce bismuth oxide into the surface layers of steel, MnO_2 was used as a carrier. Achieving an ultra-low coefficient of friction is important, but is not a sufficient condition for ensuring wear-free operation [2]. Ultra-low friction without wear was observed when a bismuth-alloyed steel disk slid over an aluminum counterbody under normal loads of up to 250 N (~5 MPa) and a sliding speed of 9 m/s in the absence of lubrication. Tribological test results demonstrate an exception to the Frenkel-Kontorova-Tomlinson model for wear-free friction. The alloy steel-aluminum pair test results suggest an innovative and promising approach for a wide range of applications.

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APPLICATION OF ATOMISTIC CALCULATIONS FOR VARIOUS Ca CONTAINING PHOSPHATES

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At the development of Ca – phosphate materials for the treatment of bone defects, it is of considerable interest to clarify the effect of isomorphic substitutions in calcium-containing phosphates on transitions between crystalline modifications (tricalcium phosphate (TCP) $\text{Ca}_3(\text{PO}_4)_2$, CaNaPO_4 , CaKPO_4), acid-base reactions of these phases in the preparation of phosphate cement materials, bioresorbability of the mentioned phosphates and hydroxyapatite (HAP) $\text{Ca}_5(\text{PO}_4)_3\text{OH}$. For the computer study of this effect, the atomistic calculation of the energies of the crystal lattices of the mentioned phosphates and the energies of the exact defects in them is relevant.

The present work shows the good applicability of the model of interatomic potentials, previously proposed for REE phosphates¹, to the calculation of the lattice energies of α and β modifications of TCP (the deviation of the crystal lattice parameters from those known from the literature data when optimizing the structure, the values of Young's modulus, zero energies of acoustic vibrational modes in the center of the Brillouin zone were taken into account). The calculations were carried out using the GULP² program. To calculate the energy of the HAP crystal lattice using the mentioned model, the parameters of the O-H interaction in the OH^- ion were determined based on previously published interaction parameters³ with varying effective charges of atoms. Lattice energies of high-temperature α - CaNaPO_4 and α - CaKPO_4 were also estimated. The parameters of the interatomic interaction potentials were calculated from the structural data available in the ICSD database.

Point defect energies (isomorphic cationic and anionic substitutions, cationic vacancies and interstitial cations) were calculated for all the phosphates considered. The obtained values of the defect energies made it possible to explain a number of observed features in the chemical behavior of the phosphates under consideration.

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DEVELOPMENTS OF ICT KSC RAS IN THE FIELD OF TECHNOLOGY OF TANTALUM CAPACITOR POWDERS

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Tantalum capacitors are characterized by high reliability, durability and high volumetric efficiency. Three types of tantalum powders are used for their production. Powders with fragmentation particle shape are obtained from ingots of high-purity metal by hydrogenation - milling - dehydrogenation method. The specific charge of such powders is 3000-7000 $\mu\text{C/g}$. To obtain higher specific charge from 8000 to 90000 $\mu\text{C/g}$, powders obtained by sodium-thermal reduction of potassium heptafluorotantalate are used. To achieve charges at the level of 100000-250000 $\mu\text{C/g}$, powders produced by reduction of tantalum pentaoxide with magnesium vapor are used. At present special attention is given to creation in the Russian Federation of own production of tantalum powder, which is an important strategic material.

Research on the technology of capacitor tantalum powders of all three types has been carried out and is being continued at ICT KSC RAS.

The paper considers the principal technological schemes of powder production. The technologies have undergone pilot industrial testing. About 4 tons of agglomerated fragmentation powders with specific charge of 4000-7000 $\mu\text{C/g}$ were obtained by the developed technology. Experimental batches of powders were used in serial production of capacitors K52-7 and K53-46, -56A, - 67 at JSC Mezon Factory, JSC “Rekond” and JSC “Girikond”. To work out the technology of sodium-thermal capacitor powders with specific charge of 8000-70000 $\mu\text{C/g}$ a plant was created, the reactor of which up to 8 kg of tantalum powder per one reduction cycle allowed to obtain. Modification modes of primary powders were worked out. Technical specifications for powders were issued. More than 250 kg of sodium-thermal capacitor powders used in production of capacitors K52-15, K52-17, K53-56 were manufactured and handed over to the customers. Research on development of magnesium-thermal capacitor powders technology is underway. Experimental batches of powders have undergone technological testing in JSC “Girikond”. Based on the results obtained, technical specifications for tantalum capacitor powders with specific charge at the level of 80000-120000 $\mu\text{C/g}$ have been developed.

LIGHT LITHIUM-CONTAINING SCINTILLATORS FOR NEUTRON DETECTION

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Our recent study was an investigation of the scintillation properties of the polycrystalline compound $\text{Li}_2\text{CaSiO}_4:\text{Eu}^{2+}$, which showed promise for use as a neutron-sensitive scintillator, with minimal disadvantages of zinc sulfide (high effective charge of the compound, opacity for environmentally friendly light scintillation and long-lasting scintillation kinetics). $\text{Li}_2\text{CaSiO}_4:\text{Eu}^{2+}$ coatings are transparent, and the gamma sensitivity of the 180 μm thick coating is 14% lower than that of a conventional Scintacor ND screen. The detection efficiency of neutrons with such a coating is 14.7%¹. Further research shows that by optimizing the activator capacitors, the light output can be increased to $\sim 104,000$ photons/neutron². It has also been confirmed that partial replacement of silicon with aluminum makes it possible to increase the reduction in photoluminescence by almost 2 times³. Such scintillation properties, with scintillation kinetics of less than 500 ns, as well as the possibility of improving properties, make the $\text{Li}_2\text{CaSiO}_4:\text{Eu}^{2+}$ scintillator a promising candidate to replace century-old ZnS.

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COMPLEX SALTS CONTAINING PLATINUM (PALLADIUM) AND METALS FROM GROUPS 5 AND 6 OF THE PERIODIC TABLE - PROMISING PRECURSORS FOR NANOSCALE METAL AND METAL-OXIDE SYSTEMS

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Much attention is currently being paid to the area of science connected with the development of methods for obtaining functional nanoscale polymetallic materials with specific properties. The presence of a second metal can lead to a synergetic effect, which is manifested in a sharp change (improvement) in the properties of polymetallic systems compared to monometallic analogues. Such materials have found a wide application in many fields of science, technology and medicine due to the variety of physical and chemical properties, such as corrosion resistance, catalytic activity, electrical conductivity, magnetic properties, anti-cancer activity, etc. We have synthesized and structurally characterized: $[\text{Pt}(\text{NH}_3)_4]\text{A}$ ($\text{A} = \text{CrO}_4, \text{Cr}_2\text{O}_7, \text{MoO}_4, \text{WO}_4$); $[\text{Pd}(\text{NH}_3)_4]\text{A}$ ($\text{A} = \text{CrO}_4, \text{Cr}_2\text{O}_7$); $[\text{Pt}(\text{NH}_3)_4(\text{NO}_2)(\text{Cr}_2\text{O}_7)]\text{NO}_3$; $[\text{M}(\text{NH}_3)_4][\text{VO}(\text{H}_2\text{O})(\text{Ox})_2](\text{H}_2\text{O})_2$, $\text{M} = \text{Pt}, \text{Pd}$; $[\text{Pd}(\text{NH}_3)_4][\text{VO}_2(\text{Ox})_2]$; $[\text{Pt}(\text{NH}_3)_4][\text{NbO}(\text{Ox})_3]_2$ ($\text{Ox} = \text{C}_2\text{O}_4^{2-}$); $[\text{Pt}(\text{NH}_3)_4]_3\text{Mo}_7\text{O}_{24}$. The isostructural nature of the complex salts $[\text{Pt}(\text{NH}_3)_4]\text{MO}_4$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) allowed us to develop methods for the synthesis and characterization of several series of solid solutions based on these compounds: $[\text{Pt}(\text{NH}_3)_4](\text{WO}_4)_x(\text{MoO}_4)_{(1-x)}$; $[\text{Pt}(\text{NH}_3)_4](\text{WO}_4)_x(\text{CrO}_4)_{(1-x)}$; $[\text{Pt}(\text{NH}_3)_4](\text{MoO}_4)_x(\text{CrO}_4)_{(1-x)}$. The thermal behavior of synthesized compounds in inert and reducing atmospheres were studied in detail. The conditions for obtaining different nanosized polymetallic powders with different phase composition were found. Thermolysis studies in oxidizing atmosphere were carried out in order to select optimal conditions for obtaining nanosized catalytically active metal-oxide particles. Nanosized $\text{Pt-Cr}_2\text{O}_3$ and $\text{Pd-Cr}_2\text{O}_3$ composites obtained by thermolysis of precursors in air atmosphere show higher catalytic activity in the processes of total and preferential CO oxidation compared to monometallic Pt and Pd powders.

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S-DOPED Zn-SUBSTITUTED BISMUTH NIOBATES: SYNTHESIS, OPTICAL AND DIELECTRIC PROPERTIES OF PYROCHLORES

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In this work, a series of Li- and Na-doped compositions of Zn-substituted bismuth niobates were synthesized by nitrate-organic precursors combustion followed by high-temperature sintering up to 1000 °C, and phase analysis was carried out using X-ray analysis and scanning electron microscopy. It has been established that the compositions are bismuth deficient relative to the original $\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$ matrix: by 7 % in the compositions $\text{Bi}_{1.4}\text{M}_{0.25}\text{Zn}_{0.65}\text{Nb}_{1.5}\text{O}_{7.8}$ (M – Li, Na) and by 14% in the compositions $\text{Bi}_{1.3}\text{M}_{0.4}\text{Zn}_{0.5}\text{Nb}_{1.5}\text{O}_{7.8}$. According to a FullProf analysis of XRD patterns using the Rietveld method, the distribution of Li^+ and Na^+ cations in the A sites, and Zn^{2+} cations in the B sites in the pyrochlore structure $\text{A}_2\text{B}_2\text{O}_6\text{O}'$, was established. As for many bismuth-based pyrochlores, a displacement of the A(96g) and O'(32e) cations relative to their ideal sites was observed¹⁻². Based on DSC data, the melting temperature of samples in air varies in the range of 1120-1180 °C and decreases with increasing dopant content. The resulting compounds are wide-gap semiconductors ($E_g^{\text{dir}} = 3.12\text{-}3.22$ eV). The dielectric properties of the compounds were studied using impedance spectroscopy (impedance analyzer E7-28, silver electrodes). The real part of the dielectric constant ϵ' varies in the range 120-190 (25 °C, 1 MHz) with the temperature coefficient of capacitance $\text{TCC} = -545\text{-}(-800)$ ppm/°C (25-280 °C). The dielectric tangent loss is 0.0015-0.0030 at 25 °C and 1 MHz. The compounds obtained in this work are promising as high-frequency dielectric capacitors up to 280 °C.

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COMPLEX COMPOUNDS OF METALS WITH ORGANIC LIGANDS AS PRECURSORS OF NANO-SIZED OXIDE CATALYSTS

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Functional materials based on simple and mixed metal oxides have attracted considerable interest due to their diverse range of applications. They are used as adhesive protective coatings, optical processors, waveguides, phosphors, acoustic-optical, storage and reading devices, and the transition from micro- to nano-sizes (nanoparticles, nanofilms and other nanoobjects) greatly enhances the beneficial properties of oxides, often introducing unique characteristics that are absent at the micro level.

Developments in the field of chemical design of nanosized oxides show the promise of using complex compounds of metal cations with organic ligands as precursors. The type and nature of electron-donating groups in an organic molecule makes it possible to directionally vary the structure of the isolated metal complexes, which directly affects the properties of the isolated nano-sized oxides. The ability to form bridging bonds makes it possible to bind two or more metal atoms, while the geometry of the ligand and the relative position of the donor centers involved in the binding of metal centers play a decisive role in the formation of the final oxide phases.

This work summarizes the results on known methods for the synthesis of metal nanoparticles and their oxides using metal-complex precursors with organic ligands and the dependence of the morphological features and properties of the resulting nano-sized objects on the nature of the precursors and methods for isolating nanoparticles.

STRUCTURE AND PHASE COMPOSITION OF MECHANOSYNTHESISED HIGH ENTROPY ALLOY CoCrFeNiTi AT LONG-TERM HEATING

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High-entropy alloys (HEAs) containing 5 or more elements in equiatomic ratio form substitutional solid solution phases with FCC or BCC structure. HEAs are characterized by ductility, corrosion resistance, low diffusional mobility, which makes them promising alloys for new functional materials¹. The aim of the work is to study the structure and phase composition of mechanical alloying CoCrFeNiTi HEA after long-term isothermal annealing. HEA powder of composition $\text{Co}_{0.18}\text{Cr}_{0.20}\text{Fe}_{0.24}\text{Ni}_{0.19}\text{Ti}_{0.19}$ was produced in the “Activator-2S” mill. Following mechanical alloying, a two-phase FCC-BCC HEA was formed, which had a defective crystal structure due to severe plastic deformation. The HEA was annealed for 200 days in vacuum quartz ampoules at 873K, 1073K, and 1273K, with periodic sampling for XRD and microstructural analyses. It has been established that isothermal annealing of the alloy leads to changes in the structure and phase composition of the HEA after only one day. Furthermore, the phase composition remains unchanged with further holding. The separation of the intermetallic σ -phase in the FCC-BCC matrix of the HEA is observed. After annealing for one day at 1073K and 1273K, two face-centered cubic phases with similar unit cell parameters were formed. The titanium depleted the HEA matrix, resulting in a composition of $\text{Co}_{0.22}\text{Cr}_{0.23}\text{Fe}_{0.29}\text{Ni}_{0.20}\text{Ti}_{0.06}$, which remained constant during the subsequent 200 days of annealing. Therefore, the CoCrFeNiTi HEA synthesized through mechanical alloying means is thermally unstable. Upon heating in the temperature range of 873-1273K, phase transitions occur, which are associated with the formation of solid substitution solutions and the separate of intermetallic compounds.

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PROBLEMS OF IMPORT SUBSTITUTION OF FUNCTIONAL MATERIALS IN THE NATIONAL AIRCRAFT INDUSTRY

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One of the main directions of the aviation industry in Russia is the development of new materials with high strength and other functional properties for long-term use in extreme conditions. At the same time, high demands are placed on the technology of production, processing and repair of these materials and structures in terms of efficiency and profitability. In this context, the developer of these materials must solve a complex scientific and technical problem.

The strengthening of sanctions against the Russian Federation has significantly hampered the development of new generation materials, as it has limited access to basic components and intermediate products. This situation affects not only the development, but also the production of popular polymer materials due to the lack of access to key chemicals.

In particular, in the manufacture of polymer composite materials, it is necessary to organize domestic production of polyamide, caprolactam, polyphenylsulfone (PPSU), polyesteresterketone (PEEK) and polyethyrimide (PEI), polyesterketonketone (PEKK), polysulfone (PSU) and other chemical products. This in turn affects the development of the production of intermediates such as organochlorine compounds, bisphenol A, bisphenol S, hydroquinone, phenyldiamine, isophthalic and terephthalic acids and others.

However, as practice has shown, when replacing imported components in existing technologies for the production of aviation materials and carrying out, significant changes are made to the formulation and production processes in order to achieve the desired, in fact, properties. In some cases, this may require re-conducting the entire complex of studies in the scope of general qualification due to significant changes in properties.

The substitution of imported materials and chemical components for domestic aviation structures requires special attention and discussion to organize new interaction chains between enterprises and minimize costs.

MULTIFUNCTIONAL PHYLLOSILICATE NANOSCROLLS

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Recently, methods of bending and folding crystalline layers of different structures and compositions to form micro- and nanoscrolls have become increasingly widespread. These processes are interesting both from a fundamental point of view – the loss of translational symmetry by the crystalline layer – and from the point of view of imparting new functional characteristics to the layers and materials based on them. To ensure scrolling, as a rule, either an external (mechanical) effect or the use of a template at the synthesis stage is required, and only in some layers the ability to scroll is due to internal reasons.

Such layers, for example, include hydrosilicates with imogolite, chrysotile and halloysite structures. A common feature of these compounds is the presence of two sublayers of different composition and structure, which leads to the occurrence of dimensional discrepancies and to bending as a natural way of compensating for it.

The talk discusses the results of the synthesis and subsequent modification of phyllosilicate nanoscrolls of the initial composition $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ with a chrysotile structure with partial replacement of cations by transition metals and semimetals (Ni, Co, Fe, Cu, Ge). Substitution by these elements allows one to vary the morphology of particles and influence their mechanical characteristics, magnetic and electronic properties. Using heat treatment in various gas environments, it is possible to obtain metal-silicate and oxide-silicate nanocomposites with the size of inclusions controlled due to spatial restrictions. The resulting materials find their use as reinforcing fillers, adsorbents, catalysts, and components of magnetically sensitive devices.

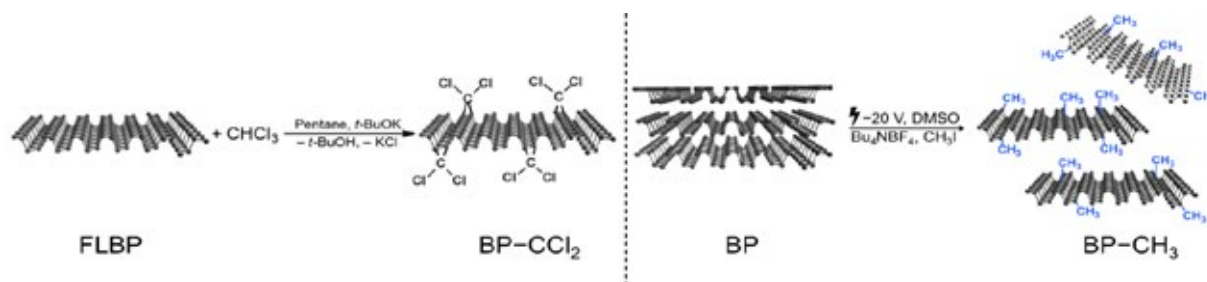
NEW APPROACHES TO THE FUNCTIONALIZATION OF FEW-LAYER BLACK PHOSPHORUS WITH ORGANIC SUBSTRATES AND COVALENT P-C BOND FORMATION

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Due to its unique in-plane anisotropic structure, high carrier mobility, and adjustable direct bandgap, 2D black phosphorus (BP) has emerged as an important graphene-like material for various micro- and optoelectronic, energy, catalytic, and biomedical applications. However, low environmental stability severely limits its processing in ambient conditions. Chemical functionalization of BP enables the tailoring of its chemical, optical, and electronic properties and improves the oxidation stability of the material¹.

Herein, we report first experimental approach for covalent functionalization of few-layer black phosphorus (FLBP) with carbene intermediates using dichlorocarbene as model reagent², as well as a facile *one-pot* approach for simultaneous electrochemical exfoliation and methylation of BP³.



The obtained materials (BP-CCl₂ and BP-CH₃) were characterized by the main physicochemical methods. Additionally, the possibility of the application of functionalized FLBP as a metal-free electrochemical hydrogen evolution catalyst is also presented.

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PECULIARITIES OF PRODUCTION OF CERAMICS FROM NANOCRYSTALLINE POWDERS OF TRANSITION METAL CARBIDES

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Due to their unique properties, transition metal carbides are one of the main components of high-temperature and hard ceramics. However, their high melting point makes it difficult to produce dense single-phase ceramics from them. One of the solutions to this problem may be the use of nanocrystalline powders, having excess free energy, owing to which sintering can take place at lower temperatures than those necessary for sintering microcrystalline powders.

In this work, we studied the sintering of dense ceramics produced from nanocrystalline powders (10-50 nm) of non-stoichiometric carbides TaC_y , NbC_y , and VC_y with a cubic structure (sp. gr. $Fm-3m$) and WC with a hexagonal structure (sp. gr. $P-6m2$), which were obtained by high-energy milling of microcrystalline powders (1-5 μm) in a planetary ball mill.

The study showed that sufficiently dense (up to 98%) and hard (20-31 GPa) ceramics can be obtained from nanocrystalline powders by conventional vacuum sintering at temperatures of 1100-1400 °C, which is 500-800 °C lower than those of sintering microcrystalline powders. However, the large specific surface area of nanocrystalline powders determines their high chemical activity and makes them very sensitive to oxygen, which interacts during heating with carbide carbon and is removed in the form of CO and CO₂, leading to partial decarburization of the carbide and the formation of a porous structure.

To prevent severe decarburization of the basic carbide during sintering, C, ZrC, Al, and SiC additives were introduced into the nanocrystalline powders to try to compensate for the loss of carbon or to bind the impurity oxygen into ZrO₂, Al₂O₃, and SiO₂ oxides before it begins to react with carbide carbon.

All additives proved to be effective in combatting decarburization and allowed the basic carbide phase to be preserved after vacuum sintering in a larger volume, but at the same time they contributed to the growth of grains and a decrease in the microhardness of the sintered ceramics.

HIGH TRANSPARENT CERAMICS BASED ON YTTRIUM-SCANDIUM-ALUMINUM GARNETS DOPED WITH RARE-EARTH ELEMENTS

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Solid solutions based on yttrium-scandium-aluminum garnets doped with rare earth elements are promising materials for creating diode-pumped ceramic solid-state lasers. Scandium cations in the garnet matrix can occupy both dodecahedral and octahedral positions in the crystal lattice, which allows them to influence a wide range of physicochemical characteristics.

The goal of the work was to identify the influence of scandium cations in the dodecahedral and octahedral positions of the crystal lattice of ytterbium-scandium-aluminum garnet doped ytterbium and erbium on the location of the Stark luminescence bands of ytterbium and erbium.

In this work, for the Y_2O_3 - Sc_2O_3 - Al_2O_3 - Yb_2O_3 and Y_2O_3 - Sc_2O_3 - Al_2O_3 - Er_2O_3 systems, the concentration-temperature ranges of existence of single-phase solid solutions, suitable for the synthesis of highly transparent solid solutions, were determined. Ceramics samples with a transmittance of more than 80% were produced by non-reactive sintering of compacts from nanocrystalline powders synthesized by precipitation from aqueous solutions. Optically transparent ceramics were studied: CA4 – $\{Y_{2.34}Yb_{0.45}Er_{0.09}Sc_{0.12}\}[Al_{1.92}Sc_{0.08}]Al_3O_{12}$ – with a low concentration $[Sc(c)]=[Sc(a)]=4$ at.%; CA20 – $\{Y_{1.86}Yb_{0.45}Er_{0.09}Sc_{0.60}\}[Al_{1.6}Sc_{0.4}]Al_3O_{12}$ – $[Sc(c)]=[Sc(a)]=20$ at.%; A50 – $\{Y_{2.26}Yb_{0.45}Er_{0.09}Sc_{0.20}\}[Al_{1.0}Sc_{1.0}]Al_3O_{12}$ – $[Sc(a)] = 50$ at.%, and $[Sc(c)]=6.67$ at.%; C50 – $\{Y_{0.96}Yb_{0.45}Er_{0.09}Sc_{1.50}\}[Al_{1.8}Sc_{0.2}]Al_3O_{12}$ – $[Sc(c)] = 50$ at.% and $[Sc(a)] = 10$ at.%. The concentrations of Yb^{3+} (15 at.%) and Er^{3+} (3 at.%) cations in all samples were the same. In the luminescence spectra of ceramics, when scandium is introduced into the dodecahedral position of the garnet crystal lattice, a narrowing of the Yb^{3+} luminescence band and a broadening of the Er^{3+} band with a simultaneous shift of the Stark bands to the red region of the spectrum are recorded. When scandium is introduced into an octahedral position, reverse effects have been recorded. At comparable concentrations of scandium cations in the dodecahedral and octahedral positions, the effects of shifts in the Stark luminescence bands are mutually compensated.

As a result, samples of high transparent yttrium-scandium-aluminum garnet ceramics doped with ytterbium and erbium were synthesized and it was determined that scandium cations in different crystallographic positions have a non-equivalent effect on the physicochemical properties.

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STUDY OF SPIN CROSSOVER IN IRON(II) COMPLEXES WITH POLYNITROGENIC LIGANDS

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Spin crossover (SCO) is one of the most remarkable phenomena in the chemistry of coordination compounds. SCO manifests itself in complexes of 3d- metals with the d^4 - d^7 electronic configuration under the influence of external influences: temperature, pressure, irradiation with light of a certain wavelength and other factors [1-4]. Complexes exhibiting spin crossover have the property of “bistability”—the ability to exist in two states: low-spin ($S=0$) and high-spin ($S=2$) with a fairly long lifetime. As a result, such compounds can serve as materials for molecular electronics devices. Polynitrogen heterocycles are promising as ligands for the synthesis of iron(II) complexes with SCO. In a number of these complexes, spin crossover is accompanied by thermochromism, which significantly expands the scope of their practical application.

The report will summarize the work of the Novosibirsk group in the field of synthesis and research of iron(II) complexes with various classes of polynitrogen heterocycles: derivatives of 1,2,4-triazole, *tris*(pyrazol-1-yl)methane and 2,6-*bis*(1*H*-imidazol-2-yl)pyridine. A study of the dependence $\mu_{\text{eff}}(T)$ in the temperature range 80-500 K showed that the received compounds exhibit high-temperature spin crossover $^1A_1 \leftrightarrow ^5T_2$, which is accompanied by thermochromism. The report will discuss the nature and features of spin crossover in iron(II) complexes with ligands of various classes.

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FERROELECTRICAL AND NONLINEAR OPTICAL PROPERTIES OF VANADATE-NIOBATES

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The report examines the features of formation, ferroelectric and nonlinear optical properties in double and triple vanadates with the structure of the whitlockite mineral. Crystalline laser matrices based on non-centrosymmetric $\text{Ca}_9\text{R}(\text{VO}_4)_7$ (isostructural with the mineral whitlockite, $\text{Ca}_3(\text{VO}_4)_2$ or $\beta\text{-Ca}_3(\text{PO}_4)_2$) activated by trivalent ions Nd^{3+} , Er^{3+} , Yb^{3+} are promising for creating new sources of coherent radiation with self-doubling radiation frequency (or without self-doubling with Bi^{3+} , Sb^{3+} cations) in the near-IR and optical ranges near wavelengths of 1.36 (0.68 μm); 1.66 (0.83 μm) and 1.03 (0.515 μm), corresponding to the 1st, 2nd and 3rd window of biological transparency, respectively, at 650 - 950 nm, 1100 - 1350 nm and 1600 - 1870 nm.

The structural, spectral, physicochemical and nonlinear optical properties of new crystalline materials based on vanadate-niobates of the general composition $\text{Ca}_9\text{R}_{0.99}\text{Eu}_{0.01}(\text{VO}_{4/7-x})(\text{NbO}_4)_x$ и $\text{Ca}_8\text{ZnR}_{0.99}\text{Eu}_{0.01}(\text{VO}_{4/7-x})(\text{NbO}_4)_x$ ($\text{R} = \text{Bi}, \text{Er}$) have been established. The regions of existence of solid solutions are determined. It was found that the samples crystallize in the non-centrosymmetric space group $R3c$ and are isostructural with calcium orthovanadate. A relationship has been revealed between the composition of whitlockite-like solid solutions, particle size, nonlinear optical and dielectric properties. Compositions with maximum values of the second harmonic generation (SHG) signal were determined. In solid solutions, the magnitude of the SHG signal increases with increasing niobium content. In the two-phase region, the SHG signal decreases. The structures of several compositions were refined using the Rietveld method. It has been established that niobium cations are located on a three-order axis and replace the vanadium cation. Using dielectric spectroscopy on ceramic samples, it was shown that when the annealing temperature of solid solutions is not high enough, two-phase samples with very close temperatures of the ferroelectric phase transition are formed.

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OXIDIZED MESOPOROUS CARBON MATERIALS BASIS FOR OBTAINING SELECTIVE SORBENTS

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It is known that the adsorption properties of carbon materials depend on the degree of surface activation as a result of oxidation and modification processes.

During the oxidation process, oxygen-containing surface-functional groups are formed on the carbon surface, which increase the hydrophilicity of the surface and promote chemical interaction with groups of sorbed compounds, and as a result, the adsorption capacity for a given component increases [1-4].

Chemical design of a selective sorbent with respect to the target impurity ion comes down to solving a dual problem - selecting a carbon matrix with an optimal combination of nano- and microstructures potentially capable of forming active centers (oxygen-containing groups) on the surface and strong chemical fixation of coordination centers on the oxidized carbon surface matrices.

The work discusses the mechanisms of interaction of iodine, chlorine, bromine, polymeric crystalline and amorphous antimony acid with oxidized carbon matrices.

Based on the studies carried out, sorbents (NUMS) were obtained that selectively extract mercury (Hg^{2+} , Hg^0) from gas and liquid media (modification of CM with iodine), NUMS-TOA, NUMS-OA effectively sorb from solutions of Au^{3+} , Pt^{4+} , Pt^{2+} , Pd^{2+} (modification UM triactylamine and octylaniline); NUMS-HA selectively extracts Cd^{2+} , Cu^{2+} from solutions (modification with humic acids); NUMS-Sb selectively extracts Na^+ , Ca^{2+} , Cs^+ , Sr^{2+} , Rb^+ from solutions (modification with hydrolyzed antimony compounds).

The processes and mechanism of sorption of Hg^{2+} , Pb^{2+} , Cd^{2+} , Ni^{2+} , Cu^{2+} , Na^+ , Ca^{2+} , Cs^+ , Sr^{2+} , Au^{3+} , Pt^{4+} , Pt^{2+} , Pd^{2+} from solutions on oxidized carbon sorbents have been studied in static and dynamic conditions.

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SOLID-STATE FRICTION STIR BASED METAL ADDITIVE TECHNOLOGIES

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Additive manufacturing (AM) is the most advanced production technique, which involves the layer-by-layer addition of materials to create a product based on a 3D digital model. This method allows for the significant reduction in time and cost of manufacturing, as well as the creation of complex-shaped structures that are not possible with other techniques. Despite the undeniable benefits of laser-based and electron beam AM for metal structures, these technologies also have significant challenges. Some of these challenges include: low structural strength of products, solidification defects, an inhomogeneous microstructure and anisotropic mechanical properties, restrictions in producing large-scale products, inert processing media, and limited choice of alloys.

Additive manufacturing technologies, which use friction heating to transfer material into a super-plastic state and high degrees of plastic deformation to create a welded joint, allow for layer-by-layer deposition of metal in a solid state, giving an approach to effectively overcome many of the aforementioned limitations. The most innovative and promising techniques of this type include the friction stir additive technology (FSAT), and additive friction stir deposition (AFSD). Unlike FSAT, which is a modification of friction stir lap welding, AFSD has purely additive nature and allows the use of raw materials in the form of powders, rods, or tubes etc. Applying the material at temperatures below its melting point, expands the application range of AM to alloys that are unweldable or immensely arduous to weld using traditional fusion welding, and simplifies the production of large-scale parts. Components manufactured by friction stir additive manufacturing exhibit a dense, fine-grained structure, that possesses significant improvements in terms of mechanical performance compared to fusion-welded materials.

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CHEMICAL STABILIZATION OF HIGH-PRESSURE INTERMETALLIC COMPOUNDS AS A PATH TO THE SEARCH OF NEW FUNCTIONAL MATERIALS

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Intermetallic compounds represent a huge class of substances with a variety of crystal structures and a wide range of important functional and structural properties. A special place among them is occupied by compounds formed by metals with different electronic structures of the valence shell, for example, d and p-metals. It is among such intermetallic compounds that superconductors, thermoelectrics, compounds with non-trivial magnetic behavior, etc. are most commonly found. Often, some compounds with potentially important functional properties can be synthesized only under high pressure conditions, in the absence of which their decomposition occurs^{1,2}. In our work we have demonstrated through specific examples how by chemical modification of the composition of such compounds it is possible to synthesize their analogues without the use of high physical pressure, without deteriorating the physical characteristics of the original matrix, and in some cases, discover new compounds or reveal the emergence of important functional properties.

The report will present new intermetallic compounds in the Re-Ga-Ge system, which were discovered during the chemical modification of *hp*-ReGa₃ by replacing gallium with smaller germanium. Thus, an isostructural compound ReGa₂Ge was synthesized, which has semiconductor properties and low thermal conductivity values, which favors thermoelectric activity. In addition, two new compounds were synthesized in the Re-Mn-Ge system: Re-substituted *hp*-MnGe, exhibiting non-trivial non-collinear ferromagnetism, as well as Mn-substituted *hp*-Re₄Ge₇, belonging to the Nowotny chimney ladder phases' family with an incommensurate crystal structure and ferromagnetic ordering below 160 K. All new compounds have been synthesized and are stable under normal pressure conditions.

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NEW TWO-DIMENSIONAL MIXED-LAYER SULFIDE-HYDROXIDE MATERIALS: SYNTHESIS ADVANCES, FEATURES, PROSPECTIVE APPLICATIONS

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Two-dimensional (2D) materials attract much attention due to their unusual physical and chemical properties. Due to the fact that along with useful properties, they display a series of restrictions such as insufficient stability in respect to oxidation, leaching etc., searching for new 2D-materials remains a significant problem. A series of natural compounds building a valleriite mineral group is well known which structure consists of alternating sulfide (FeS_{1-x} , CuFeS_2 , $(\text{Fe}, \text{Ni})\text{S}$ etc.) and hydroxide ($((\text{Mg}, \text{Al}, \text{Fe})(\text{OH})_2)$) 2D sheets self-assembled into 3D structure via excessive electrostatic charges rather than van-der-Waals interactions. Earlier, synthetic minerals have been prepared under “hard” hydrothermal conditions with rather low yield, they have not been considered in materials science, and a range of synthetic materials have been limited.

Using a developed hydrothermal technique, under comparatively mild conditions a series of phase-pure compounds including along with valleriites and tochilinites substituted with $\text{Al}(3+)$, $\text{Li}(+)$ and doped with several 3d- and 4f-elements, an earlier unknown mixed-layer material with formula of $[\text{Cu}_x\text{S}_2] \cdot 1.65[(\text{Mg}_{1-y}\text{Al}_y)(\text{OH})_2]$, where $2.2 < x < 3.0$, $0 < y < 0.25$. The optical, magnetic and electric characteristics of the samples were investigated. In particular, an intense absorption in the visible region that is likely due to all-dielectric resonances in submicrometer particles was observed. An unusual effect of impeded heat transfer across the heterogeneous 2D sheets was found. The photocatalytic effect of valleriites in the reaction of indigo carmine with trisodium citrate was discovered. For the first time, results of DFT+U ab initio simulation in GGA approximation on a series of valleriite and tochilinite structures will be presented which can shed light into the stability and characteristics of doped and modified materials, including potential applications such as nanophotonics, (electro)photocatalysis, solar energy harvesting etc.

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A PROMISING TECHNOLOGY FOR PRODUCING PRODUCTS OF COMPLEX SHAPE FROM HEAT-RESISTANT CERAMIC MATERIAL BASED ON SiC

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A new integrated approach has been developed for the production of complex-profile parts from SiC-based composite ceramics using the method of hot slip casting (HSC) of composite ceramic powders under pressure with further reaction sintering. The main advantage of reaction-sintered materials based on silicon carbide, compared to refractory metals, is the combination of properties such as long-term strength (lack of ductility) and significantly lower density, which allows the use of ceramics in high-temperature elements of gas turbine engines and other centrifugal elements of mechanical engineering, operating at extreme temperatures and needing to reduce the weight of the structure. The physical and mechanical characteristics of silicon carbide materials for specific or specified operating purposes can be increased within wide limits by adjusting the technological parameters of synthesis (molding, sintering) and modifying the structure (formation of phase and chemical composition).

The properties of the SiSiC HSC material, obtained by implementing the proposed new integrated approach for producing complex-profile parts from composite ceramics based on silicon carbide by hot slip casting under pressure with further siliconization have been studied: $\rho = 2.89\text{--}2.95 \text{ g/cm}^3$, $E = 330\text{--}360 \text{ GPa}$, $K_{IC} = 3.4\text{--}4.0 \text{ MPa m}^{1/2}$, $HV = 17.7\text{--}19 \text{ GPa}$. It can be seen that they are close to the properties of SiSiC obtained by the classical method of molding (pressing): $\rho = 3.05\text{--}3.10 \text{ g/cm}^3$, $E = 380\text{--}400 \text{ GPa}$, $K_{IC} = 3.5\text{--}4.0 \text{ MPa m}^{1/2}$, $HV = 20.0\text{--}21.5 \text{ GPa}$, which suggests the possibility of obtaining complex-profile parts with high physical and mechanical properties.

Practical results of high-temperature tests of silicon carbide ceramic materials show prospects for their use in heat-resistant structural products of complex geometry, capable of operating under bending loads at temperatures up to 1200°C in a protective environment and up to 1400°C in an oxidizing environment.

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TECHNOLOGIES FOR PRODUCING POWDER AND CERAMIC MATERIALS BASED ON ZIRCONIUM DIOXIDE FOR AIRCRAFT ENGINE BUILDING, ENERGY AND MEDICINE

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The development of modern science and technology is based on the creation and use of new functional materials and technologies for forming products based on them. Oxide materials have become widespread in industry, primarily in the creation of functional ceramic products, heat-protective coatings, and catalytic systems. Zirconium dioxide-based materials are found in a variety of functional ceramics, including yttria-stabilized zirconia used in high-temperature electrochemical devices, thermal barrier and thermal protective coatings, and mechanically resistant, corrosion-resistant, and biocompatible ceramics.

The main industrial approach to obtaining oxide materials with controlled properties today is the hydrolysis of salts in aqueous media. However, despite the simplicity, well-known and widespread use of the described approach, a huge amount of research is aimed at improving the functional properties of the described materials, expanding the areas of their application, as well as developing new, more effective methods of production. At the same time, fundamental problems associated with the study of the mechanisms of nucleation of amorphous compounds in aqueous media, primarily hydroxides and hydrated oxides, as well as the processes of growth, aggregation and agglomeration of nuclei are still unresolved and certainly hinder progress in the field of creating and improving the properties of a wide range of materials.

In this work, a comprehensive study of the processes of formation and aggregation of hydrated zirconium oxide particles under conditions of controlled double-jet deposition was carried out, and new approaches were developed based on it for the production of functional powder materials with improved properties.

SORBENT BASED ON ALUMINUM HYDROXIDE FOR SELECTIVE EXTRACTION OF LITHIUM FROM AQUEOUS MEDIA WITH HIGH SALINITY

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Over the past decades, the global consumption of lithium products has increased significantly due to the development and growth of industries related to the production of batteries and electric vehicles. The main sources of lithium are lithium-containing ores and water bodies. Several methods for lithium recovery from brines have been known, but the most promising is adsorption technology, due to its economic and environmental advantages. Among inorganic selective sorbents, the most studied and commercialized is the sorbent based on $\text{LiCl} \cdot 2\text{Al}(\text{OH})_3 \cdot n\text{H}_2\text{O}$ (DHAL-Cl). Despite the low loading capacity of 2-3 mg/g, it successfully uptakes lithium from brines with a salt content of 400 g/dm³. This work presents the results of the mechanochemical synthesis of aluminum-based adsorbent but unlike DGAL, the presented material does not contain lithium salts in its structure. Some fundamental information, including detailed sorption isotherms and sorption kinetics has been present. A study of the sorption properties of the synthesized sorbent showed that the static loading capacity with respect to the lithium cation is 30 mg/g. The maximum adsorption capacity is achieved in 4 hours at ambient temperature and the solid/liquid ratio S:L = 1:250. We have tested the new material for the treatment of brine with a salt content of more than 400 g/dm³ and lithium concentration of 0.58 g/l. The adsorption capacity is found to be 16-20 mg/l. When formation waters with a lithium content of 15 mg/l have been used, the recovery efficiency is achieved to 95%. It should be noted that the adsorbent exhibits high selectivity for lithium cations; adsorption of competing cations present in solutions have not been observed. The possibility of regeneration of adsorbent by 0.1M HCL has been shown; the desorption efficiency is about 100% without reducing the sorption capacity of the material.

The simplified synthesis, selectivity and high sorption capacity compared to other aluminum-based adsorbents make this material is promising adsorbent in lithium extraction and concentrating metals from complex solutions.

RESEARCH OF THE TRANSPORT PROPERTIES OF COMPOSITES BASED ON SUBSTITUTED AMMONIUM TETRAFLUOROBORATES AND NANODIAMONDS

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The energy and operational characteristics of various electrochemical devices are determined by the properties of the functional materials used (electrodes, electrolyte).

Substituted ammonium salts are, in a sense, solid-state analogues of ionic liquids, characterized by electrochemical stability in a wide range of voltages, due to the easy reorientation of organic groups (especially in high-temperature phases) and are characterized by plastic mechanical properties, inflammability, and relatively high values of ionic conductivity at high temperatures.¹ However, the electrical conductivity values of these materials, as a rule, are not too high ($\sigma \approx 10^{-6}$ - 10^{-5} S/cm near the melting point) for practical use.

It is known that the transport properties of such ionic compounds can be influenced through heterogeneous doping with highly dispersed additives. Thus, by introducing nanosized oxide additives (Al_2O_3 , MgO) and nanodiamonds, it was possible to increase the conductivity of $(\text{n-C}_4\text{H}_9)_4\text{NBF}_4$ by more than 3 orders of magnitude, with the best results observed when using nanodiamonds as a heterogeneous additive²⁻³. Such composites are still poorly studied, so it remains unclear exactly what factors lead to the maximum values of electrolyte conductivity.

In this work, the influence of the structure of the salt cation on the structural, thermal and transport properties of composites based on $(\text{n-C}_4\text{H}_9)_{(4-y)}(\text{CH}_3)_y\text{NBF}_4$ ($0 \leq y \leq 3$) and nanodiamonds was studied for the first time.

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DEVELOPMENT OF NEW FUNCTIONAL NANOPOROUS ADSORBENTS USING MACHINE LEARNING METHODS: FROM MODELS TO SYNTHESIS AND CHEMICAL PROCESSES

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The use of machine learning (ML) methods is the most popular and relevant direction in recent years among the global scientific community in chemistry and materials science, as evidenced by the explosive growth in the number of publications¹. Already today, ML methods are used to optimize the structure of materials, chemical transformations and processes, due to their lower resource intensity compared to traditional modeling methods. However, the main challenge for this area is the origin and quality of the resource data packages on which the training is based, which largely determines the effectiveness and reliability of the method.

As part of this study, we created our own database (DB) of reproducible methods for the synthesis of a wide range of nanoporous adsorbents with experimentally verified parameters of the porous structure and synthesis methods obtained at M.M. Dubinin Laboratory of Sorption Processes (IPCE RAS), as well as those presented in the literature and open databases.

During the study, machine learning models were developed and applied to implement an iterative process of predicting the synthesis parameters of functional adsorbents for various applications (MOF, nanoporous carbon adsorbents) - for the processes of sorption storage and separation of hydrocarbon components of natural gas, hydrogen, CO₂. The obtained model parameters were then reproduced experimentally with the production of real sorbents with their further comprehensive studies.

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STUDY OF CHEMICAL COMPATIBILITY OF GA-LLZO SOLID ELECTROLYTE AND HIGH-ENERGY DENSITY CATHODES BASED ON LI-RICH LAYERED OXIDES

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Replacing the liquid electrolyte in lithium-ion batteries (LIBs) with solid Li-conductive ceramics and switching to all-solid-state batteries (ASSBs) is considered as a promising approach to increasing the energy density of batteries, which can be achieved by reducing the weight of the final device and using a metallic lithium as high-energy anode. A further increase in energy intensity is possible through the use of new high-energy density cathode materials, such as Li-rich layered oxides¹. In turn, $\text{Li}_{6.4}\text{Ga}_{0.2}\text{La}_3\text{Zr}_2\text{O}_{12}$ (Ga-LLZO) with cubic garnet-type structure is considered as a promising solid electrolyte for ASSBs as it exhibits high Li-ion conductivity, wide electrochemical stability window and chemical resistance to metallic lithium². The goal of this study was to investigate the chemical compatibility of Ga-LLZO and high-energy density Li-rich cathode material $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$ (LNMO) at elevated temperature.

The work involved the synthesis of Ga-LLZO in the form of powder and dense (> 90 vol.%) membranes, as well as LNMO cathode material of various morphologies, which were subsequently co-sintered at different temperatures. X-ray powder diffraction studies performed on annealed samples, as well as the results of scanning and transmission electron microscopy, demonstrated that at a temperature > 700°C, a chemical reaction occurs between Ga-LLZO and LNMO to form Li_2ZrO_3 , which was not previously observed for layered oxides $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$ ($x + y + z = 1$). The formation of Li_2ZrO_3 negatively affects the toughness of the cathode/electrolyte interface and is probably caused by a larger $\mu(\text{Li})$ in Li-rich cathodes compared to classic layered oxides.

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PHASE FORMATION BY ELECTROSPARK TREATMENT WITH FUSIBLE ELECTRODES

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One of the promising methods of obtaining functional coatings on the working surface of products made of metallic materials is electrospark treatment (EST). The advantage of the technology is the local impact of electric discharge, which prevents overheating of critical parts. Flexibility of EST application is determined by a large nomenclature of electrode compositions, allowing to choose a specific brand, the use of which improves surface-sensitive properties of the product. Traditionally, refractory electrodes are used to form wear- and corrosion resistant coatings with the predominant transfer of carbides, silicides, borides contained in the electrode. However, such coatings are prone to cracking during deposition and have increased surface roughness. On the contrary, the use of fusible electrodes provides mass transfer through the melt droplet, which allows to apply low-energy EST modes and reduce surface roughness. Of particular interest is the use of electrodes based on fusible Al-Ca-Me eutectics (Me=Si; Mn; Zr; Y).

To understand the principles of phase formation control in the EST process, the influence of frequency-energy treatment modes and composition of near-eutectic electrodes on the structure and properties of coatings has been studied. The conditions of formation of reaction-active melt interacting with the treated surface and healing the structure defects during solidification are considered. It is established that at local melting the eutectic melt reacts with substrate elements (Nb, Ti, Ni), forming at solidification wear-resistant coatings containing phases that were not present either in the substrate or in the electrode. Along with improved mechanical and tribological properties, the coatings have increased heat resistance due to the effect of self-healing cracks during high-temperature oxidation.

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DEVELOPMENT OF CONTRAST AND THERAPEUTIC AGENTS BY INTRODUCING PARAMAGNETIC MANGANESE(II) IONS INTO SILICA NANOPARTICLES

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The incorporation of paramagnetic Mn(II) ions and complexes into silica nanoparticles represents a promising approach to obtaining contrast agents with high relaxivity parameters. The main reasons for high relaxivity values are the slowdown of all types of ion movement when included in nanoparticles.^{1,2} Various synthetic approaches are considered to optimize the incorporation of manganese ions into silica nanoparticles. A relationship is shown between the distribution of manganese ions in silica nanoparticles and their relaxivity values. However, high relaxivity parameters are a necessary but not sufficient condition for their use in in vivo conditions for contrasting certain tissues in living organisms. To solve this problem, synthetic approaches to covalent and non-covalent modification of the silica surface of nanoparticles containing manganese ions are also considered.

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DIFFERENT SCENARIOS OF LUMINESCENCE BEHAVIOR IN THE ENSEMBLE OF Mn-DOPED InP COLLOIDAL QUANTUM DOTS

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An important factor affecting the luminescence properties of InP:Mn nanocrystals is the possibility of delayed fluorescence due to excitation transfer from the dopant ion back to the quantum-dot levels.

Excitation-emission matrices and time-resolved luminescence spectra of the samples were analyzed using a specially developed theoretical model. The data show that the luminescence properties of polydisperse InP:Mn/ZnS nanocrystals are determined by three factors: rapid thermalization of the excitation distribution between the quantum-dot levels and the dopant levels, the high ratio of the radiative rate constants of the intrinsic and dopant luminescence, and inhomogeneous broadening due to the particle-size distribution. Depending on the nanocrystal size, qualitatively different scenarios arise. For sufficiently small particles, with fluorescence peaks shorter than ~ 460 nm, the excitation resides almost exclusively on the dopant ion and decays with a lifetime of ~ 4 ms, resulting in the phosphorescence with a peak wavelength of ~ 605 nm. For somewhat larger particles, the excitation resides predominantly on the dopant ion, but because the radiative rate constant of the dopant phosphorescence is much lower than that of the quantum-dot fluorescence, both emissions occur, the former being quenched and the latter strongly delayed and having lifetimes longer than $4 \mu\text{s}$. For even larger particles, the phosphorescence becomes almost completely quenched and the fluorescence slightly delayed. For large particles, with fluorescence peaks longer than ~ 560 nm, the excitation resides predominantly on the intrinsic quantum-dot levels and the dopant ion does not affect the luminescence properties. In a polydisperse sample, all these scenarios occur simultaneously, leading to a complicated pattern: the decay curve of the dopant phosphorescence is not monoexponential, the peak of the dopant phosphorescence in the excitation-emission matrix has a large Stokes shift, and the long-lived luminescence in the time-resolved spectra has two bands.

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BIOACTIVE ORGANIC COATINGS FOR METAL IMPLANTS

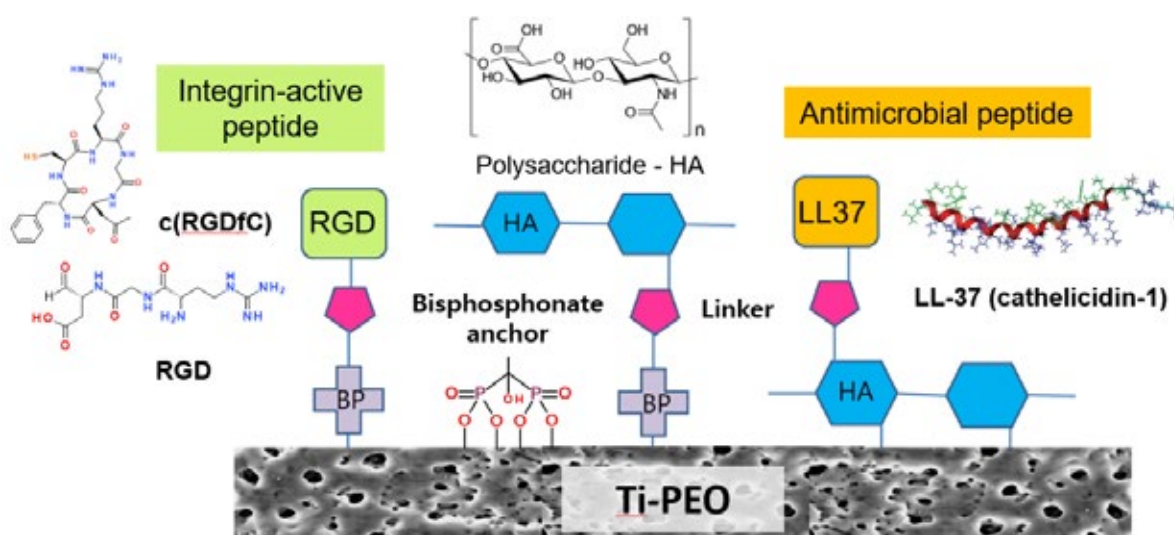
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One of the effective ways to address the issue of biocompatibility of metal implants is the use of organic coatings that provide more reliable osseointegration of the implant by activating regenerative processes, including stimulating the formation of new tissues around the device. Furthermore, the modelling of the antibacterial properties of coatings can enhance the functional performance of implants. We have developed an approach¹⁻⁴ that involves the combination of an inorganic porous oxide sublayer obtained by plasma electrolytic oxidation (PEO) and bioactive molecules with bisphosphonate anchors that provide reliable fixation of the organic layer on the surface. *In vitro* studies demonstrated that the coatings effectively regulate the biological activity of the metal surface. The approach could be further utilized for the development of the materials with improved biocompatibility.



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GENERALIZED TECHNOLOGY FOR PRODUCING INORGANIC OPTICALLY ACTIVE MATERIALS

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Using the example of inorganic scintillation materials, the procedure for developing a generalized technology for the production of optical materials is described. Historically, systematic research of scintillators and the creation of new compounds was carried out mainly in the field of improving their physical properties, such as stopping power for various types of ionizing radiation, the rate of scintillation emission and their yield, and the ability to maintain detector properties for a long time at a high dose load¹. At the same time, the issues of the relationship between technological parameters at various stages of production of crystalline optical materials and their operational properties to ensure reproducibility turned out to be undeveloped.

The key issue for achieving target properties is complex analytics of source materials and intermediate products in the production chain. In particular, control of impurity and phase purity, consumer properties of materials.

During the formation of a generalized technology of inorganic optically active materials, it was determined that by applying an approach with complex analysis at each technological stage, it became possible to establish the optimal method for the synthesis of luminescent intermediates of ternary and quaternary compounds with a garnet structure for the further production of transparent scintillation ceramics; patterns of interphase distribution of a wide range of impurity ions affecting the growth of nonlinear optical single crystals; The prospects of the approach with the formation of compositional disorder of the cation sublattice in crystalline compounds with a garnet structure for materials of ionizing radiation detectors and photonics have been established.

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STRUCTURAL MODIFICATION OF MANGANESE OXIDES (III, IV) DURING SYNTHESIS OF SELECTIVE SORBENTS

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Manganese oxides (III, IV) are characterized by a wide variety of structures, including layered and tunnel-type structures, suitable for the placement and interdiffusion of exchangeable ions¹⁻³. Based on them, it is possible to obtain new ion-exchange materials with better properties. This is achieved by modifying the composition and structure, which makes it possible to increase their selectivity, increase exchange capacity and stability during sorption-desorption cycles.

It has been experimentally shown that it is possible to control the structural transformations of manganese oxides (III, IV) during the synthesis of sorbents for alkaline earth metal ions. Thus, based on samples of the same type, purposefully changing the modifying ions in their composition (Na^+ , K^+ , H^+ , Li^+ , Ca^{2+} , Sr^{2+}), manganese oxides with different structures and properties were obtained by heat treatment (150-850° C). It has been established that the specific selectivity of ion exchangers based on manganese oxides (III, IV) to ions of individual elements or their groups is determined by textural and structural factors, and the exchange capacity by the content and acidity of OH-groups. To increase the stability of manganese oxides (III, IV) as ion exchangers during their cycling in ion exchange processes, it is proposed to replace part of the Mn^{3+} ions in the precursor with doping ions (Al^{3+} , Fe^{3+} , Fe^{2+} , Co^{2+} and Ni^{2+}) in an amount of 5-15 mol.%. Doped ions not prone to disproportionation reactions under ion exchange conditions and not exhibiting the Jahn-Teller effect. General patterns of changes in sorption properties depending on the composition and textural-structural characteristics have been identified.

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INFLUENCE OF TECHNOLOGY FOR PRODUCING ME-HYDRIDE ALLOYS AB&AB5-TYPES ON HYDROGEN SORPTION PROPERTIES

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In this work, studies were carried out on the production of FeTi & LaNi₅ alloys using the following methods: (1) electrometallurgy by alloying (VIM and VAR) pure ChM with refining microalloying of La, Ce, Mn, V and (2) methods of centrifugal SHS-metallurgy, from oxide raw materials (TiO₂, FeO, Fe₂O₃), ore concentrate (ilmenite FeTiO₃).

Using the first VIM&VAR-method, special attention was paid to the development and use of lining materials for melting that minimize the chemical interaction between the melt and the lining. When obtaining FeTi using the second method, work was focused on the maximum possible use of ore concentrate.

It was found that under same VIM modes, but using different crucible materials, O₂ content values are observed from 0.12 up to 0.03 wt. %. When using titanium iodide (TI-1) and a special lined crucible, the O₂ content was 0.018 wt. %. In the alloys obtained by VAR technology, higher concentrations of oxygen were observed (up to 0.15 wt. %) due to the lack of the possibility of refining ChM during melting, with the exception of the introduction of additional elements (REM, Mn, V) and the use of high-purity ChM.

In SHS-alloys without microalloying, similar oxygen concentration as with VIM and VAR alloys (up to 0.2 wt. %), which indicates the possible development of an alternative and more technological approach to the production of FeTi (less energy-consuming and cost-effective). An important result of the research is the possibility of direct production of the FeTi alloy from ilmenite ore concentrate.

Based on the research results, diagrams of the dependence of the studied technological regimes on the sorption-desorption properties of alloys were constructed.

DEVELOPMENT OF GRANULAR SORBENTS AgLiLSX FOR SEPARATION OF AIR AND PRODUCTION OF OXYGEN

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One of the methods for producing oxygen is the sorption separation of air in pressure swing adsorption (PSA) units, based on the selective sorption of nitrogen on low-modulus LSX zeolites with various extra-framework cations (Ca^{2+} , Ba^{2+} , Li^+ , etc.). An effective sorbent for producing oxygen with a purity of more than 95% is the Li-form of LSX zeolite. To obtain high-purity oxygen, additional purification of O_2 from the remaining argon is required. It is known that partial replacement of Li^+ with silver cations in LiLSX zeolite increases the selectivity of sorption of both nitrogen and argon from air, allowing the concentration of oxygen produced to be increased to 99% and higher. Currently, granular zeolites of the LSX type are produced by molding with various binders, while the sorption capacity of the granules is reduced.

The aim of this work is to develop effective granular AgLiLSX sorbents for air separation and production of high-purity oxygen.

In our work, granular KNaLSX sorbent was synthesized by recrystallization of the binder (metakaolin) inside the granule. This method makes it possible to obtain a sorbent in the form of a single crystalline aggregate without losing sorption capacity. The resulting KNaLSX granules were subjected to ion exchange to obtain LiLSX zeolite. Then a series of samples of granular LiLSX zeolite with varying degrees of substitution of Li^+ for Ag^+ was prepared. To assess the sorption properties and the possibility of obtaining oxygen from air, the adsorption isotherms of N_2 , Ar and O_2 at 25 °C were studied. From the K_{Henry} isotherms, the selectivity of separation of the main gases was determined as $K_{\text{Henry}}(\text{N}_2)/K_{\text{Henry}}(\text{O}_2)$ and $K_{\text{Henry}}(\text{Ar})/K_{\text{Henry}}(\text{O}_2)$. It has been established that samples of granular zeolite AgLiLSX with a high degree of substitution of Li^+ cations for Ag^+ have the highest selectivity for the sorption of both N_2 and Ar with respect to O_2 compared to LiLSX and can be used in PSA plants to produce high-purity oxygen.

The research was carried out with the support of the Development Program of Tomsk State University (Priority-2030).

PROSPECTS FOR THE USE OF TITANIUM ALLOYS FOR THE MANUFACTURE OF MEDICAL IMPLANTS

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To solve the problem of allergic reactions, the effect of “stress shielding” after the installation of medical implants, attempts are being made to develop new alloys with a lower modulus of elasticity, but with the same or higher strength and biocompatibility as used alloys¹.

One of the promising ways to solve this problem is the development of new titanium β -alloys with properties that allow the creation of orthopedic implants with a low modulus of elasticity, do not cause allergic reactions and have biocompatibility comparable to pure titanium and (α + β)-titanium alloys².

Niobium and tantalum alloying is used to produce titanium β -alloys. They increase corrosion resistance, biocompatibility of alloys and strength properties, while reducing the Young's modulus³.

Alloys of the Ti-20Nb-(5-10)Ta (at. %) system were smelted and studied. The structure, chemical composition, phase composition, static and cyclic properties, biocompatibility in vivo and in vitro, and corrosion properties were studied.

It is shown that the selected principles of alloying, using the example of specific Ti-20Nb-(5-10)Ta alloys, in the future, will allow obtaining alloys with high mechanical properties, low Young's modulus and high biocompatibility.

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FORMATION OF INHIBITED POLYMER FILMS ON DIFFERENT CONSTRUCTION METALS BY CATAPHORETIC DEPOSITION

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Corrosion protection of metal structures in different industries is one of the most important goals, ignoring which can cause enormous losses. As a result of corrosion processes, the strength and reliability of metal structures are reduced, which can lead to unfavorable consequences. The use of corrosion inhibitors is one of the ways to reduce the corrosiveness of the working environment. However, despite the variety of inhibitors, the problem of expanding their range remains relevant. In recent years, inhibited formulations (INFOR) consisting of organosilane molecules and corrosion inhibitors, the use of which leads to the formation of inhibited polymer films (IPF) on metal surfaces, are of particular interest. Previous researches have shown that the films consist of several layers: the outer layer - organosilane, is a barrier protecting the metal from the external corrosive aggressive atmosphere. If its continuity is broken, corrosion dissolution of the metal is prevented by the surface layer consisting of chemisorbed organosilane molecules and corrosion inhibitors.

Traditionally, IPFs are formed on the metal surface by dipping/exposure of the sample in the aqueous solution of INFOR. As a result, a micron, defect-free, densely bound to the metal (due to chemisorption of organosilane and corrosion inhibitor molecules) is formed on its surface. In order to optimize the process of formation of high-quality IPF on metal it is possible to use cataphoretic deposition (CPD). When using CPD, the metal sample is the cathode, which is negatively charged and the anode is positively charged. H_2 is released at the cathode and O_2 is released at the anode. Under the action of electric current, the molecules of corrosion inhibitor and hydrolyzed organosilane move to the cathode, distributing evenly over the surface of the metal product, which leads to the formation of a film. The purpose of this work was to determine the conditions under which it is possible to realize qualitative application of IPF on the surface of low-carbon steel and copper with help of CPD from the aqueous solutions of inhibited formulations. For this purpose a number of tasks were solved: to develop an effective composition of INFOR; to choose a method of surface pretreatment; to determine the optimal mode of cataphoretic deposition; to study the structure and performance properties of IPF.

ELEMENTOXANE ALUMOXANES – PRECURSORS OF HIGH-HEAT-RESISTANT CERAMIC COMPOSITES

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The development of new ceramic composites, in particular, oxide and oxy-carbide compositions, is a priority scientific task in the field of creating promising ceramic composite materials for structural and functional purposes¹.

Ceramic-forming organoelementoxanealumoxane oligomers are precursors of components (binders, matrices, barrier and protective coatings, fibers) of highly heat-resistant and chemically inert ceramic composites of oxide and oxy-carbide compositions: corundum (α - Al_2O_3), garnet ($\text{Y}_3\text{Al}_5\text{O}_{12}$), yttrium aluminum (YAlO_3 and $\text{Y}_4\text{Al}_2\text{O}_9$), yttrium disilicate – mullite ($\text{Y}_2\text{Si}_2\text{O}_7-3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), cordierite ($\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$), spinel-garnet ($\text{MgAl}_2\text{O}_4/\text{Y}_3\text{Al}_5\text{O}_{12}$), SiC-AlYO_3 compositions, as well as the above ceramics modified with refractory metal Zr, Hf or Cr oxides²⁻⁹.

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COMPLEX PEROVSKITE OXIDES AS A PROSPECTIVE THERMAL BARRIER COATINGS

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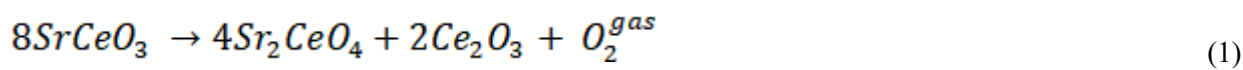
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The performance of gas turbine engines is greatly influenced by their operating temperatures, a parameter that can be enhanced by applying refractory ceramic coatings known as thermal barrier coatings (TBCs) onto nickel superalloys¹. The most widely used material for this is zirconium oxide stabilized with yttrium oxide (YSZ). However, it is limited in its application beyond 1200 °C due to factors like phase transition, prompting the quest for more efficient alternatives for TBCs².

Previous research has indicated that materials utilizing strontium cerate (SrCeO₃) exhibit low thermal conductivity and a moderate coefficient of thermal expansion, positioning them as promising candidates for TBCs³. Investigation into the melting behavior of the SrCe_{1-x}Sn_xO₃ solid solution, where x ranges from 0 to 0.5, revealed that these materials undergo incongruent melting at approximately 1700 °C, as evidenced by the following reaction:



While the melting point of strontium cerate-stannate meets the TBC criteria, additional enhancement of its properties, particularly temperature stability, is imperative. This can be achieved through the development of highly entropic compounds derived from them, such as SrCe_{0.2}Sn_{0.2}Zr_{0.2}Ti_{0.2}Y_{0.2}O_{3-d}.

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IMPURITY ABSORPTION IN A^VB^{VI} GLASSES FOR FIBER OPTICS

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The properties of A^VB^{VI} chalcogenide glasses that are most important for use in infrared fiber optics are sensitive to the content of impurities.

The main goals of development in the field of high-purity A^VB^{VI} glasses and infrared optical fibers based on them are:

- search for the sources of extrinsic optical losses that contribute at a level of 1-10 dB/km for chalcogenide glasses of various systems. This means assessing the influence of impurities and the intrinsic contribution of the glass matrix, as well as studying the influence of structural defects in the resulting optical fibers;
- further reduction in the content of limiting impurities in the glasses by 1-1.5 orders of magnitude compared to the achieved level, as well as improvement in the microuniformity of the glasses.

Optical losses of A^VB^{VI} glasses are divided into intrinsic and extrinsic ones. The current situation with glass transparency, assessed by optical losses in optical fibers, is characterized by a significant predominance of extrinsic losses compared to intrinsic ones. The communication discusses the contribution of various factors to the achieved level of optical loss. An assessment of the intrinsic optical losses is given, taking into account data on the structure of the glass and all components of the mechanism of interaction between light and the medium; determination of the predominant source of excess losses in glass and optical fibers in the loss range of 1-10 dB/km.

High-purity chalcogenide glasses were obtained, the content of limiting impurities in which did not exceed 10^{-6} - 10^{-7} wt.%. Optical fibers with minimal losses of 12–14 dB/km in the spectral range of 3–5 μm were obtained from high-purity As-S glass. Optical fibers made from high-purity As-Se, Ge-As-S-Se and Ge-As-Se-Te glasses have minimal optical losses from 40 to 150 dB/km in the wavelength range 6–9 μm .

The work was carried out with the financial support of the Russian Science Foundation, project RSF 22-13-00226.

STRUCTURE AND PROPERTIES OF LAYERED METAL-INTERMETALLIDE COMPOSITES OF THE Ti-Fe SYSTEM

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The creation of a layered structure with alternating hard (intermetallic) and soft components was carried out on layered metal-intermetallic composites of the titanium-iron system (SMIK), the complex production technology of which involves hot rolling (HR) of explosion-welded composite workpieces and heat treatment (HT) to form a layered structure¹.

Research carried out at the GP stage within the framework of the concept of this technology showed that an increase in compression of more than 70% helps eliminate uneven deformation of the layers; The minimum thickness of layers with a maximum number of layers in the composition of the SCM is ensured by a multi-pass GP with a total compression of up to 93÷95%. Studies concerning the influence of HT on the structure and properties of SCM after its HP have shown² that an increase in the carbon content in steel layers of SMIC leads to an increase in temperature and holding time during HT, necessary for the formation of the SMIC structure in the form of alternating intermetallic and ferritic layers, an increase in the thickness of the TiC interlayer; the process of formation of a layered structure occurs most intensively at 950°C, and at temperatures above 1000°C, the level of defects in the layered structure increases, up to the complete absence of its laminarity; the diffusion zone consists of single-phase layers (TiC, TiFe₂, TiFe, Ti₂Fe) and in its central part it contains a layer consisting of a mixture of two phases.

The resulting composites with a metal-intermetallic layered structure, as studies have shown, have increased tribo-technical characteristics³: with an increase in the test temperature to 500°C, their wear resistance becomes comparable to the wear resistance of U9A and 4KhMFS steels, and at 600°C 2 and 1.5 times higher.

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LONG-CHAIN AMINES AS STABILIZING LIGANDS FOR COLLOIDAL QUANTUM DOTS

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Liquid-phase synthesis in the presence of organometallic precursors in a high-boiling solvent is widely used for the preparation of colloidal quantum dots (CQDs). One of the most effective coordinating ligands is oleylamine (OLA, cis-9-octadecylamine), which is actively involved both in the synthesis itself and in the passivation of the particle surface and the formation of protective shells that prevent their aggregation. However, commercial OLA often contains various impurities, mainly elaidylamine (trans-9-octadecylamine), the content of which varies depending on the manufacturer and lot number and can be as high as 43%¹. This affects the properties of the resulting CQDs, and the separation of these isomers is an extremely labor-intensive task.

In this work, we studied the possibility of using saturated amines with a hydrocarbon chain length (C10-C18) and a higher degree of purity for the synthesis of CQDs. It has been established that with a decrease in the length of the amine molecule, the average diameter of the resulting particles and their polydispersity increase. This is due to the lower mobility of molecules with long hydrocarbon chains compared to shorter molecules². The longer the amine molecule, the lower the concentration of CQD nuclei, the precursors are consumed more slowly, and their reserves last for a longer time, and the particles are formed more homogeneously. Thus, the size of the CQD can be controlled not only by changing the temperature and time of synthesis, but also by changing the length of the hydrocarbon chain of the coordinating amine.

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LUMINESCENT MATERIALS BASED ON ORTHOBORATES AND METABORATES OF RARE EARTH ELEMENTS

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Doped lanthanum borates of different compositions, possessing high thermal stability and transparency in the UV range, are one of the highly efficient luminophores. Eu^{3+} , Tb^{3+} , Sm^{3+} , Dy^{3+} and Ce^{3+} ions are used as activators to create multicolour luminescent materials, which have high luminescence efficiency, large Stokes shift and narrow-band emission in the visible and near-IR regions when excited by UV light. Introduction of sensitising ions, for example, Sm^{3+} , Ce^{3+} , Bi^{3+} ions into the phosphor composition during synthesis, which transfer part of the absorbed energy to the activator ions, leads both to an increase in the luminescence intensity of the activator ion and to a broadening of the emission spectrum, which makes it possible to obtain a material emitting white light at the same wavelength of the excitation light.

The method used to obtain the effective material significantly affects the composition, structure, particle size and, consequently, the functional properties, as well as determines the manufacturability of the process of its preparation. Co-doped with Eu^{3+} , Tb^{3+} , Sm^{3+} , Bi^{3+} , Y^{3+} ortho- and metaborate lanthanum ions were obtained under optimal conditions of the extraction-pyrolytic method at lower temperature and time compared to known methods. The compounds were characterised by X-ray phase analysis, IR and luminescence spectroscopy. The lattice parameters of samples of different compositions were calculated. Luminescent properties of orthoborate $\text{La}_{0.95}\text{Eu}_{0.05}\text{BO}_3$ or metaborate $\text{La}_{0.95}\text{Eu}_{0.05}(\text{BO}_2)_3$ in the range of used concentrations of doping ions (0.005; 0.01; 0.02; 0.025; 0.05; 0.075; 0.1) have been studied by luminescence excitation and luminescence spectra. The compounds show intense luminescence in the broad region of 400–750 nm.

NEW Ln^{3+} BASED CONTRAST AGENTS FOR PHOTON-COUNTING COMPUTED TOMOGRAPHY

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Photon-counting computed tomography (PCCT) is a novel non-invasive imaging method combining CT and X-ray spectroscopy and allowing to visualize 3D structures of the study objects considering their chemical composition. PCCT studies often involve the contrast agents (CAs) to better visualize the morphology, structure, and features of the object. The best CA for PCCT are elements with ordinal numbers $Z > 64$ and K-edges of 40–110 keV.

The current work presents CAs based on rare earth element compounds deposited on a carbon nanomaterials (CNMs)¹ or SiO_2 ², including CAs with a core-shell structure $\text{Ln}_2\text{O}_3@\text{C}$ and $\text{Ln}_2\text{O}_3@\text{SiO}_2$. The surface of the particles can be modified by functional groups by oxidation of $\text{Ln}_2\text{O}_3@\text{C}$ with nitric acid vapors³ or treatment of $\text{Ln}_2\text{O}_3@\text{SiO}_2$ with $\text{Si}(\text{OEt})_3\text{C}_3\text{H}_6\text{NH}_2$ vapors or solution. The oxidized surface of $\text{Ln}_2\text{O}_3@\text{C}(\text{O})\text{OH}$ can be further modified by thionyl-chloride with the synthesis of $\text{Ln}_2\text{O}_3@\text{C}(\text{O})\text{Cl}$ and subsequent production of ethers $\text{Ln}_2\text{O}_3@\text{C}(\text{O})\text{R}$ ($\text{R} = \text{OPh}$, captopril) having specific selectivity properties.

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This research was supported by Russian Science Foundation (project number 22-15-00072).

LAYERED PEROVSKITES BASED ON BaLaInO_4 AS PROMISING MATERIALS FOR ELECTROCHEMICAL DEVICES IN DISTRIBUTED ENERGY

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Recent economic and socio-political challenges have transformed hydrogen from a substance used mainly in the chemical, oil refining, food and metallurgy industries into a product with high export potential. Today, there is no global hydrogen market in the usual sense of this concept. The infrastructure for its transportation has not been developed. This allows us to speak about the high prospects of the hydrogen market and the importance for Russia of implementing the strategic task of its development. It is obvious that in order for Russia to take a leading position in the global hydrogen market, it is necessary to develop its own technological competencies in the field of hydrogen energy, which would include, among other things, the development and creation of innovative solid oxide fuel cells and electrolyzers.

To create durable and highly efficient devices of this type, it is necessary, among other things, to search for and study promising materials that have a range of functional properties. Proton conductors are used as the electrolyte material in such devices. Classic materials investigated as proton-conducting matrices over the past forty years are barium cerates and zirconates, which have a perovskite structure. However, several years ago the fundamental possibility of proton transfer in layered $\text{AA}'\text{BO}_4$ perovskites was demonstrated. It was shown that the introduction of a dopant makes it possible to increase the conductivity, including proton conductivity, to ~ 1.5 orders of magnitude. In this work, the features of proton transport in doped layered perovskites based on barium-lanthanum indate BaLaInO_4 are analyzed. The influence of the nature and concentration of the dopant on the unit cell size, water absorption, and proton conductivity was assessed.

The work was carried out with the financial support of the Russian Science Foundation, project No. 22-79-10003.

LIQUID LASER MEDIA BASED ON CARBON TETRACHLORIDE

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Inorganic laser liquids (ILLs), used as active media for creating of multi-kilowatt diode-pumped circulating lasers^{1,2}, are highly toxic and aggressive. In order to create low-toxic liquid laser media, solutions of carbon tetrachloride CCl_4 activated with Nd^{3+} or Yb^{3+} were studied.

For the first time, laser-active liquids $\text{CCl}_4\text{--BCl}_3\text{--Yb}^{3+}$ were prepared: luminescence lifetime $\tau \approx 0.9$ ms and $[\text{Yb}^{3+}] \approx 0.03$ mol/L.

The conditions for the synthesis of $\text{CCl}_4\text{--GaCl}_3\text{--Nd}^{3+}$ and $\text{CCl}_4\text{--GaCl}_3\text{--Yb}^{3+}$ solutions with a concentration of active ions up to 1 mol/l were found.

The kinetics of formation and quenching of luminescent heterocomplexes in solutions of $\text{CCl}_4\text{--GaCl}_3\text{--Nd}^{3+}$ and $\text{CCl}_4\text{--GaCl}_3\text{--Yb}^{3+}$ are considered. During the preparation of solutions, changes occur in the absorption spectra, τ increases and reaches maximum values of 0.06–0.08 ms for Nd^{3+} and 0.6–0.7 ms for Yb^{3+} , the quantum yield of luminescence $\eta(\text{Nd}^{3+}) < 0.3$, $\eta(\text{Yb}^{3+}) \approx 0.9$. The rate of complexation increases both with increasing synthesis temperature and with increasing ratios of $[\text{GaCl}_3]:[\text{Nd}^{3+}]$ or $[\text{GaCl}_3]:[\text{Yb}^{3+}]$. When storing $\text{CCl}_4\text{--GaCl}_3\text{--Nd}^{3+}$ solutions, $\tau(\text{Nd}^{3+})$ slowly decreases. The reasons for the quenching of Nd^{3+} luminescence are discussed. Solutions of $\text{CCl}_4\text{--GaCl}_3\text{--Nd}^{3+}$ with $\tau(\text{Nd}^{3+}) \approx 0.25$ ms and $[\text{Nd}^{3+}] \approx 0.1$ mol/l were prepared. With increasing Nd^{3+} concentration, $\tau(\text{Nd}^{3+})$ decreases.

Spectral dependences of the gain cross section $\sigma_g(\lambda)$ Yb^{3+} in $\text{CCl}_4\text{--GaCl}_3\text{--Yb}^{3+}$ for different values of the relative inverse population β are calculated. The maximum values of $\sigma_g(\lambda)$ shift with increasing β to the region of short wavelengths and, all other things being equal, no less than in ILLs.

Liquid media based on $\text{CCl}_4\text{--GaCl}_3$ can be used to create diode-pumped laser devices.

Approaches to the synthesis of non-toxic low-corrosive organic laser liquids activated by Nd^{3+} or Yb^{3+} are considered.

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HALIDE COMPLEXES OF BISMUTH AND ANTIMONY: SYNTHESIS, STRUCTURE AND PROPERTIES

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Metal halide complexes attract the attention of researchers both because of their structural diversity and because of their physical and chemical properties. There are works showing the possibility of using these compounds in phototransforming devices, optical memory elements, piezo sensors, etc.

The purpose of this work is a systematic study of the patterns of formation of halide complex compounds of bismuth and antimony, including heterometallic, polyhalide, and the study of their physical and chemical properties

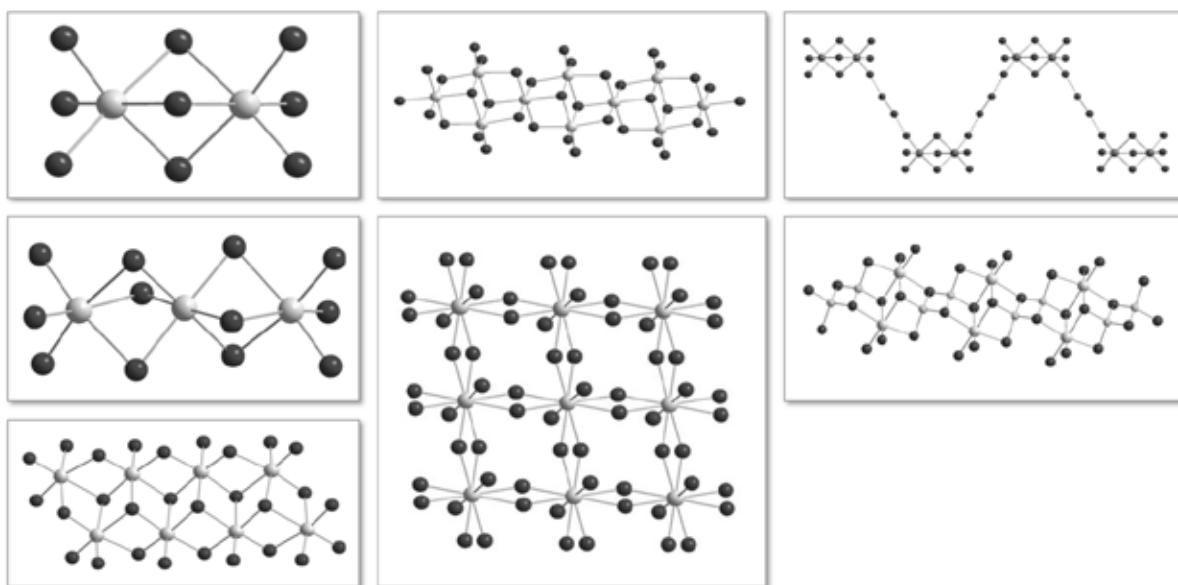


Figure 1. Structural diversity of bismuth and antimony halide complexes

This work has been supported by Russian Scientific Foundation, grant 23-73-10054.

PRODUCTION OF NIOBIUM NANOCRYSTALLINE CARBIDE BY ELECTROCHEMICAL METHOD

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The current task of modern industry in the field of metallurgy, heavy engineering, aerospace engineering and nuclear energy is to increase the operating temperatures of structural materials. Strength characteristics of composite materials depend not only on structure/phase composition of obtained materials, but also on size of matrix particles and strengthening particles in consolidated materials. Therefore, it is important to maintain a small grain size in the final material and improve the properties of the compound.

This work proposes a simple method for the synthesis of nanopowders of refractory NbC_y niobium carbide with a cubic structure using electrochemical transport reactions. The synthesis of nonstoichiometric niobium carbide nanoparticles was carried out without using high temperatures; the method used is based on the phenomenon of directed spontaneous transfer of metals by their ions in salt melts into amorphous carbon with formation of NbC_y nanoparticles without electrolysis using niobium powder, carbon and a mixture of components (K₂TaF₇ (10%) + NaCl (85%) + NaF (5%)) as starting materials. The synthesis of nanoparticles of nonstoichiometric niobium carbide was carried out without using high temperatures; the method used is based on the phenomenon of directed spontaneous transfer of metals by their ions in salt melts to amorphous carbon with the formation of NbC_y nanoparticles without electrolysis. The resulting powder was examined by X-ray diffraction, scanning electron microscopy and inductively coupled plasma spectral analysis. According to X-ray diffraction data, NbC_y nanocrystals have a cubic structure (sp.gr. *Fm-3m*), the average crystallite size is about 28 nm. The powder is rounded loose microparticles with internal cavities in the form of spheres consisting of elongated nanoparticles with a length of about 20 nm. The resulting nanopowder is an excellent additive in the production of hard alloys, exhibits good superconductivity and other functional properties. The obtained nanopowder is an excellent additive in the production of hard alloys, demonstrates good superconductivity and other functional properties.

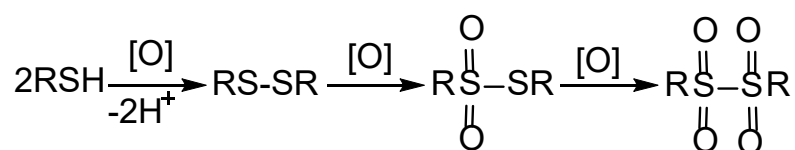
The work was carried out with the financial support of the Russian Science Foundation (project 19-73-20012-II, <https://rscf.ru/en/project/19-73-20012/>)

CATALYTIC SYSTEMS BASED ON FRAMEWORK STRUCTURES FOR RSH TO DISULFIDES COUPLING PROCESSES

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Substituted phthalocyanine metal complexes are quite perspective as a different applications¹ including thiols coupling processes catalysis², which are known as a drug compound components. The usage of phthalocyanes catalysts makes it possible carrying out the coupling at mild conditions³.



At the same time, in order to obtain materials based on metallophthalocyanines and improve their performance characteristics, their immobilization onto a solid-phase carrier is necessary. Various frame structures can act as such a carrier.

In this study, we studied the processes of adsorption⁴ of cations of some *d*-metals and precursors of phthalocyanine compounds in the pores of Fe-ZIF and Co-ZIF in order to synthesize metallophthalocyanines in the pores of an organometallic framework.

An approach has been developed to obtain functional materials based on Fe-SI and Co-ZIF with included phthalocyaninates of copper and zinc. The effect of the method of obtaining a functional material on the physical and chemical properties of the entire catalytic system is shown.

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MASS SPECTROMETRIC STUDY OF VAPORIZATION PROCESSES AND THERMODYNAMIC PROPERTIES IN THE $\text{Cs}_2\text{O}-\text{Al}_2\text{O}_3$ SYSTEM AT HIGH TEMPERATURES

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Ceramics based on the $\text{Cs}_2\text{O}-\text{Al}_2\text{O}_3$ system is a part of the multicomponent materials that are of interest for various areas of the modern engineering, including the safety problems of nuclear power and radioactive waste disposal by immobilization of cesium.¹ The urgency of studying the vaporization processes and thermodynamic properties of the $\text{Cs}_2\text{O}-\text{Al}_2\text{O}_3$ system, which was the subject of this study, was dictated by the need to synthesize and apply the ceramics based on it at high temperatures. The ceramic samples based on the $\text{Cs}_2\text{O}-\text{Al}_2\text{O}_3$ system were obtained by solid-phase and glycine-nitrate synthesis, followed by characterization using the methods of both X-ray fluorescence and X-ray phase analysis. By the high temperature mass spectrometric method² in the temperature range 1000-1300 K, it was found that the vapor over the ceramic samples based on the $\text{Cs}_2\text{O}-\text{Al}_2\text{O}_3$ system consists of atomic cesium Cs and O_2 . The partial pressures of the vapor species over the samples and the Cs_2O activities in the $\text{Cs}_2\text{O}-\text{Al}_2\text{O}_3$ system were determined at the temperature 1200 K. In assumption of the existence of a solid solution in the concentration range of 0-33 mol. % Cs_2O , the Al_2O_3 activities and excess Gibbs energies were calculated in the system under consideration, indicating negative deviations from ideality. The found component activity values were optimized within the framework of the generalized lattice theory of associated solutions³ to obtain a consistent thermodynamic description of the system under consideration.

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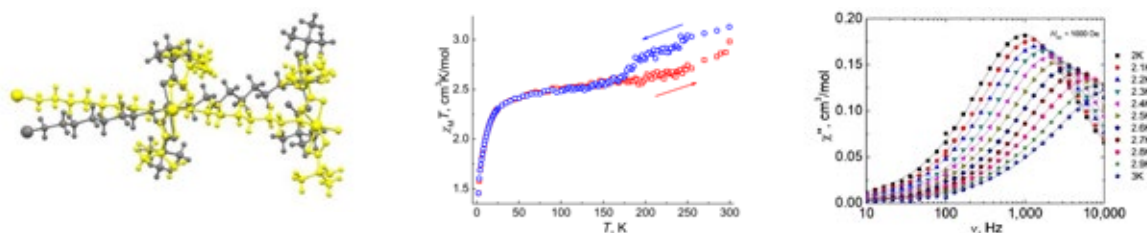
The study was carried out with the financial support of the Ministry of Science and Higher Education of the Russian Federation, grant No 075-15-2021-1383.

NEW TRANSITION METAL COORDINATION POLYMERS WITH DIIMINE AND DIAMINE LIGANDS: SYNTHESIS, STRUCTURE AND PROPERTIES

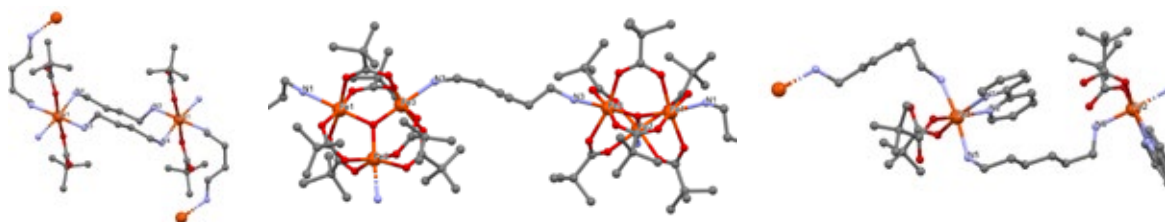
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The interaction of transition metal carboxylates with redox-active diimine and labile diamine ligands leads to the formation of new coordination polymers with controlled reversible magnetic properties. New switchable materials can be used in the development of molecular sensors and information storage devices with molecular memory^{1,2}.



In this work, we describe the synthesis of new coordination polymers of transition metals and their structure in crystal. Some properties and features of chemical reactions will be reported as part of the report.



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This work was financially supported by the Russian Science Foundation (project 23-73-01079).

FEATURES OF THE STRUCTURE OF THE BORON-OXYGEN GRID IN THE MELT $x\text{Na}_2\text{O}-(1-x)\text{B}_2\text{O}_3$ BASED ON AB INITIO MOLECULAR DYNAMICS DATA

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Experimental possibilities for obtaining information about the local structure of alkali borate melts are limited. Data on the structure with almost any degree of detail can be obtained by computer modeling methods. Therefore, calculations for melt $x\text{Na}_2\text{O}-(1-x)\text{B}_2\text{O}_3$ were performed by ab initio molecular dynamics method using VASP program code for 15 concentrations of x in the range from 0 to 0.35 at $T = 1273$ K. The supercell contained about 250 atoms and an integer number of elements Na_2O and B_2O_3 . 35,000 steps were performed for each concentration (the step is 1fs), local structural characteristics were determined by averaging over the coordinates of atoms at the last 20,000 steps using our own original program.

There are calculated the partial radial distribution functions of the atoms and bond lengths; the size of the boron-oxygen grid; the number of all XY_n units (X, Y are B, O or Na atoms); the statistical distribution of bond lengths, angles, sums of angles in all units; the number of bridged and non-bridged oxygen atoms; the number of ring structures - boroxol rings, triborate and di-triborate groups.

The concentration dependences of all characteristics are analyzed. The overwhelming number of boron atoms, from 95 to 98%, is included in the boron-oxygen grid. The basic structures, BO_3 and BO_4 , are very close to regular triangles and tetrahedra. At different concentrations, various types of ring structures prevail, what is a non-trivial fact and one can try to find its experimental confirmation. The most pronounced nonmonotonic dependence on concentration is available for the total number of rings (based on B_3O_3) and it correlates well with the nonmonotonic behavior of the viscosity measured by the vibration method by two of the co-authors of this work. In general, the work shows the prospects of the approach used to study complex oxide melts.

The calculations were carried out on the Uran supercomputer of the IMM UB RAS
The work was carried out within the framework of the state task of the IMET UB RAS

COMPOSITE MATERIAL BASED ON CHITOSAN, POLYANILINE/POLYPYRROLE COPOLYMER AND ZnO NANOPARTICLES

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In this work, a film material was obtained based on natural, biodegradable chitosan, a copolymer of polyaniline and polypyrrole, ZnO nanoparticles (SPANI/Ppyr/ZnO) from a solution containing: chitosan (500 kDa, Bioprogress, CD = 90%) – 1.5 g, acetic acid – 3.5 ml, glycerin – 4.6 ml, SPAN/PIR/ZnO – 3.8 g, the rest water up to 100 ml. SPAN/PIR/ZnO doped with anions of hydrochloric and dodecylbenzenesulfo- and oxalic acids were obtained by an oxidative polymerization reaction using ferric salt or ammonium persulfate as an oxidizing agent with the addition of ZnO nanoparticles (<100 nm (Aldrich)) in an amount of 0.1 wt. % [1]. According to impedance spectroscopy data, the conductivity of the film material was 0.1 S/cm. A composite material obtained by modifying a chitosan matrix with a conducting polymer is promising for use as a biosensor [2].

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The work was carried out within the framework of the BRFFR project № T22KITG-005 "Creation and research of new radiation-resistant nanocomposite coatings" and the SSRP "Materials Science, New Materials and Technologies" under assignment 8.4.2.2.

NITROGEN DIOXIDE SORPTION BY ZIRCONIUM METAL-ORGANIC FRAMEWORKS (Zr-MOF)

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Nitrogen dioxide (NO₂) is incredibly harmful to the environment, being one of the causes of photochemical smog and acid rains, but it also has a negative impact on human health, causing respiratory illnesses and impairing the immune system in general. The removal of nitrogen dioxide from exhaust gases and related industrial emissions is an important and rather difficult task due to the high reactivity of NO₂. The vast majority of classical sorbents (zeolites, activated carbons, metal oxides, etc.) suffer from disadvantages such as relatively low capacity and moreover are subject to degradation under exposure to this gas, which makes their use difficult.

However, there is a class of compounds with a range of properties that can help overcome these weaknesses of traditional sorbents. These are metal-organic frameworks (MOFs), which, due to the variety of metal centers and organic linkers, offer unlimited possibilities for topology modification and variation of material properties. For example, zirconium-based MOFs are of particular interest for NO₂ sorption, because of their outstanding structural and chemical stability. By using different organic linkers, it is possible to obtain compounds with different properties, which will undoubtedly influence the ability to sorb nitrogen dioxide.

In this work, the properties of three zirconium MOFs: UiO-66, MOF-801 and MOF-808 were compared using a series of physicochemical methods. The sorption capacity was determined and significant differences in their behavior were revealed; the selective sorption of NO₂ from dilute mixtures with composition close to the real one was also shown.

This work has been supported by the grants the Russian Science Foundation, RSF 22-73-10239.

STUDY OF THE FORMATION PROCESS OF GEOPOLYMERS BASED ON ALUMINOSILICATES WITH DIFFERENT PARTICLE MORPHOLOGY

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Cement-free cementitious materials based on geopolymers are environmentally friendly, have high compressive and bending strength, chemical resistance, resistance to cyclic freezing and thawing, fire and temperature resistance, the ability to vary the rheological properties of the geopolymer material, and therefore can be used in many industries, as well as in 3D printing. As precursors of geopolymer materials, aluminosilicates of natural and synthetic origin are used, which differ in particle morphology, chemical, granulometric and phase composition, which significantly complicates the study of the parameters of the geopolymerization process. In this work, we studied the patterns of formation of geopolymer materials from precursors with different particle morphologies (platelike, tubular and spherical) obtained under hydrothermal conditions.

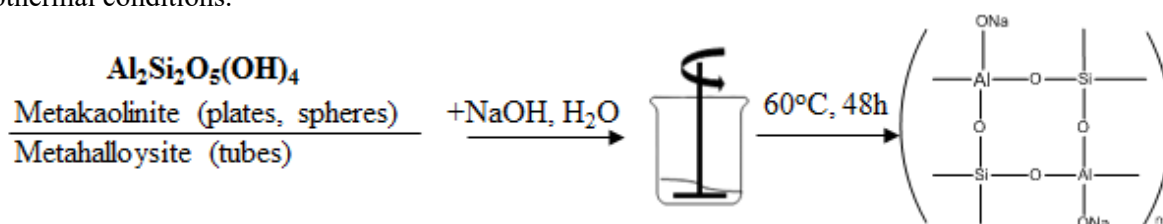


Figure 1. Schematic diagram for obtaining a geopolymer from aluminosilicate precursors

As a result of research, it was found that when synthetic precursors are used, geopolymers have a homogeneous structure and demonstrate greater uniformity in the distribution of internal stresses during compression. Based on the influence of particle morphology on strength characteristics, the following trend was established - compressive strength increases in the series: natural plates, natural nanotubes, synthetic plates and spheres. The data obtained will make a significant contribution to the understanding of the physicochemical patterns of geopolymerization and will make it possible to adapt this material for domestic additive technologies.

TOPOLOGICAL RULES FOR DESIGN OF FRAMEWORK, LAYERED AND CHAIN STRUCTURES

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Topological analysis tools are used to study the existing and potential diversity of coordination polymers and porous organic crystals of various dimensions, from molecular building blocks to frameworks.¹⁻⁵ The topology of the porous space in 1033 crystal structures of organic cages was analyzed.¹ A relationship has been established between the topology of the structural organization and the magnetic anisotropy of paramagnetic iron(III) complexes with cyclobutane-1,1-dicarboxylic acid in their salts with alkali metals.² A record degree of interpenetration was demonstrated for a network of **etb** type in new coordination polymers of zinc(II) with 1,2-bis(4-pyridyl)ethylene and pyrosmucic acid.³ The influence of network topology and the choice of anion on the luminescent properties of Zn(II) coordination polymers with 3,5-bis(4-pyridyl)-1,2,4-triazole and pivalate anion, Br⁻, Cl⁻ has been demonstrated.⁴ A set of topological representations and descriptors allowed us to reveal the potential existence of 2D nanoparticles as subnets of 3D networks.⁵ New metal-organic framework [Zn₄(THIP)(HCO₂)₃(H₂O)₄]·DMF of 4,5,6-trihydroxyisophthalic acid (H₃THIP) capable of delamination of nanosheets was synthesized, which confirmed the possibility of predicting the decomposition of frameworks into layers. The nanosheets can be used in drug delivery systems.

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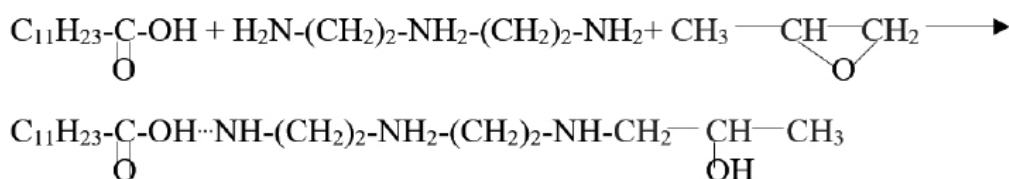
SYNTHESIS AND STUDY OF A SURFACTANT BASED ON DODECAN ACID N-(2 AMINOETHYL)-1,2-ETHANDIAMINE WITH 1,2 EPOXYPROPANE

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As a result of the gradual increase in oil spills over the past hundred years, unwanted oil pollution has recently reached alarming proportions. New surfactants have been successfully synthesized to clean the water surface of oil spills¹.

This work gives detailed information about surfactant based on dodecan acid N (2 aminoethyl)-1,2-ethandiamine with 1,2 epoxyp propane, reaction that occurs in a 1:1 molar ratio. The duration of reaction was 2-4 hours at a temperature of 70-80°C in a thermostat. The reaction proceeds according to the scheme below:



The oil-collecting and oil-dispersing ability of the synthesized surfactant was studied in laboratory conditions, both in its pure form and in the form of a 5% aqueous solution². The effectiveness of the reagent was assessed by changes in the size of the oil slick on the surface of three types of water (distilled, drinking, sea). For the spill oil was used from the Balakhani field (Caspian Sea). This synthesized product effectively removes a thin oil film from the water surface.

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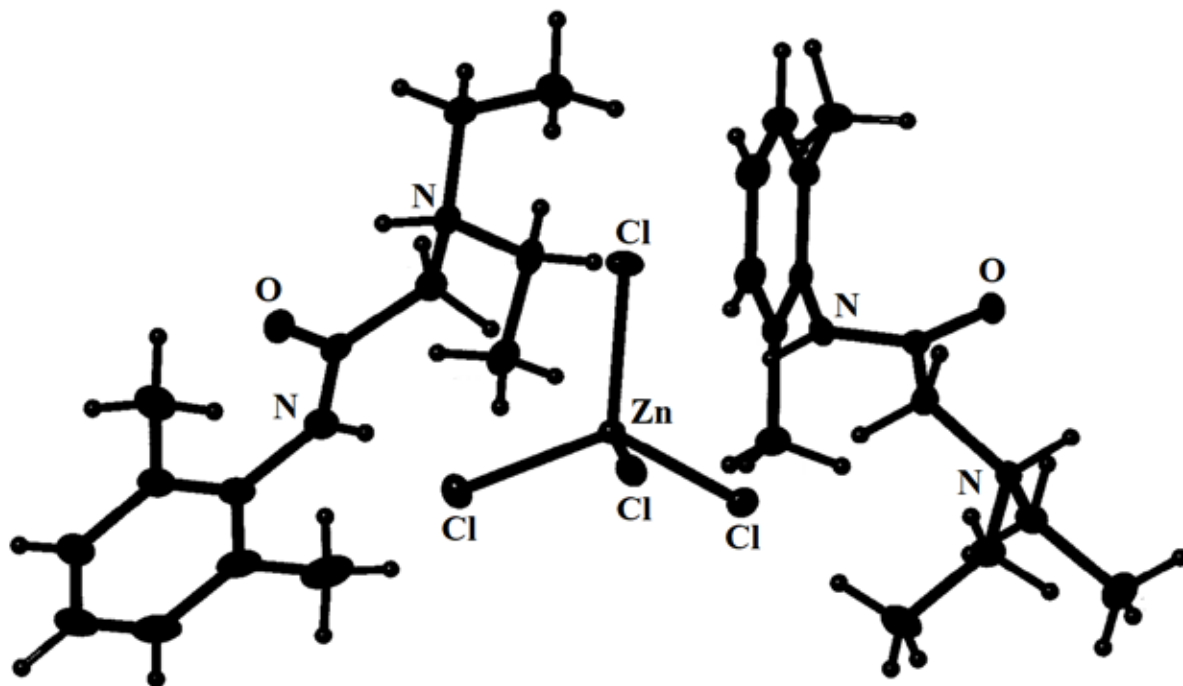
RE-REFINEMENT OF CRYSTAL STRUCTURE OF BIS(LIDOCAINE) TETRACHLORIDOZINCATE(II)

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The structure of the zinc complex of lidocaine (2-(diethylamino)-N-(2,6-dimethylphenyl)acetamide, Lid) has been studied previously^{1,2}, but the analysis was performed at low resolution¹ and protonation of the amine nitrogen atom was not taken into account². We have established that the complex crystallizes in the monoclinic space group $P2_1/c$ with $a=8.8921(2)$, $b=19.2650(3)$, $c=19.3211(3)$ Å, $\beta=95.026(2)^\circ$, and consists of slightly distorted tetrahedral anion $[ZnCl_4]^{2-}$ and two protonated cations of lidocaine $LidH^+$ in an outer coordination sphere.



H-bonds combine neighbouring complexes in pairs $2 \{(LidH)_2[ZnCl_4]\}$, while four adjacent pairs form endless layers parallel to the *ac* crystallographic plane and lying at a distance of 9.6325(3) Å from each other.

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PHYSICO-CHEMICAL PROPERTIES OF REPELLENT COMPOSITES

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Protection against blood-sucking insects is a crucial concern in developing new repellents. However, repellents can have drawbacks, particularly when applied to the skin. Certain ingredients in the formulation of products can cause skin irritation or allergic reactions, making some people sensitive to them.

The product will be based on controlled release of the repellent, using accumulated knowledge on the behavioural reactions of flying bloodsucking insects. The aim of this study is to develop a composite material with repellent action and to study its physicochemical properties.

A composite material was created using carbon nanotubes, dimethyl sulfoxide, hydroxyethyl cellulose, and repellent DEET with an active ingredient content ranging from 6 to 30 wt%. The study involved applying static stress to the material, which was applied to the substrate as a thin film, to investigate the diffusion of the repellent from the surface. The study found that the repellent diffused into the air at varying rates when the material was subjected to a voltage of 3 to 5V. The concentration of DEET in the air reached more than 2 mg/m³.

These results suggest the potential for using composite materials with controlled release to provide safe outdoor environments and effective protection against blood-sucking flying insects.

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THERMODYNAMIC PROPERTIES OF $\text{SrO-Al}_2\text{O}_3\text{-SiO}_2$ AND $\text{BaO-Al}_2\text{O}_3\text{-SiO}_2$ SYSTEMS AT HIGH TEMPERATURES

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The evaporation processes of $\text{SrO-Al}_2\text{O}_3\text{-SiO}_2$ and $\text{BaO-Al}_2\text{O}_3\text{-SiO}_2$ melts at concentration ranges of SrO and BaO from 90 to 10 mol % and the molar ratio $x(\text{Al}_2\text{O}_3) : x(\text{SiO}_2)$, equal to 3 : 2, 1 : 1 and 1 : 2, have been studied by Knudsen effusion mass spectrometry (KEMS).

The samples were synthesized by solid-phase synthesis from SrCO_3 (BaCO_3), Al_2O_3 and SiO_2 . The identification of the obtained samples was carried out by X-ray phase analysis. It was found that an increase in the heat treatment time from 12 hours to 24 hours at a temperature of 1523 K for most samples does not lead to a significant change in the phase composition. The melting temperatures of synthesized samples in the range 1815-1929 K were determined by high-temperature microscopy.

The qualitative and quantitative composition of the vapor above the studied samples was determined. It is shown that the difference in the volatility of the oxides forming the system leads to the selective evaporation of strontium (barium) and silicon oxides and the accumulation of aluminum oxide in the condensed phase. The application of the KEMS using individual strontium (barium) and silicon oxides as standards loaded into the comparative compartment of the twin effusion cell made it possible to experimentally determination of SrO (BaO) and SiO_2 activities at a temperature of 2073 K in the wide concentration range of compositions. For homogeneous melt regions, the values of aluminum oxide activity were calculated using the Gibbs-Duhem equation. The values of Gibbs energies and excess Gibbs energies are determined. It is established that the studied systems are characterized by a negative deviation from ideal behavior.

The work was performed within the framework of the state assignment for research and Development of the ISC RAS (No. 1023032900385-8-1.4.3) subsidy of the Ministry of Education and Science of the Russian Federation

NANOSTRUCTURED MAGNETIC ZEOLITE COMPOSITES FOR CESIUM- 137 EXTRACTION

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The problem of water pollution with long-lived cesium radionuclides is an urgent environmental problem. The prospect of selective removal of radionuclides is the development of simple and effective technologies based on nanostructured adsorbents. In this regard, the current work was aimed at obtaining nanostructured magnetic zeolite composites with high adsorption characteristics with respect to cesium and strontium ions.

Optimal hydrothermal synthesis conditions were established based on XRD, SEM-EDX, N₂ adsorption-desorption, VSM, and batch adsorption experimental data. The role of chemical composition, textural characteristics and surface morphology is shown. Based on modeling of the adsorption isotherm, a monolayer ion exchange mechanism is proposed. The highest Langmuir adsorption capacity of 229.6 mg/g for cesium ions was achieved in the composite obtained by hydrothermal treatment at 90 °C. The sorption characteristics of this material in relation to the ¹³⁷Cs radionuclide are superior to sorption materials of a similar type (NaA and clinoptilolite) only in sea water, where the (K_d) value for cesium can reach 1.7×10^3 ml/g, which indicates the prospects of their use for sea water purification from radioactive cesium.

It has been shown that the magnetic characteristics of zeolite composites make it possible to separate spent adsorbents from aqueous solutions using a magnet.

The work was carried out with the financial support of the Russian Science Foundation, project 23-73-01160.

PICKERING EMULSIONS STABILIZED BY TiO_2 NANOPARTICLES

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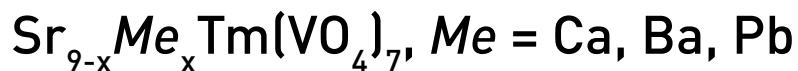
Particle-stabilized emulsions (Pickering emulsions) are of great interest in various industrial fields due to their high stability. In such emulsions particles can be not only stabilizers but also perform other useful functions. Due to their high sunscreen properties, TiO_2 nanoparticles are a promising stabilizer for Pickering emulsions. However, the main problem in using hydrophilic metal oxide nanoparticles as stabilizers is the lack of their interaction with the oil phase. To solve this problem, we developed Pickering emulsions in which the nanoparticles form hydrogen bonds with oil molecules.

TiO_2 hydrosols were synthesized by sol-gel method. Titanium butoxide was dissolved in isopropyl alcohol and added to boiling distilled water. The resulting amorphous precipitate was filtered under vacuum and washed. The washed precipitate was dispersed in 0.1 M aqueous nitric acid solution, heated to 100 °C and cooled until an opalescent hydrosol was obtained. To obtain Pickering emulsions, equal volumes of the hydrosol and a mixture of capric and caprylic triglycerides were mixed and sonicated.

The morphology, size and phase composition of the nanoparticles were characterized using transmission electron microscopy. The chemical state of the nanoparticle surface was studied using X-ray photoelectron spectroscopy. The ability to stabilize Pickering emulsions was studied based on the initial hydrosols. It was found that the high concentration of hydroxyl groups on the surface of the synthesized TiO_2 nanoparticles, allows them to interact with the carbonyl groups of triglyceride molecules, forming Pickering emulsions. The high sun protection properties of the obtained Pickering emulsions were demonstrated by encapsulating α -lipoic acid. The obtained results open new possibilities for obtaining cosmetic products with high sun protection properties.

The work was performed with the financial support of the RSF, project 20-19-00120-?

FERROELECTRIC AND NONLINEAR OPTICAL PROPERTIES



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The modern research for new materials often involves combining multiple functional properties into a single compound. Compounds based on calcium vanadate – $\text{Ca}_3(\text{VO}_4)_2$, due to their unique crystal-chemical structure, have become promising candidates for such researches. A comprehensive study of various complex calcium vanadates led researchers to a group of structurally similar complex strontium vanadates, which exhibit a range of enhanced functional properties. $\text{Sr}_9\text{Tm}(\text{VO}_4)_7$ is one representative of this group.

This study used high-temperature solid-phase synthesis to obtain solid solutions with the compositions $\text{Sr}_{9-x}\text{Me}_x\text{Tm}(\text{VO}_4)_7$, where $\text{Me} = \text{Ca}, \text{Ba}, \text{Pb}$. The samples were analyzed using the powder X-ray diffraction and second-harmonic generation (SHG) at room temperature. Single-phase samples underwent further analysis, including refinement of the unit cell parameters and dielectric spectroscopy on ceramic samples.

The results showed that the samples crystallize in the noncentrosymmetric space group $R3c$ and are isostructural to whitlockite mineral. The SHG signal value increases with the addition of Ca^{2+} and Pb^{2+} cations in the series of solid solutions, but it remains virtually unchanged when strontium is replaced with barium.

For the first time, the temperatures of ferroelectric phase transitions with a change in symmetry ($R3c \leftrightarrow R\bar{3}c$) were determined. The transition temperature depends on both the amount of substituting cation and its effective radius. As the content of Ca^{2+} cations increases, the phase transition temperature also increases, whereas replacing with Pb^{2+} decreases the temperature.

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SYNTHESIS OF THIN NANOCRYSTALLINE FILMS BY OXIDATIVE PYROLYSIS

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Thin films based on metal oxides are promising materials for the development of highly sensitive sensors, electronics, catalysis and other industries. Progress in the field of nanomaterial creating depends on the development of technologies for their production.

This study proposes a new method for the synthesis of metaloxide nanocrystalline film materials by oxidative pyrolysis, which consists of obtaining intermediate products, salts of organic metal acids, applying solutions of these salts to substrates and calcination at relatively low temperatures of 500-600 °C to obtain the target phase of the film nanomaterial¹. This makes it possible to form continuous homogeneous thin films consisting of nanocrystallites on various substrates (glass, silicon, polycor, etc.) by a simple chemical method using available equipment.

Inorganic nanomaterials thermally unstable at higher temperatures, such as multiferroic bismuth ferrite with perovskite structure used in spintronics, photonics and other applications, can be synthesized by the proposed method. Oxidative pyrolysis can also produce semiconducting oxides of p- and d-metals², their composites³, doped bismuth orthoferrite, spinel ferrites⁴ and other promising inorganic compounds with various properties.

The method allows to obtain homogeneous, optically transparent films of metal oxides with a thickness of 30-200 nm. The chemical and phase composition, morphology, crystallite size, thickness and, consequently, functional properties of the films are controlled by the synthesis conditions.

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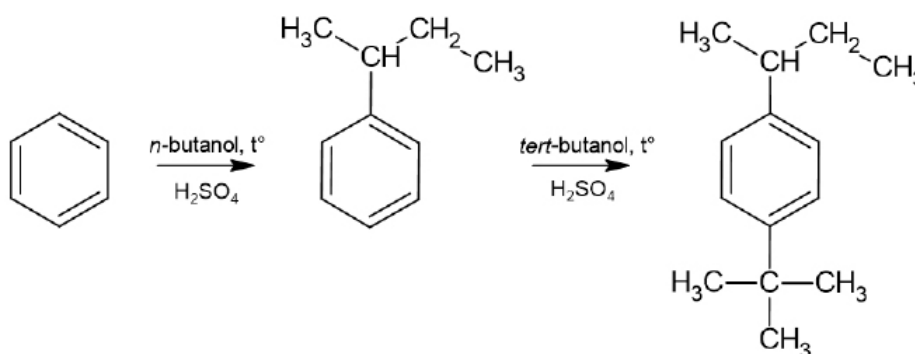
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SYNTHESIS OF *para-tert*-BUTYL-*sec*-BUTYLBENZENE

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Alkylation of aromatic hydrocarbons is one of the main synthetic methods for the preparation of alkylaromatic compounds, these processes are of great importance in organic synthesis¹. Such compounds can be used as starting materials for the hydroperoxide method for the preparation of phenols and ketones of various structures². Due to this, we investigated the regularities of the alkylation reactions of benzene and its derivatives for the preparation of *para-tert*-butyl-*sec*-butylbenzene (PTBSBB).



Scheme 1. Synthesis of *para-tert*-butyl-*sec*-butylbenzene.

PTBSBB can be obtained by alkylation of *sec*-butylbenzene (SBB) with *tert*-butanol or by alkylation of *tert*-butylbenzene (TBB) with butanol. The synthesis method based on SBB was found to be the most efficient as it is an easier to obtain precursor compared to TBB. The reaction of benzene with *tert*-butanol proceeds with the formation of double substitution by-products, and decreasing the amount of *tert*-butyl alcohol in the reaction mixture limits the yield of the target substance. The yield of PTBSBB on alkylation of SBB with *tert*-butanol was 75 %.

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REACTION SYNTHESIS OF MINERAL-LIKE SrTiO_3 CERAMICS FOR IMMOBILISATION OF ^{90}Sr WITH ADDITIONAL IN-SITU SYNCHROTRON STUDIES

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This work presents a spark plasma spark reaction synthesis (SPS-RS) of mineral-like ceramics based on SrTiO_3 with perovskite structure promising for immobilisation of Sr-90 radionuclides. A detailed study of phase transformations occurring in the reaction mixture (SrCO_3 and TiO_2) in the temperature range of 20-1000 °C was carried out using in-situ heated synchrotron X-ray radiography and TGA. The dependence of structure and composition on consolidation temperature was revealed using SEM and EDX. The optimal temperature conditions for the rapid formation of SrTiO_3 ceramics with density of 4.49 g/cm³, Vickers hardness up to 6.2 GPa, compressive strength of 279 MPa and strontium leaching rate of 10⁻⁵-10⁻⁶ g/cm²·day were determined.

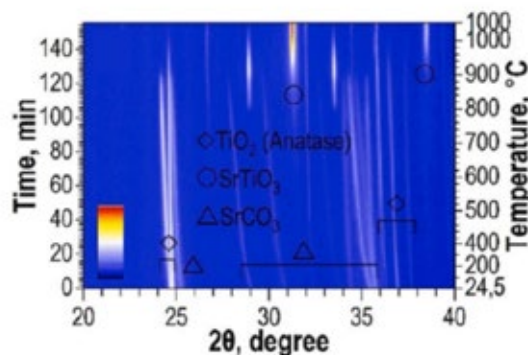


Figure 1: Time-resolved synchrotron X-ray radiography of the in-situ interaction in the reaction mixture (SrCO_3 - TiO_2) occurring in air.

The research was financially supported under the State Assignment of the Ministry of Science and Higher Education of the Russian Federation, topic No. FZNS-2023-0003

PHYSICAL AND ELASTIC PROPERTIES OF CERAMICS “IDEAL”

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The unique properties of diamond composite ceramics make it an attractive material for use in a variety of industries. Diamond-silicon carbide composite has high hardness, strength and wear resistance, making it an ideal material for the production of cutting tools, drill bits, abrasives and other products. In addition, due to its high thermal conductivity, diamond composite can be used at high temperatures. Research in the field of composite diamond ceramics is aimed at further expanding its application and creating materials with even more improved mechanical properties. Advances in this field may lead to the development of new advanced materials for various technological and industrial applications. Poisson’s ratio is one of the important parameters characterizing the mechanical properties of materials. In Ideal diamond-silicon carbide composite ceramics, Poisson’s ratio can play a key role in determining its behavior under mechanical loads.

The conducted study of the properties of Ideal ceramics included the determination of Poisson’s ratio (ν), Young’s modulus (E) and sound speed (Table 1). It has been established that the Poisson’s ratio of Ideal ceramics is close to zero, which indicates its brittle behavior under loading. The resulting value of Poisson’s ratio is significantly lower than that of crystalline diamond, which makes Ideal ceramics an exceptionally brittle material.

Table 1. Physical and elastic properties, as well as wave distribution velocities in “Ideal” ceramics

Sample No.	Density ρ , kg/m ³	Speed of sound, m/s		ν	E , GPa
		Longitudinal (C_l)	Transverse (C_t)		
1	3367	14967	10533	0,01	754
2	3367	15034	10572	0,011	760
3	3368	15108	10639	0,009	768

The work was supported by a grant from the Russian Science Foundation, project 21-73-30019.

POLYCARBOSILANES AND METALLOCARBOSILANES – BINDERS FOR SiC-CEREMICS

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Silicon carbide (SiC) is widely used in diverse fields due to its unique properties¹.

In our work samples of silicon carbide ceramics were prepared by high-temperature sintering at a firing temperature of 1900 °C in an argon atmosphere.

Samples for sintering were prepared by semi-dry cold molding on a hydraulic press from green silicon carbide micropowders and binders based on toluene solutions of polycarbosilane (PCS) and metallopolycarbosilanes (MPCS: AlYPCS, HfTaPCS, ZrTaPCS)^{2,3} (40–50 wt % concentration), providing plasticity and mold ability to ceramic mixture. The samples were cured in air for 12 hours at ambient temperature. After high-temperature sintering, ceramic samples were fired in air at 1500 °C.

The thermal conductivity of the obtained samples (Fig. 1) was studied by the laser flash method in a nitrogen atmosphere in the temperature range from ambient temperature to 500 °C. The results of the study showed that the thermal conductivity of the obtained samples decreases with increasing temperature.

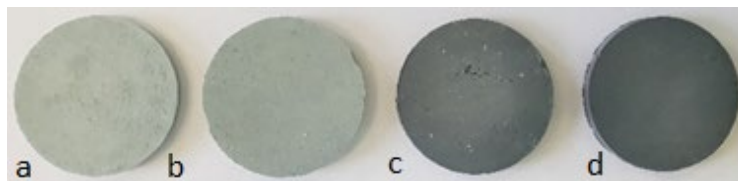


Figure 1. Samples of the prepared binder-based ceramic material: a – PCS; b – AlYPCS; c – HfTaPCS; d – ZrTaPCS

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INFLUENCE OF RUBBER WASTE PYROLYSIS TEMPERATURE ON THEIR PHYSICAL AND CHEMICAL PROPERTIES

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Research the influence of rubber waste pyrolysis conditions on the composition and properties of liquid pyrolysis products is an urgent research task. Pyrolysis of tire rubber was carried out in a screw-type reactor in a nitrogen flow at temperatures 450-550°C. The optimal temperature of pyrolysis is 500°C. The following indicators were determined: density, kinematic viscosity, refractive index, average molecular weight, carbon, hydrogen, sulfur content, aromatic hydrocarbon content, iodine and acid numbers, calorific value, flash point. The characteristics of liquid products of rubber pyrolysis are compared with the properties of commercial petroleum products: motor gasoline, diesel fuel, marine fuels and heating oil.

Liquid products of tire pyrolysis are a mixture of hydrocarbons of various classes that boil over a wide range of temperatures, and therefore they can be considered as a synthetic analogue of fuel. Compared to natural fuel, they are characterized by a higher content of olefins, dienes and aromatics. Pyro-gasoline does not correspond density, mass fraction of sulfur, content of olefinic hydrocarbons and benzene, their values are higher than the standard values to the requirements of motor gasoline (GOST R 51105-97). Diesel fractions isolated from pyrolysates in terms of density and sulfur content exceed the values established by GOST 32511-2013 for petroleum diesel fuels, while the kinematic viscosity of the resulting products is lower than its standard value. At the same time, the distillation residue of liquid pyrolysis products (fuel oil) in terms of density, viscosity, sulfur content, heat of combustion and flash point can be classified as certain grades of marine residual fuels according to GOST 32510-2013 or heating oil grade 100 according to GOST 10585-2013.

Hydrotreating of liquid pyrolysis products on Pt- and Ni/Mo-based catalysts was carried out. It was found out, that pyrolysis oil can be hydropurified together with fuel and petroleum products using Ni/Mo catalyst.

MODIFICATION OF CONTRAST AGENTS BASED ON SILICA NANOPARTICLES TO INCREASE THEIR CONTRAST AND BIOCOMPATIBILITY

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Magnetic resonance imaging contrast agents based on manganese(II) ions are currently being developed to replace existing gadolinium(III) ion-based contrast agents. Manganese(II) ions-doped silica nanoparticles are potential contrast agents due to their relatively high relaxivity values. The accuracy of magnetic resonance imaging results can be increased by using a dual contrast agent, which allows to achieve noticeable contrast simultaneously on T_1 - and T_2 -weighted images. The possibility of obtaining double contrast agents by simultaneously introducing iron oxide nanoparticles and manganese(II) ions into silica nanoparticles is being considered. Silica nanoparticles are not completely biosafe, because silanol groups present on their surface can disrupt the chirality of proteins and hazard cell membranes. It is known that high surface activity of naked silica nanoparticles results in their high hemolytic activity leading to damage of red blood cells. Synthetic approaches to covalent and non-covalent modification of the silica surface to increase their hemocompatibility are considered. The conditions for the adsorption of denatured bovine serum albumin protein on the surface of silica nanoparticles are also discussed in detail. The influence of silica surface modification on the magnetic relaxation properties and cytotoxicity of manganese(II) ions-doped silica nanoparticles is estimated.

The work was supported by the Russian Science Foundation, project №22-13-00010.

PROTECTIVE DIFFUSION ALUMINIDE COATINGS FOR TITANIUM AND ITS ALLOYS

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One of the most promising functional coatings with a high level of heat resistance, creep resistance and thermal stability are coatings based on titanium aluminides. The main methods for obtaining such coatings on the surface of titanium and its alloys are spraying technologies, SHS, and various deposition options. The main disadvantages of these methods include high energy intensity, complexity of technological equipment, limited possibilities for shaping and technological processing of the finished product.

In this work, a combined method is proposed, including explosive welding and heat treatment, as well as hot-dip aluminizing. Its advantages are that it allows, at the design stage:

- assign the required thicknesses of layers of initial dissimilar metals and alloys, obtain high-quality explosively welded workpieces, which, if necessary, are subjected to shaping operations;
- assign heat treatment modes that ensure, as a result of the occurrence of homogeneous (solid-solid state) and heterogeneous (solid-melt state) reactions at the interlayer boundaries of the resulting flat and curved workpieces, the formation of coatings of a given thickness, phase and chemical composition with the calculated ratio of matrix and intermetallic components of the structure.

The developed technology made it possible to obtain coatings with a thickness of 150-300 μm based on the TiAl_3 intermetallic compound, which have high hardness ($\sim 4.2\text{-}6.8$ GPa), low density (~ 3500 kg/m^3) and high aluminum content (~ 63 wt.%), protecting the substrate from high-temperature (up to 900°C) corrosion and wear, as well as to realize high adhesion strength to the titanium base (at the level of titanium properties) and bring the shape of the resulting semi-finished product as close as possible to the shape of the finished product.

This work was supported by the Russian Science Foundation, project no. 24-29-00231.

RELAXATION PROCESSES IN ORGANOPLASTICS BASED ON PARAARAMIDE FIBERS

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Polymer composite materials based on aramid fibers (organoplastics) have a unique set of mechanical characteristics¹. The study of temperature changes in mechanical characteristics makes it possible to find optimal solutions for realization of the greatest strength of fiber in the composite material.

In this paper the temperature and frequency dependences of complex modulus of organoplasty, elementary paraaramide fibers Rusar-C and polymer binder EDT-10 are studied using the dynamic mechanical analyzer. Some results of experiments at a frequency of 1 Hz are shown in Finger 1.

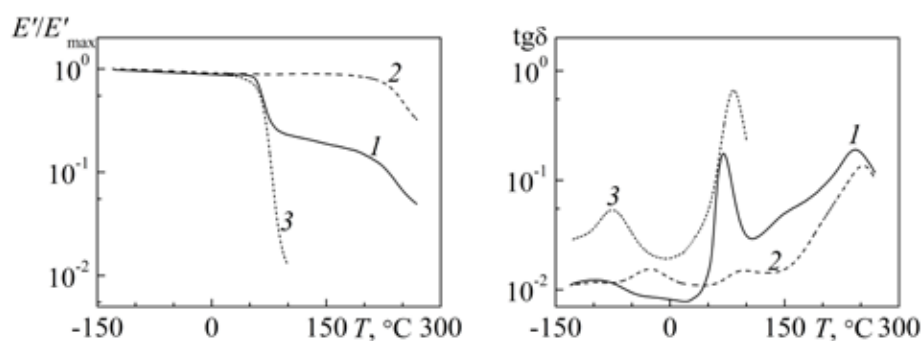


Figure 1. Temperature dependences of the relative values of the storage module (E'/E'_{\max}) and the loss tangent of the phase angle ($\text{tg}\delta$) of samples of organoplasty (1), fiber Rusar-C (2) and binder EDT-10 (3)

Two main relaxation processes are realized in organoplasty, which are registered by the inflections of the dependencies $E'/E'_{\max}(T)$ and maxima of the dependencies $\text{tg}\delta(T)$ at $+70^\circ\text{C}$ and $+243^\circ\text{C}$, which correspond to the glass transition of the polymer binder and fiber. The detected displacements of the maxima of the dependencies $\text{tg}\delta(T)$ organoplasty relative to the maxima of the glass transition of the binder ($+97^\circ\text{C}$) and fiber ($+253^\circ\text{C}$) indicate a change in the segmental mobility of their macrochains. The features of relaxation processes in organoplasty and its constituent components are discussed based on the results of studying the temperature-frequency dependences of the complex modulus.

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HYDROTHERMAL SYNTHESIS OF NANOMATERIALS BASED ON NOBLE AND NON-FERROUS METALS

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The work addresses the issues of synthesis under hydrothermal conditions of nano-sized metal mono- and bimetallic powders (Pd, Pt, Ir, Ni, Ni-Pt) and functional materials with various combinations of noble metals (Pd, Pt, Ir, Pd-Au, Pt-Au, Pd-Pt, Pd-Ir) on carbon supports, such as nanotubes, sibunit, mesoporous carbon materials. Today, it is relevant to develop methods for producing metallic and functional materials without the use of stabilizing additives, which, when adsorbed on the surface, can have a negative effect, for example, on catalytic properties. Carrying out the synthesis of materials using closed systems (autoclaves) is very important both from the point of view of environmental aspects and for economic reasons: high energy efficiency and stoichiometric consumption of reagents, ease of standardization of conditions and the possibility of scaling processes [1-3]. The properties and application of materials significantly depend on the size, shape, and composition of particles, which can be smoothly varied during hydrothermal synthesis. For example, under hydrothermal conditions, depending on the experimental conditions, iridium powders with particle sizes from 8 to 200 nm and a specific surface area of up to 25 m²/g have been synthesized. A method has been proposed for uniformly depositing Ir nanoparticles with sizes of 5-8 nm onto carbon supports. Positive catalytic effects of materials in the processes of anodic oxidation of water were discovered.

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HYDROTHERMAL SYNTHESIS OF NEW LAYERED SULPHIDE-HYDROXIDE 2D MATERIALS

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The work considers the issues of obtaining monophase two-dimensional layered 2D materials, analogues of natural minerals of the vallerite group $\text{CuFeS}_2 \cdot 1.53[(\text{Mg,Al})(\text{OH})_2]$, which have unique physicochemical properties [1]. Such materials are formed by alternating 2D layers of metal sulfides and magnesium and aluminum hydroxides. The formation of a number of phases under hydrothermal conditions at temperatures from 120°C in a wide range of Fe:Cu:Mg:Al:S molar ratios has been studied. The hydrothermal treatment time varied from 1 to 120 hours. The samples were characterized by X-ray phase analysis, scanning and transmission electron microscopy with X-ray spectral microanalysis, X-ray photoelectron spectroscopy, and X-ray absorption methods. Optimal conditions for the production of a number of monophase materials have been determined and it has been established that the sulfide layers in them are similar to nukundamite and mackinowite. A key factor, along with the temperature and duration of hydrothermal treatment, is the introduction of excess S^{2-} . It has been established that the formation of the vallerite phase proceeds through the stage of formation of intermediate products: erdite ($\text{NaFeS}_2 \cdot 2\text{H}_2\text{O}$), haycockite ($\text{Cu}_4\text{Fe}_5\text{S}_8$) and chalcocite (CuFeS_2). The introduction of Al^{3+} impedes the Fe^{3+} transfer from sulfide layers into hydroxide ones, which paves the way for control over the structure of materials and their final properties. The possibilities of modifying materials with lanthanides and 3d metals, which, depending on conditions, can be incorporated into sulfide and/or hydroxide layers, have been shown [2]. For the first time, a new sulfide-hydroxide monophase material with chalcocite-like sulfide layers was synthesized and characterized.

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DEVELOPMENT OF HIGH-FLAMMABLE GLASS PLASTICS BASED ON EPOXY OLIGOMERS MODIFIED WITH COPPER PHOSPHATES

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Polymer composite materials based on epoxy resins are widely used, but have the disadvantage of flammability. One of the ways to reduce it is to modify the polymer matrix with metallophosphate particles synthesized in situ. In particular, there is information in the literature about the ability of copper metal to inhibit radical processes in the condensed phase. The goal of the work is to develop binder formulations for creating low-flammability fiberglass plastics based on epoxy oligomers modified with copper phosphates.

Solutions of copper hydrogen phosphate in phosphoric acid in the concentration range from 0.25 to 2.0% wt were used as a modifier. The modifier content varied from 0.25 to 8.0% wt. in relation to the binder, including epoxy resin ED-20 and triethylenetetramine. It has been established that the modifier under study reduces the level of physical and mechanical characteristics, probably due to the formation of developed structures during curing, which we identified using optical and scanning electron microscopy. The best values are characterized by samples containing 1.5% wt. modifier - the breaking stress and modulus of elasticity during static bending reach 89.2 MPa and 3.9 GPa, respectively. The oxygen index value does not exceed 25.1% vol.

For a more significant reduction in flammability, it is necessary to increase the content of the modifier, which was achieved by using it as a hardener without triethylenetetramine. The resulting material is characterized by oxygen index values of up to 33.6% vol. Its combustion was accompanied by a high intumescent effect: the swelling coefficient exceeds 85. The level of physical and mechanical characteristics of this series of samples is significantly higher, the breaking stress and elastic modulus during static bending reach 120 MPa and 4.2 GPa, respectively.

The developed binders can be used as CMC or BMC pastes to produce polymer composite materials, for example, by direct pressing.

The work was carried out with funding from the Russian Ministry of Education and Science within the framework of the State Budget FZUS-2024-0001.

ENCAPSULATION OF TEA POLYPHENOLS INTO MELAMINE BARBITURATE SUPRAMOLECULAR ASSEMBLY

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Polyphenols^[1] contained in green tea, such as epicatechins and gallic acid derivatives, are interesting as antioxidants and anticancer drugs. However, there is still a problem in isolating water-soluble polyphenols from tea extracts.

To improve the stability and bioavailability of polyphenols, methods can be used to encapsulate them in supramolecular assemblies that are able to control release depending on conditions (pH, temperature). For example, melamine barbiturate (Mel-BA), whose structure is based on hydrogen bonds.^[2]

The study created and studied assemblies of melamine barbiturate with green tea extract (Mel-BA-GT). This material was studied by X-ray phase analysis, IR spectroscopy, EPR, DSC, SEM and fluorescence microscopy.

The probability of hydrogen bonding between polyphenols, melamine and barbituric acid was estimated using quantum chemical calculations (B3LYP). The amount of encapsulated polyphenols and antioxidant activity were assessed by DPPH test of green tea extract before and after encapsulation. The particles were also modified with hexachloroplatinic acid and, as a result of platinum adsorption, microswimmers were obtained, which can be used as a polyphenol delivery system.

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INFLUENCE OF THE TOPOLOGICAL STRUCTURE OF CRYSTAL SUBSTANCES ON THEIR MECHANICAL PROPERTIES

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The study of the ‘structure-property’ relationships of crystalline substances and materials is one of the main tasks of modern materials science. The objects of research in works in this area are diverse: starting from simple structures such as carbon allotropes, ending with complex compounds with potential applications in industry, for example, metal-organic frameworks¹ (MOFs). An important stage of the research is the prediction of new substances and materials using various mathematical models.

We propose a new approach to the generation of novel crystal phases using the model of “natural tiling” – the division of crystal space into minimal cavities containing neither atoms nor bonds – tiles, inside which the processes of transformation of the structure of matter are carried out. Using this approach in the *ToposPro* program package (<https://topospro.com>), we modeled 72 new carbon allotropes, four of which, according to DFT calculations, have a Vickers hardness close to diamond (94.6-95.0 GPa). It was found that three of them are characterized by a similar topological structure of tilings, and the fourth allotrope contains void types of diamond and lonsdaleite structures, and is an intermediate structure on the path of their solid-phase transformation into each other.

We have created a collection of topological types of cavities (tiles) most commonly found in MOFs (more than 60 types of tiles) and carbon allotropes (more than 40 types of tiles), and found correlations between the type of tiles and the mechanical properties of crystal structures. These data were used to extend the *Topological Types of Tiles* database (TTT collection), which is located on the TopCryst Internet resource (<https://topcryst.com>), and the SACADA carbon allotrope database that we are developing at <https://www.sacada.info>.

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SYNTHESIS OF MIXED OXIDE NANOPARTICLES IN PLASMA DISCHARGE UNDER ULTRASONIC TREATMENT

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In this work, mixed metal oxide nanoparticles were synthesized in a plasma discharge under the influence of ultrasonic cavitation. Brass and bronze wires were used as discharge electrodes, and thus nanoparticles of copper and zinc oxides, as well as copper and tin oxides, were synthesized.

Ultrasonic influence on a liquid-phase medium in the mode of developed cavitation affects the conditions of electrical breakdown between the discharge electrodes in the reaction chamber due to the fact that cavitation bubbles in the electric field are able to line up in chains, thus changing the medium from liquid-phase to vapor-liquid, and in this case, the discharge itself has a falling current-voltage characteristic, similar to the current-voltage characteristic of an anomalous glow discharge in a gas.

Typical discharge parameters during the synthesis of nanoparticles are the following: DC voltage 50-70 V, current 4-5 A. Such parameters were chosen, on the one hand, based on the need to ensure the maintenance of a stable discharge, and on the other hand, to create reproducible conditions for synthesis of solid-phase nanoparticles.

Nanoparticles of copper and tin oxides, as well as copper and zinc oxides in the form of an aqueous suspension, synthesized in a plasma discharge under the influence of ultrasound, were studied by the method of dynamic light scattering and it was shown that the synthesized particles have a distribution peak in the size range of 50-60 nm, with intensive ultrasonic cavitation during the synthesis process, the distribution peak shifts to the region of 30-40 nm. Measuring the electrokinetic potential of the surface of the initial nanoparticles in an aqueous dispersion medium made it possible to establish that, under the influence of ultrasound, particles of mixed metal oxides acquire additional active adsorption sites capable of interacting with the functional groups of the polymer matrix.

The work was carried out with the financial support of the RSF, project No. 24-19-00161.

IRON OXIDE NANOPARTICLES WITH A WIDE SIZE DISTRIBUTION OBTAINED BY ELECTROPHYSICAL METHODS: PROSPECTS FOR BIOAPPLICATIONS

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Electrophysical methods of electric explosion of the wire (EEW) and laser target evaporation allow to obtain the large quantities of magnetic nanoparticles (MNPs) of iron oxides, which are widely requested for biological applications. In addition to high productivity and large batch size, these methods make it possible to vary the dispersion parameters of MNPs batches by selecting different technological conditions. The shape of the EEW and LIM MNPs is very close to being spherical.

Biocompatible iron oxide MNPs can be fabricated by different techniques, which provide both a larger or smaller MNP batch size and a certain average size range. Biological applications require the production of stabilized aqueous suspensions of MNPs. Typically, researches make the efforts in order to obtain batches of MNPs with a very narrow size distribution for further suspension synthesis using electrostatic, steric, or combined stabilizations. In this work, we used a batch (above 30 g) of iron oxide MNPs with a wide size distribution from 4 nm to 180 nm, with an average size of about 21 nm, synthesized by the electrophysical EEW method. Based on the same batch, two aqueous suspensions were obtained using different synthesis techniques and the electrostatic way of stabilization with the additions of the natural stabilizer, sodium citrate. In the first case, a standard technique based on ultrasonic treatment was used. In the second case, the suspension was obtained by co-grinding of 5 g of the iron oxide MNPs for 1 hour in an aqueous medium with the addition of Na₃C₆H₅O₇ in a ball mill. Next, the resulting suspensions underwent a standard characterization procedure and were used for comparative analysis in biological experiments with a culture of human bone marrow mesenchymal stromal cells grown as a monolayer either without or in the presence of MNPs at their selected concentrations in the nutrient medium.

The work was carried out with financial support from the Priority 2030 Program.

A METHOD FOR PROCESSING THE SPENT MELT OF TITANIUM CHLORINATORS

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Chlorination of titanium slag at “AVISMA” LLC is carried out in a melt chlorinator by passing of anodic chlorine gas through a NaCl melt, into which titanium slag and anthracite are continuously dosed. As impurities accumulate, the melt is periodically drained into a hydraulic removal bath, into which water is continuously supplied at the rate of $10 \pm 2 \text{ m}^3$ per 1 ton of melt. The resulting pulp is sent to a hydraulic pond, where a coarse part of the insoluble residue is deposited. Acidic effluents are sent to acidic sewers, and the water-insoluble residue is disposed to a landfill of production and consumption waste. At the same time, irretrievable losses of titanium dioxide (about 7%) significantly reduce the technical and economic indexes of production. Repeated use of this residue as an integral part of the charge for chlorination is unacceptable due to the high residual acidity $\text{pH} = 3-4$.

Table.1 Chemical composition of chlorinated slag

TiO_2	Al_2O_3	SiO_2	Fe_2O_3	Cr_2O_3	Others
87,58	5,87	3,23	0,83	0,67	1,82

To neutralize the insoluble residue, it is proposed to wash additionally with lime milk with CaO mass concentration at least 100 g/dm^3 on a washing tray installed under the discharge hopper of the water-insoluble residue from the hydraulic pond of the titanium chlorinator. This makes it possible to neutralize the insoluble residue to a $\text{pH} \approx 12$, reduce the content of metal oxides such as zirconium, manganese, chromium, vanadium, silicon, aluminum, which will allow it to be converted into an environmentally safe product suitable for the long-term storage in an open area and further washing with natural precipitations to a neutral pH value. At the same time, the content of titanium dioxide does not change.

COMBINED TECHNOLOGIES FOR PRODUCING WEAR-RESISTANT MAO-COATINGS

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One of the promising technologies for hardening surfaces is microarc oxidation (MAO), which makes it possible to form coatings with high physical and mechanical properties. Using the MAO method, it is possible to strengthen the surface of valve group metals, but most machine parts are made of steel of various grades, therefore, for wider practical use of MAO, a combined method is used, which includes aluminizing the substrate using cold gas dynamic spraying (CGDS) followed by strengthening using the MAO method. New promising methods have been proposed to increase the wear resistance of MAO coatings by creating a precursor CGDN layer on a metal base (Fig. 1).

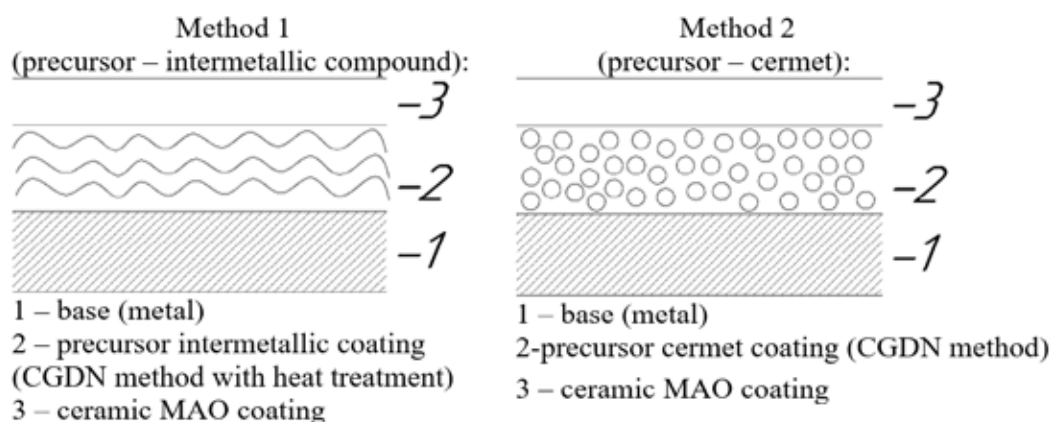


Figure 1. Technological methods for forming precursor layers

It has been experimentally shown that an MAO coating can be strengthened with ceramic particles (using SiC as an example) not only through an aqueous electrolyte solution, but also through the formation of a precursor CGDN layer. It has been established that the introduction of 5–10% wt. SiC in MAO coating leads to an increase in the wear resistance of the aluminum surface by 3.4 times.

A method for producing a functional-gradient coating to protect metals from high-temperature influences, in which the precursor layer undergoes a transition into a strengthening intermetallic compound, is also proposed. To form an intermetallic structure, a mixture of Al and Ni powders was sprayed gradiently, then an Al layer, which was strengthened by MAO. After this, during heat treatment, the remaining Al is converted with the previous Ni layer into intermetallic compounds, which makes it possible to increase the wear resistance of the aluminum surface by 3.8.

The work was supported by a grant from the Russian Science Foundation, project 21-73-30019.

BUILDING A DIGITAL TWIN OF AN ICP-CVD PROCESS

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Next generation nanoelectronics requires development of new thermally and mechanically stable materials with relative permittivity (k) as close to 1 as possible. In June 2020, Hong et al. presented ICP-CVD-deposited amorphous boron nitride (a-BN) with very low k of 1.78¹. This a-BN also turned out to be thermally, chemically, and mechanically stable, and having high breakdown voltage, thus fulfilling all requirements for practical applications. A three-nanometer thick layer of this material was obtained by low-temperature remote inductively coupled plasma–chemical vapor deposition (ICP-CVD) with borazine as the precursor. Two years later Lin et al. conducted seemingly identical synthesis but obtained a compound with noticeably different properties². When synthesis conditions were identical (based on the information in the article) to those of the Hong experiment, the boron to nitrogen ratio (B:N) was ~ 2.64 , whereas the B:N in the original article films was 1.0. To obtain the same B:N, Lin's team had to explicitly add nitrogen molecules to the gas flow. To understand why supposedly equivalent conditions, lead to different products we have constructed a digital twin of this system to comprehensively reconstruct the ICP-CVD process, encompassing all its intricate details and established the most likely reason for the discrepancy between Hong's and Lin's experiments. Our comprehensive model utilizes an active-learning interatomic potential known as MLIP³ for molecular dynamics simulation. The designed workflow allowed us to establish, that the films morphology heavily depend on the particles reaching the substrate. This approach not only unveils hidden process dependencies but also establishes a versatile framework for computational modeling.

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SYNTHESIS OF PERFLUOROCARBOXYLIC ACIDS TRIMETHYLSYLIL AMIDES FROM THE CORRESPONDING ESTERS

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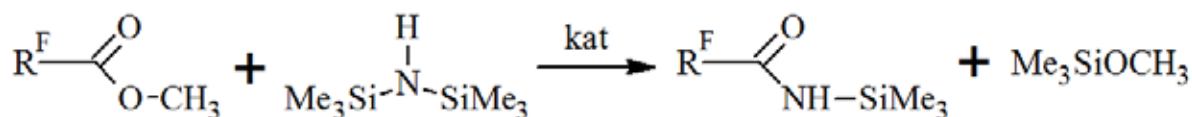
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One of the widely used protecting and functional groups in organic chemistry is trimethylsilyl group (TMS). Its introduction into an organic compounds leads to a decrease in its melting point and increases solubility. For example, trimethylsilyl ethers are easily distilled, which allows them to be analyzed by chromatographic methods.^{1,2}

As a rule, TMS-derivatives can be prepared from the compounds with an active hydrogen atom by treating with trimethylchlorosilane in the presence of a tertiary amine or hexamethyldisilazane.

The conditions for synthesis of trimethylsilylamides from the corresponding methyl esters and hexamethyldisilazane have been found. The reaction is carried out with high yield at temperature of 20 – 60 °C in the presence of catalytic amount of nitrogen Lewis bases according to the scheme:



Trimethylsilyl amides of several perfluorocarboxylic acids have been synthesized and described, including: propionic ($\text{R}^{\text{F}} = -\text{C}_2\text{F}_5$), butyric ($\text{R}^{\text{F}} = -\text{C}_3\text{F}_7$) and enanthic ($\text{R}^{\text{F}} = -\text{C}_6\text{F}_{13}$) as well as some difunctional derivatives of perfluoroadipic ($\text{R}^{\text{F}} = -\text{C}_4\text{F}_8-$) and perfluorosuberic ($\text{R}^{\text{F}} = -\text{C}_6\text{F}_{12}-$) acids. The substances mentioned above may be used for preparing of the corresponding nitriles with high yield.

Structures of prepared trimethylsilylamides were described by ¹⁹F and ¹H spectroscopy.

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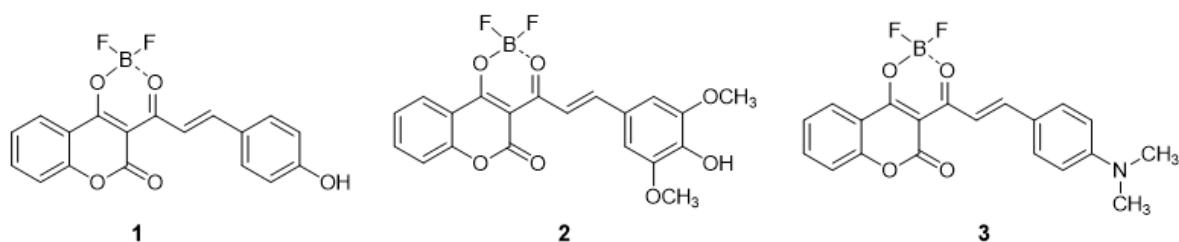
PHOTOPHYSICAL PROPERTIES OF BORDIFLUORIDE COMPLEXES OF COUMARIN DERIVATIVES

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It is known that modulation of the photophysical properties of fluorophores is possible by introducing a difluorinated boron center.¹ This allows the maximum fluorescence absorption and emission wavelengths, solvatochromism, and sensor properties of the fluorophore to be changed.

In our work, the photophysical properties, as well as solvatochromism and anion-sensitive ability of three synthesized boron complexes based on coumarin were assessed.²



The photophysical properties of the complexes were studied in various solvents and in the solid state. It was found that compound **1** in a chloroform solution has the highest fluorescence quantum yield – 33%, while positive solvatochromia in fluorescence absorption and emission was also observed with increasing solvent polarity. In addition, in the presence of various anions, borodifluoride complex **1** changed the color of the solution with subsequent quenching of the fluorescence emission intensity, which, according to the NMR spectra, is associated with deprotonation and the formation of a quinone base.

It should also be noted that all synthesized boron complexes based on coumarin were introduced into polymer matrices. At the same time, was identified the possibility of using these compounds as temperature sensors.

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SYNTHESIS AND RESEARCHING THE PROPERTIES OF BIOCIDAL MATERIALS BASED ON ORGANOSILICON RAW MATERIALS AND PHMG

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Today, an urgent task is to create organic materials with bactericidal properties. For example, silica gel or siloxane polymers are very widely used in everyday life, medicine, cleaning systems, and so on¹. However, such materials lack antibacterial activity.

It is possible to give the material antibacterial properties using chemical modification. One of the most promising bactericidal modifiers are guanidine and its derivatives². Many of them are commercially available, cheap and eco-friendly. For these reasons, the production of organosilicon materials modified with guanidine is a promising direction.

In this work, we have developed two methods for modifying SiO₂ particles with polyhexamethyleneguanidine (PHMG), and also investigated the antibacterial activity of suspensions and a layer of these particles. In the case of suspensions, the bacteria died after some time (depending on the concentration of particles). At a concentration of 5 mg/ml, all colonies died after 2-4 hours. When passing water infected with gram-negative bacteria through a layer of these particles, all bacteria died.

Based on the data obtained, it is possible to judge the possibility of widespread use of the obtained particles in gas, water treatment, etc. Also, these modification techniques can be used not only for particle modification, but also for many other compounds.

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THERMAL AND STRUCTURAL STABILITY OF SOLID SOLUTIONS TiZrHfTa , TiHfNbTa

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The use of multicomponent alloys of complex composition, in which there are no dominant elements, is one of the modern concepts in the design of new materials. Huge interest in high-entropy alloys (HEA) is caused by the prospects of their practical application and the fundamental nature of the problem of structure formation in multicomponent solutions of complex chemical composition.

The presence of elements of different radii and valence causes a distorted crystal structure with a very high density of defects, providing low and practically temperature-independent electrical conductivity . The authors of [1] showed the promise of practical application of a multicomponent metal material based on TiZrHfNb for the creation of sensitive elements of strain gauge transducers operating in extreme conditions.

Alloys TiZrHfTa , TiHfNbTa were prepared in an electric arc furnace from pure metals by direct alloying and annealed at temperatures of 250 °C , 400 °C with holding increments of 10, 25, 50, 100, 200, 400, 800 hours . In the cast state, they form single-phase solid solutions having a cubic crystal structure of the Im-3m type. The microstructure of the alloys has a dendritic grain growth pattern. During heat treatment, relaxation processes occur in these alloys. In the TiZrHfTa alloy , decomposition into two similar phases occurs at 250 °C , and into three at 400 °C. The TiHfNbTa alloy retains its original single-phase structure throughout the entire heat treatment (800 hours) at 250 °C , however, at an annealing temperature of 400 °C, precipitation of the second phase is observed. The studied alloys have a weak temperature dependence of the electrical resistance, as in the case of the previously studied TiZrHfNb HEA [1].

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STRUCTURAL AND MAGNETIC PROPERTIES OF MECHANOACTIVATED OXIDE HoMnO_3

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There is ongoing interest in hexagonal manganites, in which magnetic ordering and ferroelectricity (multiferroics) coexist, due to their potential application as converters and information storage devices [1]. Varying the composition, microstructure, thermal and mechanical processing parameters leads to changes in physical properties and expands the prospects for their application. In this work, nanostructured manganite HoMnO_3 was obtained by mechanical activation (MA), containing, along with the thermodynamically stable hexagonal phase (h - HoMnO_3), a metastable ortho-phase (o - HoMnO_3), for which the crystal structure and magnetic properties were studied.

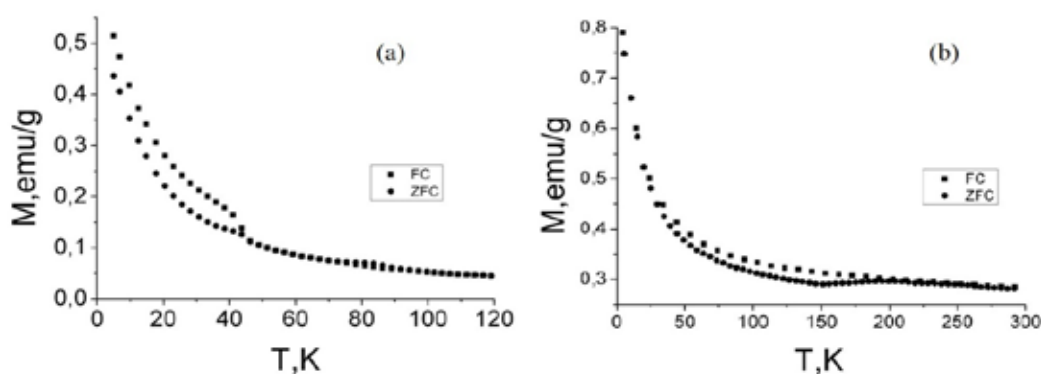


Figure 1. ZFC and FC curves in a magnetic field of 0.01 T for the initial (a) and mechanically activated HoMnO_3 manganite for 60 seconds (b) .

The decrease in temperature T_N (Mn) of the MA sample (60 s) and magnetization M at $H = 2$ T and $T = 5$ K is explained by the increasing influence of the surface of nanoparticles. Anomalies in the temperature dependences $dM(T)/dT$ of MA samples at $T \sim 7, 9, 12, 15$ K are associated with the ordering of holmium ions and spin- reorientation transitions in the Mn sublattice in the h- HoMnO_3 and o- HoMnO_3 phases .

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The work was carried out according to the State assignment of the Institute of Metallurgy and Metallurgy of the Ural Branch of the Russian Academy of Sciences.

CONTROL AND MECHANISM STUDY OF TWO DIMENSIONAL SUBNANO LAYERED SPACE OF NON Pt CARBON BASED OXYGEN REDUCTION CATALYSTS

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Carbon materials have advantages such as rich pore structure, large specific surface area, easy control of surface chemical properties, favorable reduction of metal phases, and low cost [1]. Carbon based carriers not only introduce heteroatom anchoring points to fix metal single atoms, but also have a positive effect on the electrocatalytic process of ORR by doping heteroatoms with carbon. The “spatial confinement” strategy is an effective way to solve the problem of low metal loading and aggregation of metal particles or clusters. The multi-level pore structure can maximize the utilization of active sites, enhance material mass transfer ability, and enhance ORR catalytic activity. Porous carbon materials with different morphologies and pore sizes were prepared

In response to the shortcomings of low exposure of active sites, low utilization of metal atoms, and slow mass transfer rate in electrocatalytic ORR process, starting from the construction and optimization of nanospace confined structures and molecular assembly processes, the guest (short chain quaternary ammonium salts, etc.) and the host (two-dimensional layered materials, etc.) are first subjected to ion exchange, and the interlayer spacing of the two-dimensional confined space is modified and optimized. Targeted construction of rich bimetallic active sites porous structure coupling sites, ultimately achieving *in situ* preparation and optimization of high-performance porous ORR catalysts doped with bimetallic single atom active sites.

The development of this study is expected to obtain efficient and inexpensive porous bimetallic single atom ORR catalysts, which will help deepen the understanding of the active site structure and catalytic laws of catalysts, and provide theoretical and practical basis for the development of new high-performance catalysts and the commercial application of green environmental protection energy systems such as fuel cells and metal air batteries.

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SPECTRAL PROPERTIES OF HYBRID COMPLEXES BASED ON AMMONIUM HEXAVOLPHRAMOMANGANATE AND PHTHALOCYANINES

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Phthalocyanines are macroheterocyclic compounds with a unique and very diverse arsenal of properties¹. Studies on solubilisation of hydrophobic phthalocyanine molecules in aqueous media are currently underway. This work deals with the interaction of phthalocyanines with water-soluble heteropolycompounds (HPCs). The anions of HPC have high hydrophilic properties and have several coordination centres of different types.

In this work, the interaction of zinc phthalocyanine and chlorinated aluminium phthalocyanine with ammonium hexavolphramomanganate $(\text{NH}_4)_4[\text{MnW}_6\text{O}_{18}(\text{OH})_6] \cdot 6\text{H}_2\text{O}$ in aqueous media was comparatively investigated. The formation of hybrid organic-inorganic structures was observed by electron absorption spectroscopy and spectrofluorimetry.

Comparison of spectra of individual compounds and their hybrid structures in a concentration series of solutions, the initial concentration of which is 10^{-6} mol/L, shows that the joint presence of organic and inorganic components in solution leads to the formation of coordination compounds. Experimental data showed that the hybrid complexes have a stoichiometric composition of 1:1 and are characterised by a binding constant of 10^4 - 10^5 L/mol. These values are in agreement with the fluorescence quenching data and the value of the Stern-Folmer constant.

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The work was carried out within the framework of the project "Research on the problems of recycling waste of natural origin for the practical use of the products obtained" (122122600056-9).

SPECTRAL PROPERTIES OF ALUMINIUM PHTHALOCYANINE IMMOBILISED ON SILVER NANOWIRE SUBSTRATES

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Physicochemical properties of phthalocyanines significantly depend on their aggregation form and intermolecular interactions. The most promising properties are possessed by compounds in which phthalocyanine macrocycles are packed in stacks, layers or chains.

The adsorption of phthalocyanine molecules onto a nanostructured surface followed by their aggregation may lead to the formation of new hybrid materials with unusual optical properties. Of particular interest is the determination of the shape of the chromophoric molecules, since the spectral properties of individual molecules and their chains formed as a result of aggregation are different¹. In the present work, a new material based on aluminium phthalocyanine AlOHPc(SO₃H)₄ and silver nanowires has been prepared and characterised.

In this work, phthalocyanine molecules within a hybrid nanomaterial based on silver nanowires differing in thickness were comparatively studied by electron absorption spectroscopy, spectrofluorimetry, and Raman light scattering (including SERS). It was shown that, when the SERS spectrum is excited by low-power and high-power laser radiation, there is a redistribution of intensities, indicating that different vibrational modes are excited.

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The work was carried out within the framework of the project "Research on the problems of recycling waste of natural origin for the practical use of the products obtained" (122122600056-9).

1,8- AND 4,5-DIAZAFLUORENYLIDENE DERIVATIVES: SYNTHESIS AND PHYSICO-CHEMICAL PROPERTIES

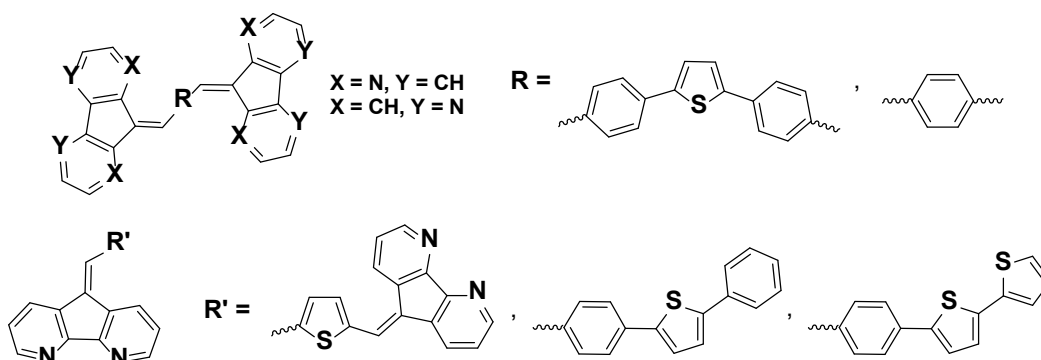
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Fluorenylidene derivatives, such as 2,5-bis((9H-fluoren-9-ylidene)methyl)arylenes, exhibit high conformational mobility, polymorphism, and aggregation-induced emission¹. Such materials are used in light-emitting devices, sensors, bio-imaging, etc.

Replacement of some carbon atoms in the fluorene fragment with more electron-withdrawing nitrogen atoms leads to changings in physico-chemical properties. For example, 4,5-diazafluorenylidene derivatives may have chelating ability, which is necessary for the preparation of coordination compounds based on them². 1,8-Diazafluorenylidene derivatives can form planar structures due to intramolecular non-covalent interactions.

In this work, approaches to the synthesis of 1,8- and 4,5-diazafluorenylidene derivatives shown below have been developed, and their physico-chemical properties have also been studied. It was shown that some of the obtained compounds have aggregation-induced emission. The quantum yield in the crystalline state reaches 10%. Coordination compounds were also obtained based on 4,5-diazafluorenes.



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DEVELOPMENT OF TECHNOLOGY FOR THE PRODUCTION OF A GLASS-CARBON ELECTRODE FOR THE DETERMINATION OF HEAVY METAL IONS BY INVERSION VOLTAMMETRY

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Currently, there is a need to determine the concentration of heavy metals in aqueous solutions in the ranges of 10^{-9} - 10^{-13} in various industries, unfortunately, most methods allowing the quantitative determination of heavy metals in the specified concentration range differ in expensive apparatus¹. The most acceptable method of analysis is based on inversion voltammetry using solid-state electrodes.² The design of the solid-state electrode is shown in figure 1.

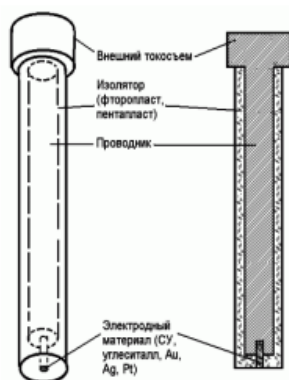


Figure 1. Electrode construction made of solid inert materials

Based on the above, a technology for the production of a glass-carbon electrode for the voltammetric analysis of heavy metals in aqueous solutions was developed, which allows measurements to be carried out in low concentration ranges.

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ULTRA-STABLE NANOFIBER LUMINESCENT COMPOSITE MATERIALS BASED ON POLYTETRAFLUOROETHYLENE AND PEROVSKITE NANOPARTICLES

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Perovskite nanocrystals of the composition CsPbX_3 ($X = \text{Cl, Br, I}$) possess outstanding characteristics, such as high quantum yield and narrow luminescence spectral characteristics, which makes them potentially applicable as LEDs, lasers, solar cells, luminescent solar concentrators, photodetectors, display backlights etc. However, such structures are extremely susceptible to moisture and air atmosphere, their luminescent properties quickly degrade under their influence. Therefore, to preserve their properties, it is advisable to encapsulate these nanoparticles in protective polymer structures for integration with applied light sources. It should be noted that the nanocrystal size (diameter about 5 – 10 nm) provides excellent optical properties, and upon agglomeration their effectiveness is lost, so the encapsulant must maintain a monotonic dispersion of the nanoparticle array. At the same time, a related goal is to develop a simple and convenient method for the synthesis of perovskite nanoparticles, ensuring the formation, in fact, of nano-sized particles and their simultaneous encapsulation.

In this work, luminescent materials based on fluoroplastic and perovskite nanoparticles of the composition CsPbBr_3 were obtained by electrospinning. Solutions of precursors were added into the spinning solution where in situ nanoparticles formation took place. It was found that CsPbBr_3 nanoparticles are effectively encapsulated in nonwoven fibers with a diameter of $0.6 \pm 0.1 \mu\text{m}$. The resistance of the developed material to external factors was demonstrated. Strong and bright luminescence at a wavelength of 508 – 510 nm under excitation with $\lambda_{\text{ex}} = 380 \text{ nm}$ persisted for at least 9 months.

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GENERATION OF SENSOR SIGNAL IN TIN DIOXIDE OBTAINED BY PEROXIDE-ASSISTED SOL-GEL METHOD

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Peroxide-assisted sol-gel method for the synthesis of functional materials makes it possible to obtain nanocrystalline semiconductor oxides with a complex of microstructural parameters optimal for use in gas sensors from solutions of hydroperoxostannates sol particles of p-elements (Sn, Sb, Ge, Te). Using of templates makes it possible to obtain functional materials with a given morphology and unique properties.

In this work, SnO₂ samples with 3D (SnO₂-3D-i) and quasi 2D (SnO₂-2D-i with graphene oxide (GO) as sacrificial template) morphology were obtained by peroxide route, as well as comparison samples by calcination β SnO₂·xH₂O (SnO₂-ref-i). (i – annealing temperature, 300 or 500 °C, time – 24 hours). SnO₂-2D-500 has unique characteristics (CSR, specific surface area). Raman spectroscopy and TPR H₂ methods have been used to establish the presence of oxygen deficiency in SnO₂ samples synthesized at 300 °C without GO. For SnO₂-2D-300, no oxygen deficiency was detected, and the sample also did not demonstrate a sensor signal to CO (Fig. 1, left). In the case of samples obtained at 500 °C, SnO₂-2D-500 demonstrated a sensor signal value similar to 3D and significantly greater compared to the reference sample. The same patterns were observed in case of NH₃ (Fig. 1, center). For acetone (Fig. 1, right), no low-temperature maximum response was observed for SnO₂ samples obtained at 300 °C.

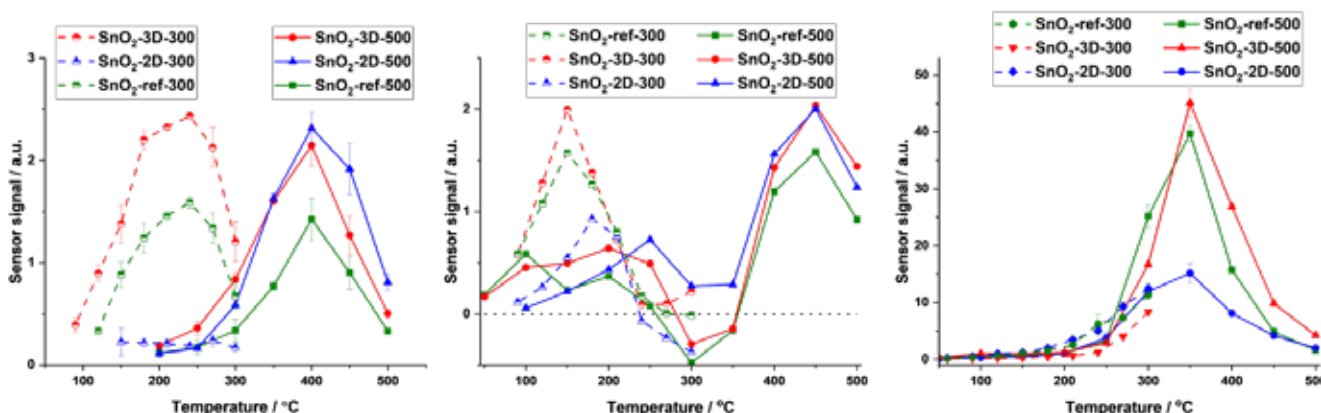


Figure 1. Sensor signals for different reducing gases CO (left), NH₃ (center), acetone (right)

AN INNOVATIVE METHOD FOR ONE-STEP SYNTHESIS OF NANO-SIZED SYSTEMS OF Fe, Ti, Si, B CARBIDES.

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Nanoparticles of Fe, Ti, Si, B carbides were first obtained using the innovative method of induction-flow levitation. The sizes obtained using the technology range from 3 nm to 1 micron. This is achieved by varying the parameters of nanoparticle synthesis, such as pressure, power, type and flow rate of the refrigerant gas and reaction gas. Fe₃C, TiC, SiC, B₄C nanoparticles were prepared using argon as a refrigerant gas (99.999%). Various gases were used as a carbon source, such as methane, acetylene, carbon monoxide, and benzene vapor. The morphology of the obtained nanoparticles was studied by SEM and TEM. Elemental and phase analysis were studied using SEM-EDS, XRD, HRTEM methods. ICP-MS analysis showed high purity of the resulting NPs. The average size was obtained from SEM, TEM, XRD, DLS and BET data. The study shows that the IPL method makes it possible to obtain nano-sized powders of the composition Fe₃C, TiC, SiC, B₄C with a high degree of purity. The dependence of the composition on the type of reagent gas used was also determined.

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The work was carried out with financial support from the Ministry of Science and Higher Education of the Russian Federation within the framework of scientific project No. FWSR-2022-008 and the Russian Science Foundation, project 20-79-10097. The work was carried out By the support of the federal academic leadership program “Priority 2030” of the Ministry of Science and Higher Education of the Russian Federation.

INVESTIGATION OF THE SPRAY DRYING PROCESS OF SUSPENSIONS CONSISTING OF COMPOSITE NANOPARTICLES BASED ON TUNGSTEN

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Obtaining products of complex shape with high physical, mechanical and operational characteristics by rapidly developing additive manufacturing technologies is impossible without development in the direction of reducing the grain size of metal powder particles in the structure and increasing its uniformity. One of the possible ways to obtain such materials is the plasma treatment of pre-granular nanopowders obtained as a result of plasma chemical synthesis.

The aim of this work was to obtain mechanically strong nonporous nanopowder microgranules of various tungsten-containing systems (W-Ni-Fe, W-Cu and W-C-Co) in the size range from 20 to 70 microns by spray drying of a suspension consisting of nanoparticles. Nanopowders of these systems with an average size of 50-70 nm, obtained at the plasma chemical synthesis of nanopowders developed at IMET RAS¹, were used as feedstock in the granulation process. Experimental studies of the spray drying process were carried out on the Buchi Mini Spray Dryer B-290 laboratory unit equipped with a Buchi B-295 circulating gas circuit.

During the experiments, the effect of the suspension composition was studied: the dispersed medium, the concentration of the dispersed phase and the binder component, as well as the flow rate of the suspension fed into the spray nozzle. As a result of the experiments performed, the possibility of obtaining granules of various shapes with a yield of a particle fraction with a size from 20 to 70 microns to 80% was established. It is shown that the main parameters of the spray drying process, determining the yield of the target fraction, were the concentration of the binder and the consumption of the suspension.

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The work was carried out with the financial support of the Russian Science Foundation, project No. 22-19-00112.

SYNTHESIS AND RESEARCH OF COMPOSITE MATERIALS BASED ON FERROCYANIDES FOR CAESIUM EXTRACTION FROM LIQUID MEDIA

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The synthesis of composite materials based on mixed K-Co and K-Cu PCs in composition with siloxane-acrylate emulsion and polyethylene has been carried out. The sorption properties of the obtained sorbents were studied with respect to ^{137}Cs extracted from model solutions. Table 1 presents the values of distribution coefficients (K_p) of ^{137}Cs during sorption from model solutions using different industrial sorbents.

Table 1. Distribution coefficient (K_d) values of ^{137}Cs on different sorbents

Name sample	K_d ^{137}Cs values, cm^3/g during sorption from solution		
	0,1 mol/dm ³ NaNO ₃	1,0 mol/dm ³ NaNO ₃	SW/5
	22600	21800	38000
FOC Cu-PE	21800	11200	20800
FOC Cu-PE	19000±400	2400±100	-
BGL	1800±100	64± 3	-
CL(Hol)	680±20	20± 2	-
NaA	84000±2500	60000±2000	-

The results of the study show that the highest sorption characteristics with respect to ^{137}Cs are possessed by the sample of FC K-Cu-PE, the K_p value for which exceeds the values for industrially used sorbents (Table 1). The developed sorption materials represent a prospect for synthesis of effective and practically demanded selective sorbents obtained in a simple and cheap way.

This work was financially supported by the Russian Science Foundation, project 23-73-01160.

FORMATION OF THE $\text{Bi}(\text{Al}_{1-x}\text{Fe}_x)_3(\text{PO}_4)_2(\text{OH})_6$ WITH ALUNITE-LIKE STRUCTURE UNDER HYDROTHERMAL CONDITIONS

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In recent years, there has been an active study of natural minerals and the development of new functional materials and technologies based on their synthetic analogues. This interest is primarily due to the possibility of obtaining new compounds with unique properties¹. Alunite supergroup phosphates are a broad class of inorganic compounds with the chemical formula $AB_3(\text{PO}_4)_2(\text{OH})_6$, where A – Ce, La, Nb, Sm, Ca, Sr, Pb, Ba, Bi and B – Al, Fe, V, similar in their structural parameters of the crystal lattice². The relevance of obtaining and studying such phosphates lies in the prospect of using them, in particular, as matrices for toxic and radioactive waste^{3,4}.

Of interest are studies aimed at studying the formation of $\text{Bi}(\text{Al}_{1-x}\text{Fe}_x)_3(\text{PO}_4)_2(\text{OH})_6$ compounds and determining the miscibility limit of x_{Fe} in the structure. An analysis of the scientific literature showed the lack of data on the preparation of the $\text{BiFe}_3(\text{PO}_4)_2(\text{OH})_6$ compound with an alunite-like structure in laboratory conditions.

Using the procedure for the synthesis of $\text{BiAl}_3(\text{PO}_4)_2(\text{OH})_6$ under hydrothermal conditions at a temperature of 200°C, described in work⁵, and adapting it for the introduction of iron into the system, a series of solid solutions of $\text{Bi}(\text{Al}_{1-x}\text{Fe}_x)_3(\text{PO}_4)_2(\text{OH})_6$ were obtained and the miscibility limit of x_{Fe} was determined. The obtained samples were characterized by XRD and SEM methods.

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MATERIAL DURABILITY ASSESSMENT TAKING INTO ACCOUNT BIODEGRADATION PROCESSES

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Practically all industrial and construction materials can be negatively affected by microorganisms. As a result of the impact of bacteria, mycelial fungi, physical and chemical properties of materials and their commercial appearance deteriorate. The damage caused to objects as a result of bio-damage amounts to tens of billions of dollars annually. In addition, micro-mycetes cause mycoses in humans and animals, and lead to spoilage of manufactured food products. In order to increase the durability of materials and improve the environmental situation in buildings, it is necessary to take measures that reduce or eliminate aggressive biological effects.

Our research, conducted for more than 30 years by engineers, chemists, biologists, physicists and physicians, covers: a comprehensive and systematic study of biological corrosion and resistance of materials in biological media used in modern construction and mechanical engineering; research of biochemical processes of interaction of materials and media with the establishment of the mechanism of these reactions and the isolation of physical and chemical processes; identification and the classification of biological media that have a destructive effect with the release of strains of microorganisms; establishment of mathematical dependencies of biodegradation of materials taking into account temperature, humidity, structural and other factors and development of methods for assessing and predicting durability; search for effective methods to increase the biological resistance of materials, development of methods for biological protection of buildings and structures taking into account the resource of reliability in operation; training of specialists capable of managing biochemical processes and ensuring the safety of buildings and structures.

3D PRINTED NEW MATERIALS BASED ON MAGNESIUM PHOSPHATES FOR BIOMEDICAL APPLICATIONS

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Chemically similar physiological phosphates are of significant fundamental interest for resorbable, highly porous materials development for bone tissue engineering. To realize their innovative potential, it is necessary to develop and/or select carefully a method for synthesis of new physiological phosphates powder analogues, to comprehensively study the physicochemical properties of both powder, ceramic and composite materials, mechanical properties, biocompatibility *in vitro* and *in vivo* of biomaterials based on them and macroporous scaffolds.¹

The new type of highly porous, degradable magnesium phosphate (MgP) biomaterials announced in this study, which are designed to not only repair damaged bone, but also have a profound therapeutic effect on bone remodeling or therapy, has been produced using 3D-printing for the first time.

From a materials science point of view, the problem is related to the design of the chemical and phase composition of implants. The requirement for resorbability suggests a transition to more soluble MgP materials compared to calcium phosphates (CaP). The requirement for implant strength, from a mechanical point of view, assumes that such a material will have increased mechanical strength in compression both due to a more advanced microstructure and due to higher theoretical strength compared to traditional CaP ceramics. The engineering aspect is associated with the implementation of osteoconductive properties, which are determined by the presence of a connected system of macropores (at least 100 μm in size), carried out by stereolithographic 3D printing.

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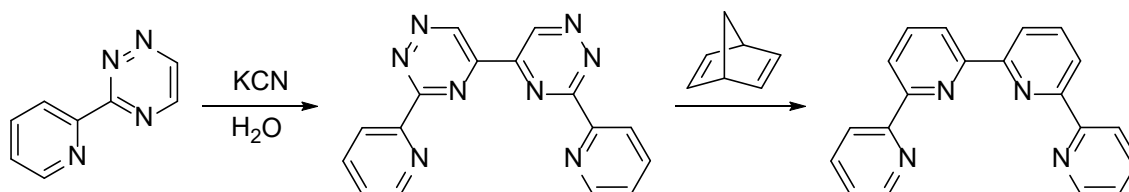
NOVEL APPROACH TO THE SYNTHESIS OF QUATERPYRIDINE LIGANDS

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Quaterpyridine ligands are an important N-heterocyclic scaffolds that have found application in supramolecular chemistry, catalysis, bioanalysis, and as a components of solar cells.¹ However studying this class of compounds is limited by the complexity of their synthesis.

We found that dimerization of 3-(pyridin-2-yl)-1,2,4-triazine in the presence of KCN followed by transformation of the bitriazine moiety *via* the Boger pyridine synthesis leads to the formation of 2,2':6',2'':6'',2''':6'''-quaterpyridine in good overall yield.



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TECHNOLOGICAL METHODS FOR PRODUCING STABLE BITUMEN BINDERS MODIFIED BY RECYCLE POLYETHYLENES

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An effective way to modify bitumen binders to improve process characteristics and reduce susceptibility to temperature changes is to add polymers to them. An environmentally and economically beneficial method can be the use of recycled polyethylenes as modifiers. However, polymer-bitumen binders (PMB), especially those based on thermoplastic polymers, have a big drawback - instability during high-temperature storage.

The purpose of the work was to study the factors influencing the stability of PMB during high-temperature storage: the composition of bitumen and the structure of recycle polyethylenes, the conditions for preparing PMB.

In the course of the research, a new approach to the rapid analysis of PMB homogeneity using the calorimetry method was developed. It has been established that paraffin-naphthenic hydrocarbons have a stabilizing effect on PMB, and asphaltenes have a destabilizing effect; the critical concentration of asphaltenes was determined, below which they do not have a negative effect on the stability of PMB during high-temperature storage.

For the first time, the fact of high-temperature segregation in PMB not only of the polymer component (floating), but also of the asphaltene fraction (sedimentation) was recorded.

It has been shown that the production of stable polymer-bitumen binders is possible only under conditions of complete amorphization of the polymer in bitumen, which can be achieved by selecting the conditions for preparing PBB. It was found that to obtain stable PBB based on low-density polyethylene, it is achieved at a mixing speed of 1200 rpm and a mixing time of 600 minutes.

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OXIDATION OF THE COBALT-NIOBIUM AND COBALT-TANTALUM ALLOYS ALLOYED WITH RHENIUM IN AIR AT 1375 K

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The addition of rhenium to the cobalt-niobium and cobalt-tantalum alloys to enhance their strength properties results in a reduction of their resistance to high-temperature oxidation¹. Previous studies have investigated the phase composition and microstructure of the oxidized zone after exposure to air at 1200 K using SEM, PXRD, and EPMA methods². The oxidized zone was found to consist of three layers: an outer layer of CoO, an intermediate layer of Nb₂Co₄O₉ or Ta₂Co₄O₉, and an inner layer of rhenium particles. Alloying with up to 9 at.% of rhenium improved the adhesion between the oxidized zones and the alloys. However, it also led to an increase in the width of the oxidized zones.

The study conducted oxidation of the alloys with the same composition at 1375 K for 15 minutes. The microstructures of the resulting oxidized zones lack intermediate layers. Ternary oxide particles are unevenly distributed in the oxidized zones, while pure rhenium particles are larger and concentrated near the inner boundary of the outer layer. The outer layer contains lacunae, indicating the diffusion of gaseous Re₂O₇ through the surface of the alloys (Figure 1).

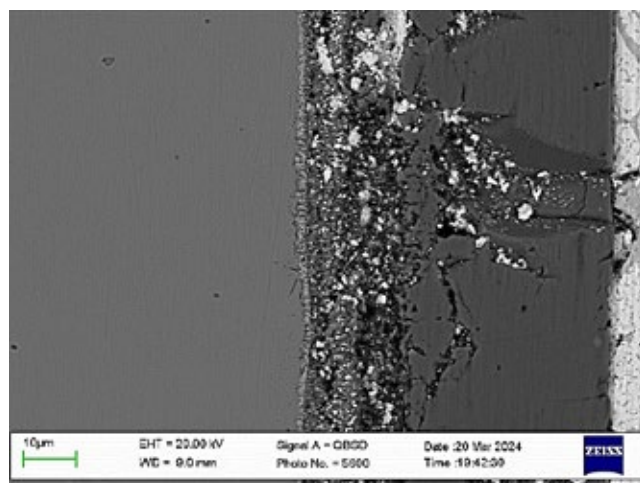


Figure 1. Oxidized zone of the Co-Nb-Re alloy (oxidation at 1375 K for 15 min).

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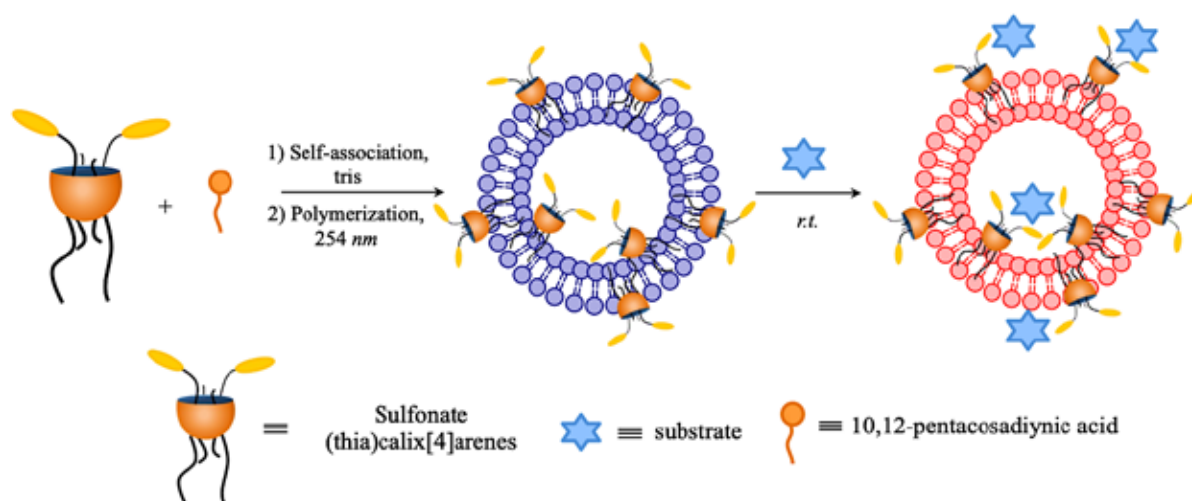
MODIFIED POLYDIACETYLENES BASED ON SULFONATE (TIA)CALIX[4]ARENAS

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Colorimetric sensors have remained relevant in the last decade as they can be used for qualitative/quantitative detection of substrates with the naked eye, saving significant time and resources. One of these polymers, unique in their properties, are systems based on 10,12-pentacosadiynic acid (PCDA). UV treatment of PCDA results in the formation of blue polymers that exhibit a color change to red under the influence of various external stimuli (pH environment, temperature) and in response to the substrate. This allows this polymer to be used as an active material in various applications such as chemosensors, biosensors, ion sensors, temperature sensors and molecular switches.

Our group has prepared polymers based on pentacosadiynic acid and sulfonate (thia)calix[4]arenes in the 1,3-alternant conformation (Scheme). Optimal conditions for obtaining colloiddally stable systems (irradiation time, monomer ratios) were selected. The sensory abilities of modified polydiacetylenes in relation to amino acids and heavy metals have been studied.



Scheme. Schematic representation of the preparation of modified polydiacetylenes.

The work was carried out with financial support from the Russian Science Foundation № 23-73-01140.

SORBENTS FOR LANTHANIDE IONS BASED ON Co(II) - MOF's

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The work reports methods of synthesis of metal-organic frameworks based on Co(II) compounds with 2-ethylimidazole and terephthalic acid at various metal/linker ratios. Synthesized metal-organic frameworks (MOF's) have shown efficiency as sorbents for the extraction of rare earth metal ions Yb³⁺, Er³⁺, Sm³⁺, Nd³⁺ and Pr³⁺ from liquid-phase systems. A high rate of establishing sorption equilibrium was found. It is achieved with a contact time in the range of 30-40 minutes.

The particles of all obtained MOF's are a microheterogenic system with an average particle size of 0.05-0.1 microns. The parameters of the porous structure of the synthesized samples were found by the method of low-temperature nitrogen adsorption. The study of the adsorption of Yb³⁺, Er³⁺, Sm³⁺, Nd³⁺ and Pr³⁺ ions from aqueous solutions at temperatures of 298.15 and 313.15K proved the sorption efficiency of the obtained frame structures, which is confirmed by a high degree of extraction of metal ions. Adsorption is spontaneous in all cases. The values of the differential heats of sorption for the studied temperature range indicate the exothermic nature of the process. Ion sorption is realized with a decrease in the entropy of the system. The linearization of experimental data on ion adsorption is achieved in linear coordinates of the Langmuir isotherm and the theory of volumetric pore filling for zeolites.

The study was supported by the Russian Science Foundation, project No. 22-73-10158.

ANTIOXIDANT ACTIVITY OF CERIA SOLS STABILIZED BY BIOACTIVE LIGANDS

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Nanocrystalline cerium dioxide is considered as one of the most promising nanobiomaterials because of its diverse biological activities. Most likely that the mechanism of biological activity of CeO_2 is related to its ability to mimic the functions of different enzymes, i.e. to act as an enzyme-like material, and to catalyze biochemical reactions involving reactive oxygen species. Additional modification of the biochemical activity of cerium dioxide can be achieved by modifying the surface of the nanoparticles with biologically active compounds.

In the present work, stable colloidal solutions of cerium dioxide were obtained by thermohydrolysis (95°C) of ceric ammonium nitrate followed by stabilisation with low molecular weight ligands, including ammonium citrate, sodium ascorbate and potassium urate in molar ratios of ligand: CeO_2 corresponding to grafting densities of the ligands on the CeO_2 nanoparticles.

The characteristics of the obtained materials were investigated by powder X-ray diffraction analysis, transmission scanning electron microscopy, UV-visible, Raman and IR spectroscopy, dynamic light scattering. Comparative analysis of antioxidant activity of the obtained materials was carried out by recording the kinetics of luminol oxidation in the presence of alkylperoxyl radical source 2,2'-azobis(2-amidinopropane) dihydrochloride using the chemiluminescence method. The antioxidant properties of cerium dioxide and individual ligands were quantitatively compared.

The work was supported by the Russian Science Foundation (project 24-13-00370).

MODELING AND CHARACTERIZATION OF THE MIDDLE- AND HIGH-ENTROPY $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$ -BASED PHASES

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The search for a solution to the problems of unsatisfactory compatibility of traditional solid oxide fuel cell (SOFC) cathode materials with electrolyte materials and significant polarization resistance at the electrode/electrolyte interface stimulates the development of novel cathodes based on medium- and high-entropy oxides. In the present work, the prediction and validation of complex oxide phases obtained by multidoping the conventional $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$ (LSCF) perovskite cathode was carried out on the A- ($\text{La}_{1-x-y}\text{Ln}_x\text{Sr}_y\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$, Ln = Pr, Nd, Sm, Eu, Gd) and on the B-sublattice ($\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{1-x-y-z}\text{Co}_x\text{Mn}_y(\text{Ni,Cu})_z\text{O}_3$).

On the basis of a complex of calculations (Goldschmidt tolerance factor, change of mixing entropy, size-difference and valence-difference stability factors), a model evaluation of phase and structural stability of the studied oxides was performed and the ranges of existence of medium- and high-entropy phases were predicted.

A number of multidoped compositions were obtained by the method of pyrolysis of citrate-nitrate compositions, their phase composition was analyzed by X-ray powder diffraction data, and the crystal structure of single-phase samples was elucidated by neutron diffraction data.

First-principles calculations of the electronic structure of high-entropy phases based on LSCF have been performed by the electron density functional theory (DFT) method using the VASP software package. Based on the analysis of the structural stability of the phases in a wide range of dopant concentrations, a factor contributing to the thermodynamic stability has been identified.

The crystal structure data of the samples obtained using model approximations showed satisfactory agreement with the results obtained from powder neutron diffraction data.

The work was financially supported by the Russian Science Foundation, project 23-23-00083.

WETTING ABILITY, ADHESION WORK OF SYSTEMS BASED ON NONIONIC SURFACTANTS WITH CARBON C-DOTS ON SURFACES

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Lyomesophases are promising media for various biomedical applications¹. In this aspect, the rheological characteristics of lyotropic media and their adhesive properties are necessary. This work presents the results of assessing the wetting of model surfaces with different free surface energy by hybrid lyotropic liquid crystalline media based on nonionic surfactants: tetraethylene glycol monododecyl ether ($C_{12}EO_4$) and decaethylene glycol ($C_{12}EO_{10}$), doped with C-dots in water-decanol media, forming lyomesophases and gel-like structures. The surface tension of the samples under study was determined and the work of adhesion of the systems to the substrates was calculated. As an example, Figure 1 presents an assessment of the contact angle of lyomesophase on glass, nylon and polydimethylsiloxane (PDMS).

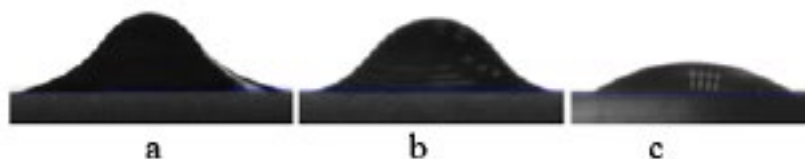


Рисунок 1. Photographs of $C_{12}EO_4$ -based LLCs obtained on a Kruss Easy Drop DSA 20E device on the surface of glass (a), nylon (b), PDMS (c).

The study of wetting and adhesion interaction of hybrid systems with hydrophobic surfaces established the influence of introducing carbon dots into the LLC system and showed the possibility of controlling these characteristics of lyomesophases and gels by varying the composition and type of C-dots, which will make it possible to predict the mechanism of drug delivery by LLC transport systems.

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The work was supported by Vladimir Potanin Foundation.

OBTAINING SiO_2 COATING ON THE TREATED SURFACE OF CARBON FIBERS

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Carbon fibers are widely used in composite materials as a reinforcing component. In aluminum matrix composites, carbon fibers react chemically to form aluminum carbide, which leads to a decrease in the properties of the entire material. Therefore, applying an oxide coating to the fibers will not only prevent the formation of Al_4C_3 , but also protect the fiber from degradation.¹ In order to increase the interfacial interaction at the fiber/coating interface, the carbon fiber surface is treated.^{2,3} In this work, carbon fibers were treated with 1,1-dihydroperoxycyclohexane (DHPC) to form functional groups on their surface. Using electrochemical deposition from sol-gel solutions, SiO_2 coatings were deposited to the surface of the fibers.

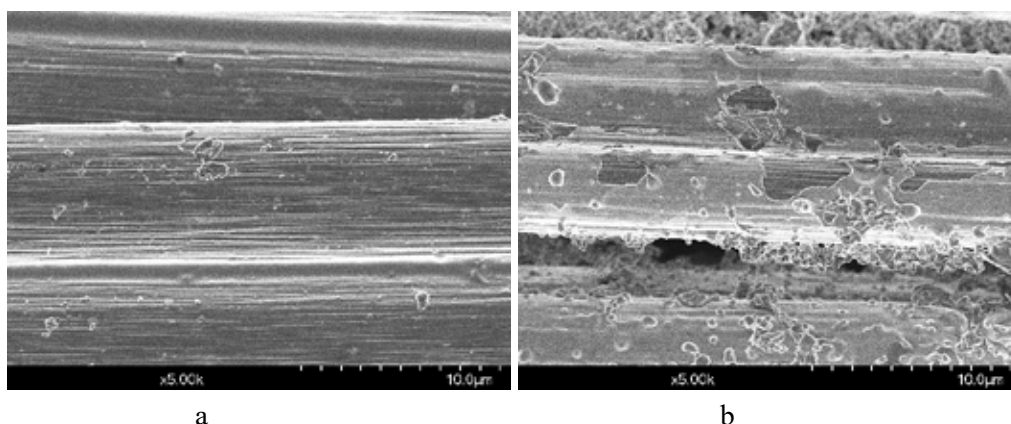


Figure 1. SEM images of the surface of carbon fibers: a) after treatment with DHPC; b) with SiO_2 coating

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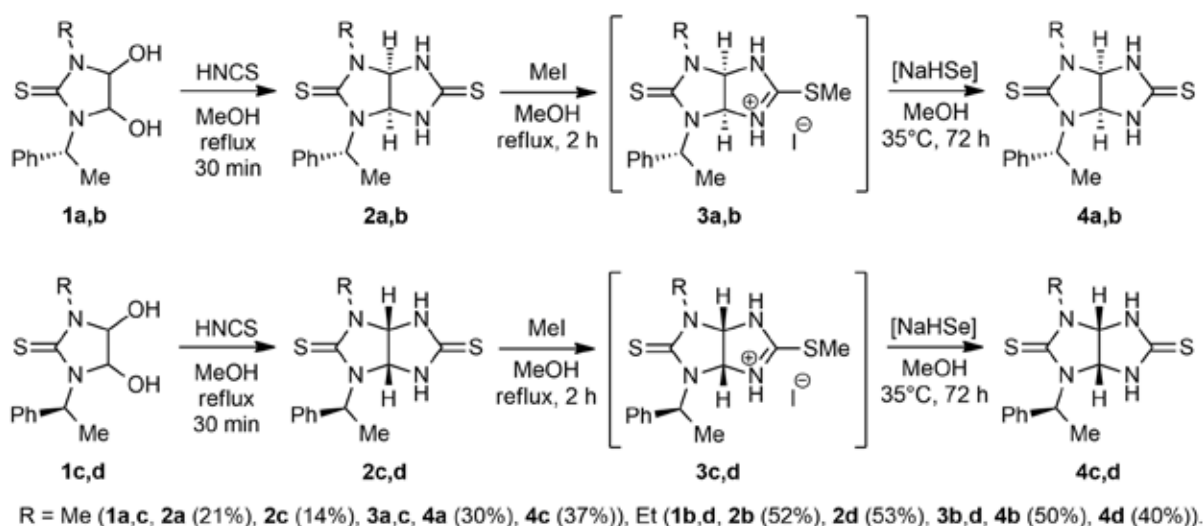
SYNTHESIS OF ENANTIOMERICALLY PURE THIOSELENOGLYCOLURILS – NEW POTENTIAL FUNGICIDES

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5-Selenoxohexahydroimidazo[4,5-d]imidazol-2(1H)-ones (seleno-glycolurils) are a class of bicyclic biureas that exhibit fungicidal activity.¹ To date, no approaches have been developed to the synthesis of enantiomerically pure selenoglycolurils, so this problem is of current interest.

In this work, using the example of the reaction of 4,5-dihydroxy-1-methyl-3-(1-(R(S))-phenylethyl)imidazolidine-2-thiones **1a-d** (DHIT) with HNCS, we show that the reaction proceeds highly diastereoselectively with the predominant formation of 1-alkyl-3-(1-(R(S))-phenylethyl)thioglycolurils **2a-d** (yield 14-53%, scheme 1). The resulting compounds **2a-d** were methylated with MeI to obtain isothiuronium salts **3a-d**, which were further selenized to the target enantiomerically pure thioselenoglycolurils **4a-d** (yields 30-50%).



Scheme 1.

Target selenoglycolurils **4a-d** were submitted for the study of antifungal activity.

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STRUCTURAL-PHASE CHANGES AND LUMINESCENT PROPERTIES OF LIQUID CRYSTAL SYSTEMS BASED ON SURFACTANTS WHEN DOPED WITH CARBON C-DOTS

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Lyotropic liquid crystals (LLC) are promising media for theranostics in the biomedical field^{1,2}. This paper presents the results of studies of structural-phase changes and luminescent properties of the systems based on nonionic and zwitterionic surfactants: tetraethylene glycol monododecyl ether ($C_{12}EO_4$), decaethylene glycol monododecyl ether ($C_{12}EO_{10}$), N,N-dimethyldodecylamine oxide ($C_{12}DMAO$) and C-dots (CD) in water-decanol media, forming lyomesophases and gel-like structures. The Fig. 1 shows examples of texture observed on polarizing and fluorescent microscopes.

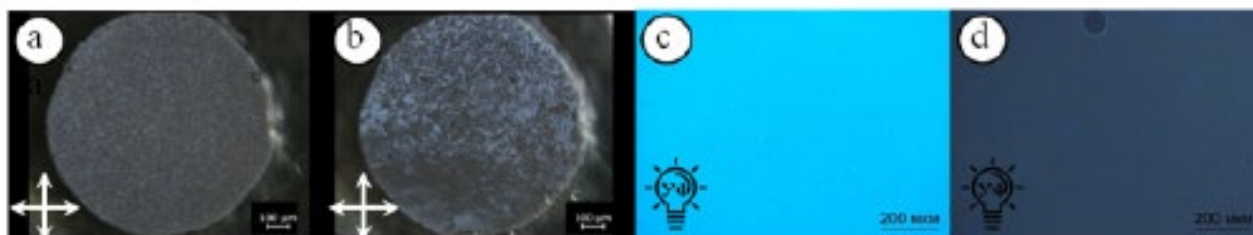


Figure 1. Photographs of LLCs based on $C_{12}EO_{10}$, obtained on a polarizing and fluorescence microscope: a, c – with “blue” CDs, b, d – with “yellow” CDs.

Thus, introducing carbon dots into the LLC system leads to obtaining hybrid supramolecular-organized optical media with pronounced luminescent properties. Investigations by complexes of physicochemical methods demonstrated the possibility creation and controll the polarized luminescence of lyotropic mesophases by varying the composition and type of C-dots.

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The work was supported by Vladimir Potanin Foundation.

MAGNESIUM TITANATES AS REAGENTS FOR PRODUCING $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ NANOTUBES WITH AN INNER CHANNEL FILLED WITH A TITANIUM OXIDE COMPONENT

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The purpose of this work was to study the processes of solid-phase formation of magnesium titanates as precursors for filling hydrosilicate nanotubes of the composition $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ with the titanium oxide component.

Magnesium titanates were obtained by solid-phase synthesis. Mixtures of MgO (“analytical grade”) and TiO_2 (anatase “Aldrich”) were used in the molar ratio $\text{MgO}:\text{TiO}_2 = 1:1, 1:2, 2:1$. Grinding and mixing of the reagents was carried out in a planetary mill (Pulverisette FRITSCH) for 30 minutes at a speed of 450 rpm. Tablets were pressed from the mixtures and subjected to multi-stage firing (850, 1100 and 1250°C) with intermediate grinding in a mill.

The obtained and characterized reagents, magnesium titanates, were used to fill the internal channel of nanotubes with the titanium oxide component, which occurs during the synthesis of hydrosilicate nanotubes with a chrysotile structure.

The phase composition of the samples was determined from X-ray diffractometry data using the RietveldToTensor¹ program. The microstructural parameters and composition of the samples were determined by transmission electron microscopy and elemental microanalysis.

It has been shown that it is the use of titanium oxide substances that makes it possible to introduce titanium dioxide into the internal channel of nanotubes in the greatest amount compared to other methods of introducing TiO_2 ² into it.

Thus, the prospects of the “reaction method” of filling the nanotube channel with the required components using reagents of the appropriate composition have been established.

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The work was supported by the Russian Science Foundation grant No. 24-13-00445 dated 05/08/2024

INFLUENCE OF COATING CONDITIONS ON THE PROPERTIES OF CATALYTIC $\text{CeO}_2\text{-ZrO}_2$ AND Mo_2C LAYERS OBTAINED BY SOL-GEL METHOD

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Molybdenum carbides are catalysts of many reactions including the conversion of light hydrocarbons. One of the ways to intensify these reactions is to use membrane catalytic systems in the reaction. The efficiency of membrane catalysts in a certain chemical reaction is mainly determined by the architecture and porous structure of the catalyst.

Catalytic layers (membrane catalysts) based on $\text{CeO}_2\text{-ZrO}_2$ and Mo_2C were obtained in this work. The influence of coating conditions on their main characteristics were established.

Catalytic layers were obtained by dip coating method using $\text{CeO}_2\text{-ZrO}_2$ and molybdenum blues sols. A microfiltration membrane based on $\alpha\text{-Al}_2\text{O}_3$ was used as a support. Compositions with different pH value of dispersion medium, concentration of dispersed phase and polymer content were prepared using the listed sols. The contact time, substrate dipping/extraction rate were varied during coating applying. The assessment of preliminary modification of the support was estimated to prevent infiltration of sol particles into the pores of the support. The obtained samples of membrane catalysts were characterized in terms of layer morphology, thickness, depth of infiltration of sol particles, and porous characteristics.

It was found that for the Mo_2C catalytic layer (10 μm) on the external surface of the support preliminary modification of the substrate using PEG was necessary. The contact with the sol should be from 3 to 10 s to form a layer of particles on the support. To obtain a defect-free coating it is sufficient to repeat cycle “application-drying-heat treatment” twice. The concentration of molybdenum blue should be at least 5 wt. %. Preliminary modification of the substrate is also necessary to obtain the $\text{CeO}_2\text{-ZrO}_2$ catalytic layer on the external surface of the substrate. In this case the optimal option is to create an intermediate layer of Al_2O_3 .

The research was carried out within the state assignment of Ministry of Science and Higher Education of the Russian Federation (FSSM-2023-0004).

NEW INORGANIC PHOTOLUMINOPHORES ACTIVATED BY BISMUTH AND YTTRIUM IONS ON THE BASIS OF HIGH-SILICA NANOPOROUS MATRICES

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Materials activated by bismuth and yttrium ions can be used to create broadband fiber amplifiers, for LEDs, for display applications, in solar cells^{1,2,3}. Bismuth-containing composite materials (BCMs) with variable content of yttrium oxide have been synthesized by impregnation of silicate porous glass matrices (composition by analysis, wt. % $0,30\text{Na}_2\text{O} \cdot 3,14\text{B}_2\text{O}_3 \cdot 0,11\text{Al}_2\text{O}_3 \cdot 96,45\text{SiO}_2$) in acidified water-salt solutions of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ in the presence of $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ with their subsequent heat treatment (in the range of 650–870 °C)^{4,5}.

The study presents the results of a comprehensive investigation of BCMs by optical, infrared and luminescence spectroscopy methods. It has been established that BCMs exhibit photoluminescence in a wide spectral range (230–900 nm) due to the presence of various active centers⁶, as a result of which they can be considered as new promising solid-state inorganic photoluminophores.

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SYNTHESIS OF CHIRAL DERIVATIVES OF 2,2'-BIPYRIDINE

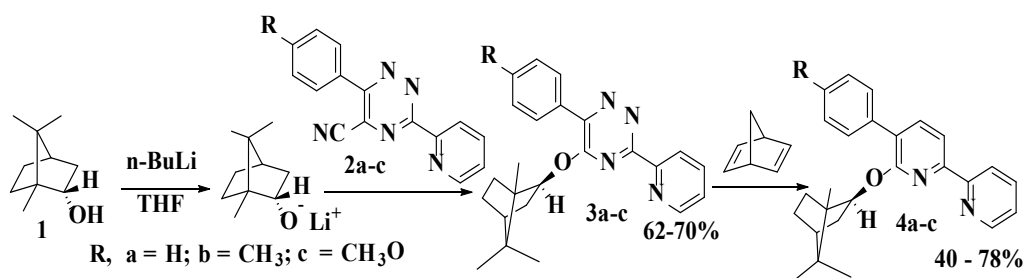
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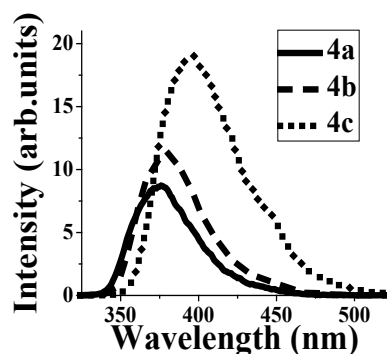
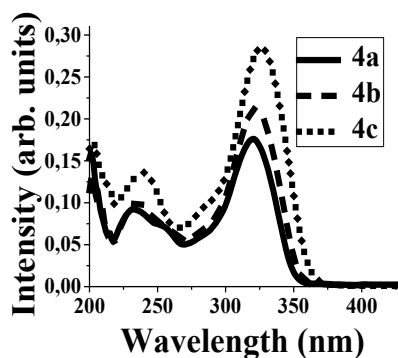
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2,2'-Bipyridines are widely used as push-pull fluorophores and/or chelating metal ligands due to their high redox stability and ease of functionalization¹. Chiral compounds based on 2,2'-bipyridines can be used as ligands for asymmetric synthesis. An effective approach to obtaining 2,2'-bipyridines is the so-called. "1,2,4-triazine methodology"² due to the possibility of transforming 1,2,4-triazines into pyridines.

As part of the work, 2,2'-bipyridines with fragments of the O-nucleophile borneol were synthesized as possible ligands or fluorophores. To functionalize 1,2,4-triazine 2a-c, the S_N^{ipso} reaction was carried out with borneol **1**. To obtain chiral 2,2'-bipyridine ligands **4a-c**, the Boger reaction was carried out with norbornadiene.



Below the graphs of absorption (left) and emission (right) are presented. Compound **4c** has the highest emission intensity.



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THE DYNAMICS OF CHANGES IN PHYSICOCHEMICAL PROPERTIES OF METAL-CONTAINING NATURAL POLYMERS FILMS

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Materials based on natural high-molecular compounds are an interesting object of research. Inclusion of cations of platinum group elements in polymer matrixes causes changes in physicochemical properties of materials¹.

In this study, polymer films based on chitosan, agar-agar and gelatin with the inclusion of Pt(II), Pd(II), Rh(III) and Ir(IV) cations were obtained². The films' properties such as surface morphology by scanning electron microscopy, antioxidant properties and thermal stability were investigated. The correlations between the short-term strength and maximum tensile strength of the films, as well as swelling coefficients in aqueous and buffer solutions, and the composition and age of the samples were found.

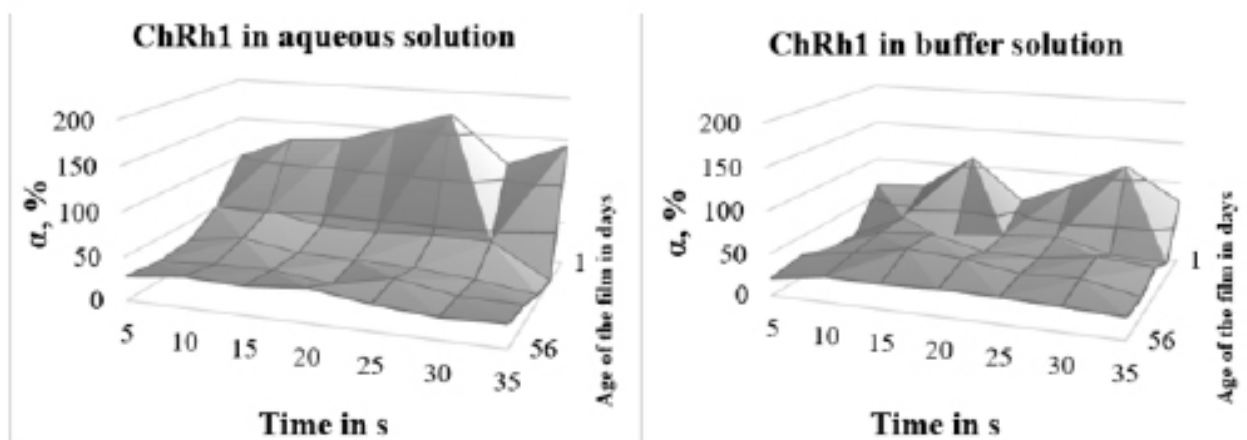


Fig. 1. Dynamics of the film ChRh1 swelling coefficient change

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DEVELOPMENT OF MULTIFUNCTIONAL MICROPOROUS IONIC POLYMERS FOR ADSORPTION AND CATALYTIC CONVERSION OF CO₂ INTO CYCLIC CARBONATES

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Carbon dioxide (CO₂) is one of the main factors of global climate change, while CO₂ is a widespread, cheap and renewable source of carbon C1. The binding of CO₂ to three-membered ring compounds, such as epoxides, through a cycloaddition reaction is one of the most widely studied ways of fixation, due to overcoming the thermodynamic inertia of the CO₂ molecule and 100% saving of atoms.

Porous organic polymers based on ionic liquids (PILs) are promising candidates for the effective adsorption and catalytic conversion of CO₂ into cyclic carbonates. The introduction of fragments of ionic liquids (IL) into the polymer structure allows them to combine their advantages: a large specific surface area and high microporosity of the polymer structure are effective for capturing CO₂; IL have an affinity for CO₂, and their anions are active nucleophiles for opening the epoxy ring.

We have developed highly porous polymer catalysts for the conversion of CO₂ into cyclic carbonates based on imidazolium with various functional groups (-COOH, -NH₂, -OH, etc.) and counterions (-Cl, -Br, -I). The catalysts have a crosslinked polymer structure, have a high specific surface area (up to 750 m²/g) and abundant porosity. The adsorption capacity of the obtained catalysts reaches 0.83 mol/g of CO₂, and the yield of the target product is more than 90% during the catalytic reaction under conditions of 70 °C and 3 atm of CO₂ occurs in less than 5 hours.

The work was carried out By the support of the federal academic leadership program "Priority 2030" of the Ministry of Science and Higher Education of the Russian Federation.

SPECTRAL CHARACTERISTICS OF RAMAN SCATTERING OF SORPTION COMPOSITIONS BASED ON ACRYLAMIDE FOAM GELS AND NANOSORBENTS

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Sorption composites based on polymers with sorption properties and sorbents of inorganic and organic nature, which are characterized by the size of macro, micro, meso pores and high specific surface area for the penetration of sorbed substances and sorbents with functional groups with which sorbed substances can interact, are relevant for practical work for cleaning contaminated waters. Sorption composites were produced by microwave heating for 30-60 seconds of suspensions, which included components for the polymerization of polyacrylamide gel and dispersion media of various natures. Samples were separated from acrylamide foam composites to determine the sorption properties in relation to model solutions of metal salts. Acrylamide foam composites with inorganic substances: manganese oxide and graphenes were studied by the Raman method using changes in the spectral characteristics of the sorption components from colloidal to aggregative states. For sorbents of different natures used in (SC), the characteristic areas of functional connections that interact with the sorbed substances are determined. Of the organic compounds, chitosan, pyrolyzed and oxidized waste from processing plant raw materials were considered. The possibility of manufacturing sorption structures from (SC) in the form of granules, networks and others allows us to solve practical problems in the localization and purification of polluted waters.

The work was carried out with financial support from the Ministry of Science and Higher Education of the Russian Federation (state registration number of the research topic 122041400110-4).

SYNTHESIS OF HIGH-ENTROPY LAYERED DOUBLE HYDROXIDE WITH COMPOSITION MgNiCo/AlFeY BY COPRECIPITATION METHOD FOLLOWED BY MICROWAVE-HYDROTHERMAL TREATMENT

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Layered double hydroxide (LDHs), also known as hydrotalcite-like compounds, is the class of natural and synthetic inorganic compounds with the general formula $[M(II)_{1-x}M(III)_x(OH)_2]^{x+} [A^{n-}_{x/n} \cdot yH_2O]^{x-}$, where M(II) and M(III) are cations of divalent and trivalent metals, respectively, and A^{n-} is a n-valent anion. The structure of LDH is a system of positively charged brucite-like octahedral hydroxide layers alternating with interlayer anions and water molecules. The structure is stabilized due to electrostatic interactions between layers and interlayer anions. These compounds are known for a number of useful and even unique (“memory effect”) properties.¹

The compositional flexibility of LDHs makes them promising compounds for the obtaining of high-entropy materials (HEM). At this moment, mainly two- and three-cationic LDHs have been synthesized, while HE-LDHs contain six or more cationic components homogeneously distributed in the crystal structure. It is assumed that maximizing configuration entropy makes possible to stabilize the system and gives to materials cumulative properties, which were not appeared previously by each individual element of the system.²

This work presents the successful synthesis of a six-cationic layered double hydroxide with the composition MgNiCo/AlFeY, obtained by coprecipitation method followed by microwave-hydrothermal treatment. The synthesized material was investigated by X-ray diffraction, elemental and FTIR analyses. Also, the behavior of the sample upon heating was studied.

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The work was supported by the Russian Science Foundation (grant No. 24-23-00182)

OSTEOCONDUCTIVE COMPOSITE SCAFFOLDS BASED ON METHACRYLATED POLYCAPROLACTONE FOR BONE TISSUE REGENERATION

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The manufacturing of materials that can induce the restoration of damaged bone tissue, eventually being completely replaced by native bone, was revealed as an urgent problem of modern regenerative medicine. In addition, an important parameter is the osteoconductivity of the implant, what can be ensured by the specified porous architecture. The most promising way to form a three-dimensional architecture of bone implants is 3D printing from photocurable materials.

The composite materials presented in the current work were prepared from a polymer matrix of methacrylated polycaprolactone filled with amorphous calcium phosphate (ACP), which was stabilized with sodium tripolyphosphate¹. The addition of oleic acid made it possible to obtain a uniform distribution of particles in the volume of the material. The addition of ACP leads to an increase in Young's modulus and a decrease in the contact angle. A further increase in the hydrophilicity of the composite surface can be achieved by treatment in 1M citric acid and 0.05M sodium hydroxide. The gyroid structure was printed on an Ember Autodesk 3D printer with a DLP projector with a maximum radiation at 405 nm. It has also been shown that staining in DMEM did not reveal a significant change in pH, which allows further testing on cells.

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The work was carried out with financial support from the Russian Science Foundation (grant No. 22-19-00219).

HYDROPHOBIC COATINGS BASED ON ORGANIC ACIDS SALTS

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The development of new hydrophobic materials is an actual task.

This report presents data on new hydrophobic materials based on stearates, myristates, di-(2-ethylhexyl)phosphates of *d*- and *f*-elements, obtained by interfacial synthesis at the interface of two immiscible liquids. The material of interfacial formations (MIF) is formed quite quickly. Taken from the system and transferred to a plate (glass, aluminum, copper, iron) 10 minutes after bringing the phases into contact, MIF is hydrophobic.

It has been established that MIF has adjustable wettability, which, in particular, depends on the duration of MIF formation. As the synthesis time increases, the hydrophobicity of MIF increases, tending to a certain constant value. Among the studied organic acids, MIFs based on lanthanide di-(2-ethylhexyl)phosphates are more hydrophobic, the contact angle reaches 135°. The influence of the nature of the metal on the contact angle of the material transferred to different carrier has been studied.

If 1,2-dichloroethane is used as a diluent for stearic acid, then, regardless of the nature of the metal, the resulting MIF has a contact angle close to 90°. In the case of toluene and heptane, the material is hydrophobic, and in the case of heptane the contact angle is larger. MIFs based on stearate salts of *f*-elements are more hydrophobic than in the case of *d*-elements. In the series of *d*-elements, the difference in wettability is insignificant and the contact angle is close to 120°.

Higher values of the contact angle for MIF with *f*-elements are due to a large amount of metal salt accumulated in the MIF, lower water content in the material composition, a higher proportion of crystallinity, and greater roughness surfaces.

Over the course of two months, the contact angle of MIF based on zinc stearate changes slightly and is equal to 112.5°.

The work was carried out with the financial support of a grant from the Government of the Tula Region in the field of science and technology DS/104 dated September 27, 2023 and the Ministry of Science and Education of the Russian Federation within the framework of the scientific project of the laboratory "Laboratory of Smart Materials and Technologies" project No. FSSM-2024- 0005).

EFFECT OF MECHANICAL ACTIVATION ON POROUS STRUCTURE OF ASPHALT-BASED CARBON

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Carbon sorbents can be synthesized from carbon-containing materials using pyrolysis and activation methods at high temperatures. Chemical activation with KOH is one of the most effective in the formation of a porous structure. However, the features of the process (excessive use of alkali, difficulty of homogeneous mixing, need for a separate washing the carbon from alkalis step) limit the scale of application. Recently, many efforts have been made to search for effective, fast, simple technologies for producing porous materials. Mechanical activation (MA) begins to grow in popularity in this field.

As a result of the study of the effect of MA on the formation of the porous structure of carbon materials: It is shown that MA of asphalt with KOH leads to the formation of carbon samples with high porosity structures. It is found, that grinding, homogeneous mixing of reagents and the development of primary porosity occur by the MA. It is also shown that rise KOH/asphalt ratio from 1 to 4 increases the textural characteristics. It is important to note that, MA contributes to reduce the KOH/carbon precursor ratio necessary for effective activation to 1-2 and obtain microporous carbon materials with high textural and adsorption characteristics. In addition, reduction of the KOH/asphalt ratio from 4 to 1-2 leads to the the average pore size decreases and formation of predominantly ultramicroporous sample. Thus, the results of this study demonstrate the high adsorption capacity of porous coals of petroleum asphalt. Accordingly, this research focuses on solving environmental pollution problems and expanding existing approach for synthesizing new carbon materials for energy storage.

This work was supported by the Ministry of Science and Higher Education of the Russian Federation within the governmental order for Boreskov Institute of Catalysis (FWUR-2024-0039).

SiC FIBERS BASED ON POLYCARBOSILANES: STRUCTURE AND PROPERTIES

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Noncore SiC fibers are used in various branches of industry such as nuclear power, aerospace, automotive, etc. They have low density, chemical, corrosion and heat resistance.

The researches of GNIChTEOS prepared β -SiC fibers based on polycarbosilane (PCS). PCS has a high ceramic yield and good fiberization ability ^{1,2,3}. Using the method of melt spinning, fibers were prepared from PCS, whose curing occurred when heated to 200°C in air. Further heat treatment of the fibers took place in an inert atmosphere at a temperature of 1100-1900°C.

The resulting fibers were studied by SEM and X-ray diffraction analysis. It was found that upon thermal treatment up to 1100°C, the samples remain X-ray amorphous, and upon further processing up to 1500°C, the fibers have a crystalline β -SiC structure. The highest tensile strength was shown by β -SiC fibers heat-treated in vacuum up to 1500°C. Their strength amounted up to 2000 MPa with a fiber diameter of 10-25 microns. At a temperature of 1700°C a noticeable softening of the fibers was observed, which, according to SEM analysis, is associated with the growth of silicon carbide grains. When processed up to 1800 - 1900°C, β -SiC fibers began to sinter.

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DEFECTS, THERMODYNAMICS AND ELECTRONIC STRUCTURE OF the ORDERED RUDDLESSEN-POPPER PHASES

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Ruddlesden-Popper layered ferro-manganites are considered among promising candidates for thermochemical energy storage devices, oxygen membranes, as well as thermoelectric materials. In order to deeply understand the potential for practical application of these compounds, it is necessary to study their thermodynamic properties, as well as the features of their electronic structure. In particular, knowledge of defect chemistry and the band structure of the oxides is the basis for targeted modification of their composition and the production of materials with the desired properties.

A set of the oxides $\text{Sr}_4\text{Mn}_{2-x}\text{Fe}_{1+x}\text{O}_{10-\delta}$ ($x = 0, 0.5$ and 1) was studied in the present work. The samples were synthesized by the glycine-nitrate method and characterized using X-ray diffraction. Employing a combination of thermogravimetry and iodometric titration methods, the absolute oxygen content in the samples was determined. Coulometric titration was applied to determine the equilibrium dependencies of the relative oxygen non-stoichiometry $\delta = f(p(\text{O}_2), T)$. The calculation of the electronic spectra and thermodynamic functions of the processes of the oxygen vacancies formation was carried out within the framework of the electron density functional method (DFT).

Based on the obtained experimental data and the results of the first-principles calculations, a defect equilibrium model was developed and verified. Theoretical spectra of the density of states are calculated. It has been revealed that $\text{Sr}_4\text{Mn}_{2-x}\text{Fe}_{1+x}\text{O}_{10-\delta}$ samples have a broad range of oxygen non-stoichiometry. In this case, $\text{Sr}_4\text{Mn}_{1.5}\text{Fe}_{1.5}\text{O}_{10-\delta}$ phase has the greatest stability and oxygen capacity in the studied $p(\text{O}_2)$ range. Using the obtained $\delta = f(p(\text{O}_2), T)$ dependencies, the partial molar functions of oxygen in $\text{Sr}_4\text{Mn}_{2-x}\text{Fe}_{1+x}\text{O}_{10-\delta}$ were calculated and the thermal effects of oxygen exchange were assessed.

This work is carried out under support of Russian Science Foundation (grant №22-19-00129).

PRODUCTION SILICON CARBIDE COATINGS FOR POWER MICROELECTRONICS

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Silicon carbide is a promising semiconductor for modern power devices due to its unique properties: wide bandgap, high critical electric field strength and high saturation drift rate¹. Additionally, high thermal conductivity and thermal stability allow SiC-based devices to operate at extremely high power levels while maintaining the ability to dissipate large amounts of excess heat generated. A comparison of the properties of basic semiconductor materials is presented in the figure.

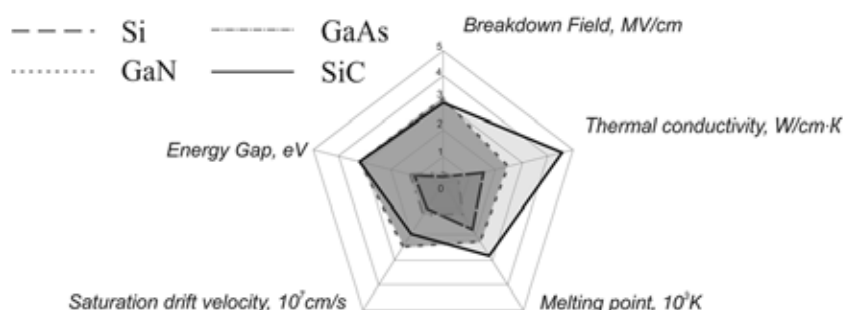


Figure 1. Basic physical properties of popular semiconductors.

Modern methods for producing SiC coatings in microelectronics are: growing crystals from a congruent melt or by sublimation; by chemical vapor deposition (CVD). An analysis of literature data² showed that CVD has a number of advantages: the quality of SiC coatings due to the use of high-purity starting compounds; constant Si/C ratio due to controlled substance content in the gas environment; continuous supply of gas mixtures of stable composition in flow-through reactors of cold storage facilities.

SiC-based devices have found application in DC motors, asynchronous motors, synchronous motors, as well as in hybrid and electric vehicles, renewable energy sources, and switching power supplies.

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EXPLORING SEMICONDUCTOR PEROVSKITE NANOPARTICLES CsBX_3 (B = Pb, Mn; X = Br, Cl): SYNTHESIS, STRUCTURE, AND OPTICAL BEHAVIOR

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Over the past years, the active development of biovisualization technologies has opened up the possibility of early detection of various diseases and diagnosis using fluorescent tomography¹. One of the promising materials considered for various biological applications is semiconductor nanoparticles, particularly those with a perovskite structure of CsPbX_3 (X = Br, I, Cl), which possess excellent physical and optical properties such as high carrier mobility, bright fluorescence in the visible spectrum, etc.².

In this study, a modified method for obtaining perovskite nanoparticles of the composition CsBX_3 (B = Pb, Mn; X = Cl, Br) is proposed³. Depending on the composition of the perovskite nanoparticles, their shape, sizes, and values of the elementary cell parameters varied. In summary, the study demonstrates the effect of changing the chemical composition of perovskite nanoparticles on the optical properties of the material.

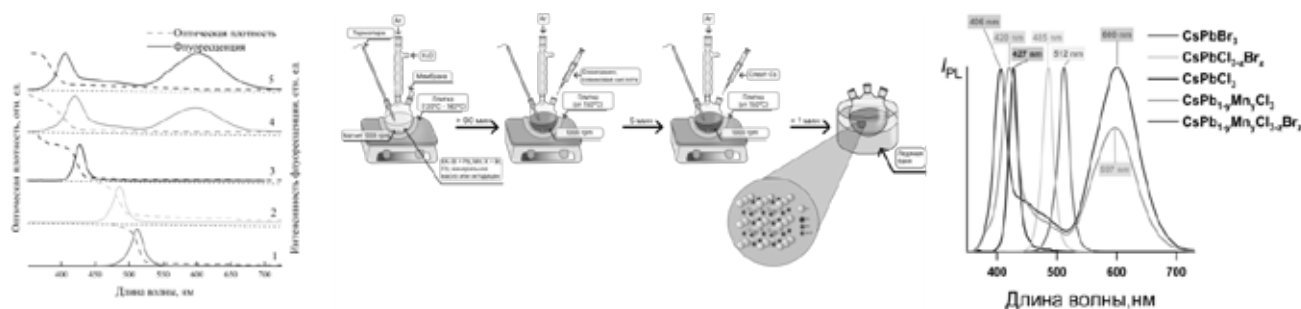


Figure 1. Absorption and emission spectra and the synthesis scheme by the hot injection method.

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BIOCIDAL ADDITIVES IN MEMBRANE TECHNOLOGY

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Non-modified and modified resin acids are valuable resources for the synthesis of imides exhibiting biocidal properties. Rosin (GOST 19113) and rosin terpene maleic resin (TU BY 600012243.087-2022) were used as initial raw materials.

It is known that rosin, as a commercial product, consists of a number of resin acids. Since rosin is a multicomponent system and its composition changes seasonally, its qualitative analysis was carried out using modern research methods - NMR spectroscopy. The quantitative composition of the identified resin acids of the used rosin, mol. %: abietic acid – 44.0; dehydroabietic acid – 5.2; isopimaric acid – 6.3; neoabietic acid – 13.6; palustric acid – 19.4; pimaric acid – 8.4 and sandaracopimaric acid – 1.0.

When heating the rosin in the presence of maleic anhydride, abietinic, neoabietic and palustric acids participate in the isomerisation process and are converted into maleopimaric acid, the remaining acids do not react. Thus, the maximum amount of maleopimaric acid formed in the reaction products may be ~ 77%. However, secondary processes leading to a decrease in its content in the mixture are not excluded¹.

New biocides can be obtained directly from purified oleoresin (turpentine), bypassing the stage of distillation into rosin and turpentine, which will reduce their cost and increase their competitiveness.

Synthesised imides are introduced into the compositions of moulding solutions for obtaining composite membranes for nano- and ultrafiltration and filtration, which exhibit biocidal properties against a wide range of microorganisms.

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The study was supported by a grant from The Belarusian Republican Foundation for Fundamental Research, joint project with Uzbekistan X23UZB-086.

LUMINESCENT PROPERTIES OF PHOTOACTIVE (*E*)-(4-ARYLBUT-1-EN-3-IN-1-YL)-*o*-CARBORANES

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Targeted synthesis of metal-free π -conjugated *C*-substituted *ortho*-carboranes is a promising direction for the development of luminescent materials with tunable emission properties. For example, (*E*)-(4-arylbut-1-en-3-in-1-yl)-*o*-carboranes **1–4** (Figure 1), prepared using the previously developed Cu(I)-catalyzed coupling of vinyl acetylene *o*-carborane with arylboronic acids, are characterized by polychromatic luminescence (Figure 2).

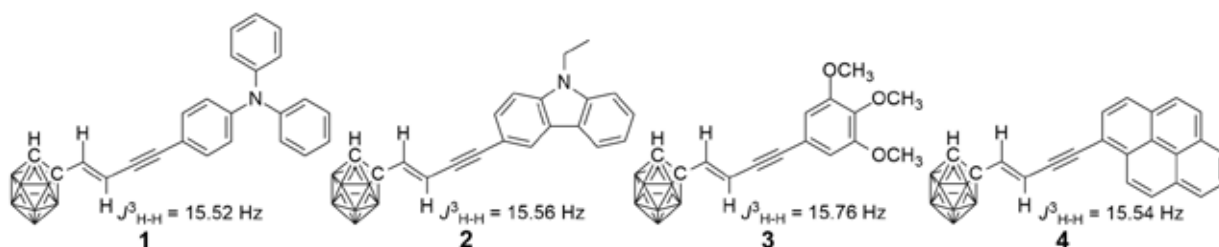


Figure 1. (*E*)-(4-arylbut-1-en-3-in-1-yl)-*o*-carboranes

In this work, quantum chemical calculations have used to find out the electronic transitions that cause the emission patterns of compounds **1–4**, including triplet states (Table 1).

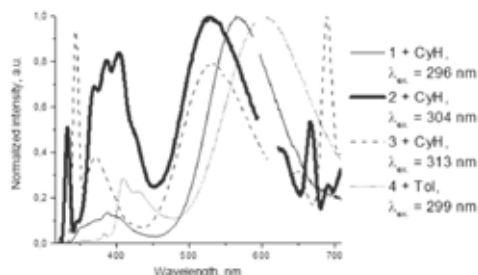


Figure 2. Emission spectra of compounds **1–4** solutions ($C = 10^{-5}$ M; 25 °C)

State	Transition	Contribution	Characteristics
$S_0 \rightarrow S_1$	HOMO \rightarrow LUMO	85%	E = 3.3241 eV $\lambda = 373$ nm $f = 1.4384$
	HOMO \rightarrow LUMO+4	5%	
$S_0 \rightarrow S_2$	HOMO \rightarrow LUMO+1	75%	E = 4.1238 eV $\lambda = 300$ nm $f = 0.0170$
	HOMO \rightarrow LUMO+2	4%	
	HOMO \rightarrow LUMO+5	4%	
$S_0 \rightarrow S_3$	HOMO-1 \rightarrow LUMO+3	9%	E = 4.4154 eV $\lambda = 280$ nm $f = 0.2145$
	HOMO \rightarrow LUMO+4	79%	
$S_0 \rightarrow T_1$	HOMO-1 \rightarrow LUMO+1	28%	E = 1.8202 eV $\lambda = 680$ nm $f = 0.00$
	HOMO \rightarrow LUMO	64%	
$S_0 \rightarrow T_2$	HOMO-7 \rightarrow LUMO+4	15%	E = 3.0284 eV $\lambda = 409$ nm $f = 0.00$
	HOMO-1 \rightarrow LUMO	23%	
	HOMO \rightarrow LUMO+4	32%	
$S_0 \rightarrow T_3$	HOMO-1 \rightarrow LUMO+3	16%	E = 3.269 eV $\lambda = 379$ nm $f = 0.00$
	HOMO \rightarrow LUMO+3	48%	

Therefore, the developed synthetic approach makes it possible to obtain promising phosphorescent luminophores for photofunctional materials.

The research was supported by a grant from the Russian Science Foundation № 24-13-20023, <https://rscf.ru/en/project/24-13-20023/>.

THE APPLICATION OF HIGH-MOLECULAR COMPOUNDS TO INCREASE THE EFFICIENCY OF ELECTROFLOTATION PURIFICATION OF CaCl_2 PROCESS SOLUTION

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In the production of calcium chloride¹ by dissolving carbonate rock in hydrochloric acid, the co-products are Fe^{3+} , Al^{3+} and Mg^{2+} chlorides. The purpose of the work is to determine the most effective type of high-molecular substances for application in the process of electroflotation (EF) and filtration (F) extraction of impurities Fe^{3+} , Al^{3+} and Mg^{2+} in the form of slightly soluble compounds from the CaCl_2 process solution. The pH of the environment of model solutions is in the pH range 6,5 – 7,0. The extraction efficiency (α , %) is presented in table 1.

Table 1.

Solution, g/l: CaCl_2 – 300; Impurities, mg/l: Fe^{3+} – 50; Al^{3+} – 10; Mg^{2+} – 10	α , % (EF)			α , % (EF and F)			C (residual), mg/l (EF and F)		
	Fe^{3+}	Al^{3+}	Mg^{2+}	Fe^{3+}	Al^{3+}	Mg^{2+}	Fe^{3+}	Al^{3+}	Mg^{2+}
Without additives	74	20	0	99,9	97	1	0,05	0,3	0,1
Superfloc C-454 (C)	77	94	18	91	93	47	4,50	0,70	5,30
Praestol 2540 (A)	81	87	41	99,7	99,9	18	0,15	0,01	8,20
Praestol 2500 (N)	38	71	5	96	93	6	2	0,7	9,4
Septapav (C)	4	6	12	95	99	12	2,5	0,1	8,8
NaDDS (A)	7	4	4	95	53	7	2,5	4,7	9,3
PEO-1500 (N)	6	4	20	99	99	9	0,5	0,1	9,1
Betapav A1214.30 (Amph.)	77	45	9	98	57	10	1	4,3	9
$i_v = 0,6 \text{ A/l}$, $t = 30 \text{ min.}$, $C(\text{surf., flocc.}) = 5 \text{ mg/l}$.									

The greatest α for impurities is achieved in the presence of flocculant Praestol 2540 (anionic). The electroflotation process is not effective with the addition of a surfactant, since the particles of the dispersed phase are formed too small (less than $50 \mu\text{m}$)². Filtration increases $\alpha \text{ Fe}^{3+}$ and Al^{3+} to 99% and higher, C (residual) – 0,15 and 0,01 mg/l, respectively.

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SYNTHESIS OF IMIDAZOTHIAZOLOTRIAZINES AND THEIR TRANSFORMATION INTO IMIDAZOTHIAZINOTRIAZINES

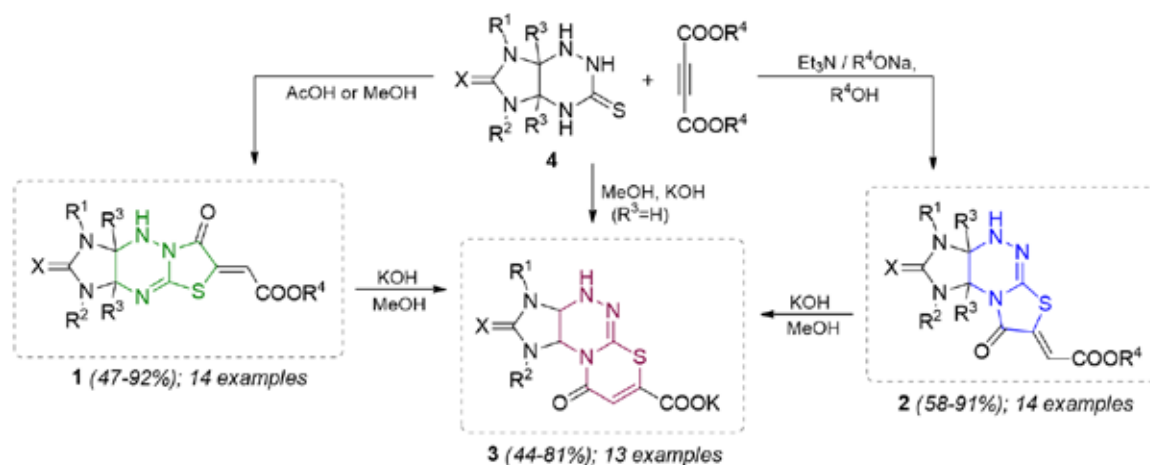
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Rearrangements and transformations of heterocyclic compounds play an important role in organic chemistry and provide broad opportunities for the synthesis of new heterocyclic systems¹.

This work proposes effective highly selective methods for the preparation of three different heterocyclic systems **1–3** based on regioselective cyclization of imidazo[4,5-*e*]triazine-3-thiones **4** with dialkylacetylenedicarboxylic acid esters and directed transformation of the resulting imidazo[4,5-*e*]thiazolo[3,2-*b*]triazines **1** and imidazo[4,5-*e*]thiazolo[2,3-*c*]triazines **2** in imidazo[4,5-*e*][1,3]thiazino[2,3-*c*]triazines **3** (Scheme).



X=O, S; R¹=Me, Et; R²=Me, Et, Ph; R³=H, Ph; R⁴=Me, Et

The conditions found for the selective formation of the starting imidazothiazolotriazines **1**, their isomerization into structures **2**, and transformation into structures **3** made it possible to obtain a wide range of compounds of each heterocyclic system in individual form.

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The study was supported by a grant from the Russian Science Foundation № 23-73-01252.

SYNTHESIS OF Ti_3SiC_2 MAX PHASE CERAMIC MATERIALS REINFORCED WITH C/SiC COMPOSITE FIBERS

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There is a pressing demand for structural ceramic materials tailored to withstand harsh operating conditions, offering prolonged service life for components in technical systems against severe factors like high temperatures, aggressive environments, and mechanical and thermal stresses. Among the prospective candidates for such applications are silicon-containing MAX phases, notably Ti_3SiC_2 .

This paper presents the outcomes of our research on synthesizing ceramic matrix composites utilizing the Ti_3SiC_2 MAX phase, reinforced with C/SiC composite fibers featuring a “core-shell” structure. An innovative approach was employed, combining processes of self-propagating high-temperature synthesis and infiltration of the reaction melt, facilitated by uniaxial hot pressing of samples at temperatures ranging between 1350–1400 °C and pressures below 5 MPa. A distinctive aspect of the technique was the utilization of reaction layer compositions comprising alternating layers of titanium foil, a polymer film laden with SiC particles, and a reinforcing tape of C/SiC composite fibers (see Fig. 1). The impact of the reinforcing fibers on the microstructure and phase composition of the resulting ceramic materials was thoroughly investigated.

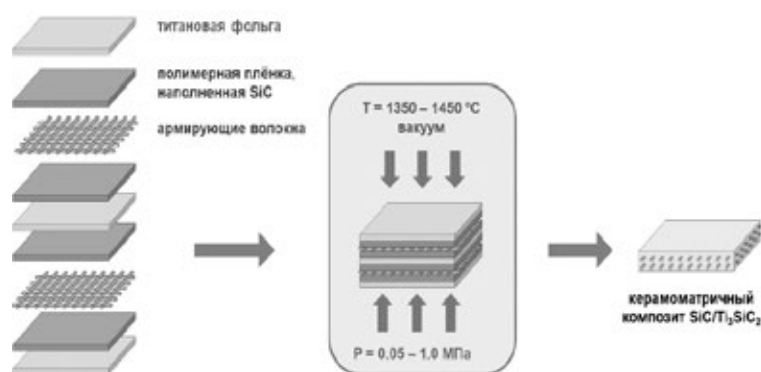


Figure 1. Scheme for obtaining ceramic material

The work was carried out with the financial support of the Russian Science Foundation, project № 23-29-00629 (<https://rscf.ru/en/project/23-29-00629/>).

APPLICATION OF TITANIUM COATING ON C/SiC COMPOSITE FIBERS USING SOL-GEL TECHNOLOGY

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Ceramic matrix composites featuring a SiC-based matrix reinforced with continuous carbon fibers exhibit enhanced strength characteristics, rendering them highly promising for harsh operating conditions. These materials find diverse applications, spanning from heat-loaded components in spacecraft and rocket engines to friction discs in high-speed railway transport. Despite their potential, carbon fiber-reinforced ceramic matrix composites face limitations in practical implementation due to the intricate manufacturing process required to achieve a homogeneous, pore-free ceramic matrix with restricted access of the matrix material between the reinforcing fibers. The primary concept of this study is to utilize fiber reinforcing elements as the only source of matrix material, enabling the formation of a homogeneous SiC-based pore-free ceramic matrix uniformly distributed within an array of regularly oriented carbon fibers through pressure sintering methods. This research showcases successful results from the introduction of sintering additives via titanium coating on C/SiC composite fibers using sol-gel technology. The sol-gel process involves utilizing complexes like $[\text{Ti}(\text{OC}_4\text{H}_9)_{4-x}(\text{O}_2\text{C}_5\text{H}_7)_x]$ as precursors, demonstrating notable effectiveness in the synthesis

The work was carried out with the financial support of the Russian Science Foundation, project № 23-29-00392 (<https://rscf.ru/en/project/23-29-00392/>).

HYDROPHOBIC MAGNETIC SORPTION MATERIALS BASED ON LAYERED DOUBLE HYDROXIDES FOR SELECTIVE EXTRACTION OF PETROLEUM PRODUCTS FROM LIQUID MEDIA

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Oil pollution of marine areas in regions of intensive fossil fuel extraction poses a serious threat to the safety of aquatic ecosystems. Oil sorbents for eliminating oil pollution must have the properties of selectivity, high capacity, and the ability to quickly collect from the surface of the water.

This work proposes a sorption material based on melanin modified with a composite coating of magnetic Fe_3O_4 particles in a matrix of layered Zn-Al-LDH double hydroxide intercalated with various organic ligands (diffraction patterns are shown in Fig. 1a). Intercalation of Zn-Al-LDH with sodium stearate allows one to achieve the required hydrophobicity property (Fig. 1b). During the modification of the material, high values of sorption capacity with respect to ESPO oil are maintained (Fig. 1c). The materials are promising for further use as oil sorbents due to their high capacity, hydrophobicity, and magnetic susceptibility.

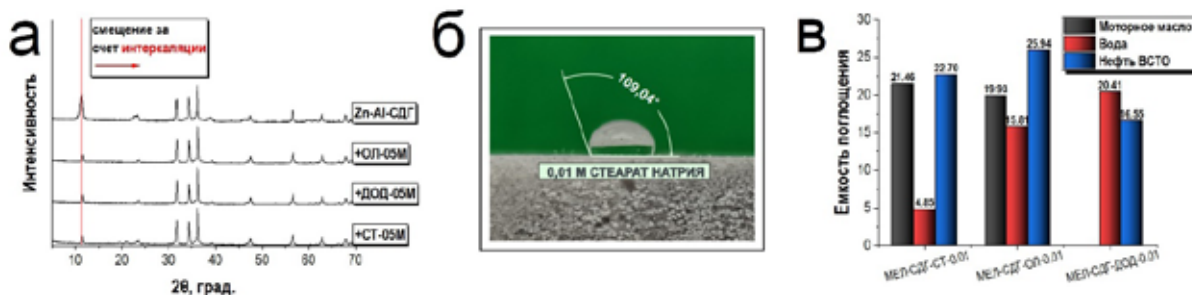


Figure 1. Diffraction patterns of modified materials (a), contact angles of the surface of the sponge material and water (b), and absorption capacity values of various absorbents by modified materials (c)

The work was supported by a grant from PJSC NK "Rosneft" within the framework of the project «Chemical engineering of selective magnetic sorption materials for the elimination of oil spills and control of environmental pollution of the environment»

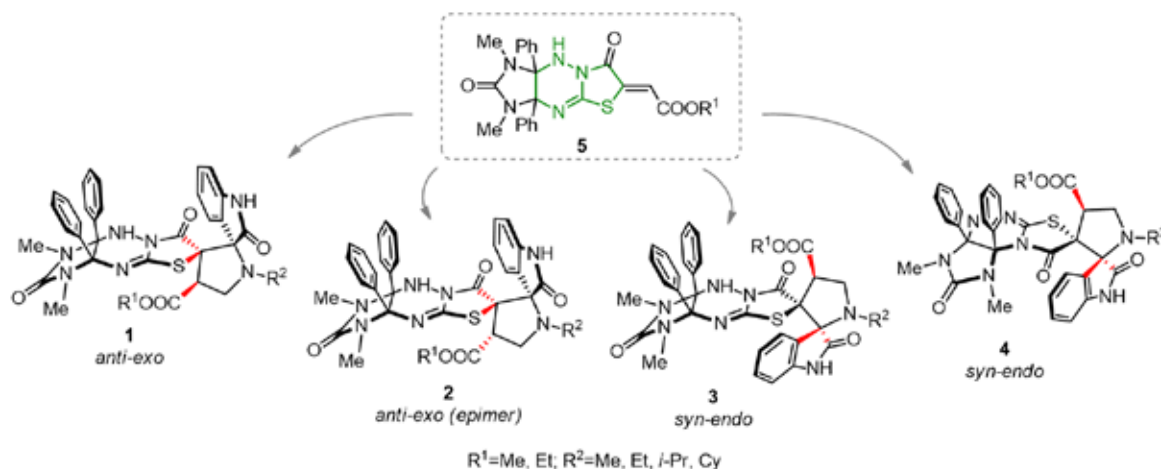
SYNTHESIS OF NEW SPIROCYCLIC OXINDOLE DERIVATIVES AND THEIR ISOMERIZATION PATHWAYS IN BASIC MEDIUM

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Spiro-linked oxindoles with a pyrrolidine ring are a valuable class of heterocyclic compounds that have become popular since the beginning of the 21st century since the discovery of valuable pharmacological properties in a number of natural alkaloids¹. Over the past two decades, synthetic spiropyrrolidine oxindoles have appeared with pronounced antiproliferative and immunomodulatory properties.

We have developed effective approaches to the targeted preparation of four series of isomeric dispirocyclic imidazothiazolotriazine-pyrrolidine-oxindoles 1–4 based on the [3+2]-cycloaddition reaction of azomethine ylides to functionalized imidazothiazolotriazines 5 and various rearrangements and transformations of the resulting cycloadducts into new isomers².



Changing the reaction conditions, as well as the order of individual stages, makes it possible to specifically obtain each of the isomers 1–4 in an individual form.

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The work was carried out with the financial support of the Russian Science Foundation, project no. 23-73-01252.

IDENTIFYING SELECTIVELY ANTIMICROBIAL METAL AND METAL-OXIDE NANOPARTICLES FOR TARGETED ERADICATION OF PATHOGENIC BACTERIA

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Microbial infections caused by bacteria, viruses, or fungi pose significant health risks, with antibiotics being the primary treatment. However, their non-selective nature and overuse contribute to antibiotic resistance [1]. Inorganic nanoparticles (NPs) offer a promising alternative due to their ability to combat infections by disrupting bacterial metabolism, damaging cell membranes, and inhibiting biofilm formation [2]. At the same time, size, shape, roughness, surface charge, and other specific properties of NPs facilitate varied interactions with bacteria compared to antibiotics which have a specific mechanism of action. This diversity in mechanisms of action of NPs poses challenges in developing a generalized theory to predict the antimicrobial effects across various bacterial strains [3]. The need becomes more pronounced when considering selectively toxic nanoparticles tailored to exert antimicrobial activity exclusively against pathogenic bacteria. These challenges spur investigations into developing theoretical models based on a data-driven approach, allowing correlation among poorly formalized parameters. Although machine learning has been used for predicting antimicrobial activity of NPs, overall, to our knowledge, no study has evaluated its capability to discover selectively antimicrobial NPs.

Our approach involved compiling comprehensive databases to characterize nanoparticles and their antibacterial activity. We trained CatBoost regressor model on unique datasets consisting of 489 samples for minimal concentration prediction. The ML model achieved a mean cross-validation R^2 score of 0.82 with RMSE of 0.46 respectively. Subsequently, we combined ML with genetic algorithm (GA), a screening platform that enables high-throughput identification of NPs with selective antimicrobial activity. With this platform we for the first time identified CuO NPs exhibiting selective antimicrobial against pathogenic *Staphylococcus aureus*. CuO NP with key parameters including NP synthesis with green methods, nanorods in shape, average NP size of 30 nm, and reaction time of 2 hours showed a minimal bactericidal concentration (MBC) of 62.52 $\mu\text{g/ml}$ against *Staphylococcus aureus* whereas it achieved MBC of 455.37 $\mu\text{g/ml}$ for non-pathogenic *Bacillus subtilis*. Hence, the selectively antimicrobial CuO NP demonstrated higher toxicity against pathogenic *Staphylococcus aureus* compared to non-pathogenic *Bacillus subtilis*, with a concentration difference of 392.85 $\mu\text{g/ml}$. The antimicrobial selectivity of NPs is attributed to a complex interaction between the NPs and diverse microbial strains. The findings of this study present a novel and promising methodology for identifying selectively antimicrobial NPs capable of eradicating pathogenic bacteria without harming non-pathogenic ones.

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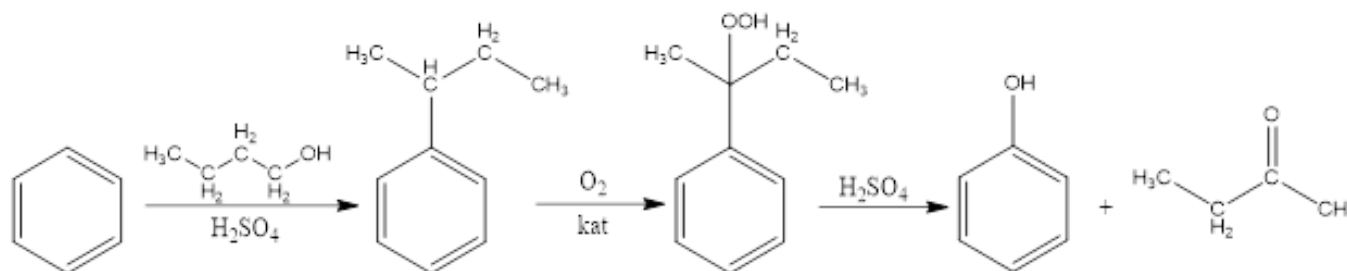
HIGHLY EFFECTIVE TECHNOLOGY FOR PRODUCING METHYLETHYLKETONE – A VALUABLE PETROCHEMICAL SYNTHESIS PRODUCT

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Methyl ethyl ketone (MEK) is a valuable, commercially important product of basic organic and petrochemical synthesis, widely used in the polymer, paint and varnish, leather, and oil refining industries. Existing technologies 1,2 for obtaining this compound are characterized by low yields and selectivity in the formation of the target product.

In this regard, an urgent task is to develop an effective technology for obtaining MEK as an alternative to existing ones and eliminating their shortcomings. A hydroperoxide method has been proposed for the production of MEK together with phenol, consisting of three stages:



Scheme 1.

The starting sec-butylbenzene was obtained by alkylation of benzenen-butanol with a yield of more than 90%. The regularities of the aerobic liquid-phase oxidation of sec-butylbenzene to its hydroperoxide in the presence of hydroperoxide initiators, organic phthalimide catalysts, and also in the absence of any additives have been studied. The influence of various technological parameters on the process of acid decomposition of sec-butylbenzene hydroperoxide to phenol and MEK was studied. The target products were isolated from the reaction mixture in yields of over 80%. The structures of the intermediate and target products were confirmed using modern physico-chemical methods of analysis. Mathematical (kinetic) models of the processes of sec-butylbenzene oxidation to hydroperoxide and its decomposition have been compiled.

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COMPOSITE BIO-CERAMIC MATERIALS FOR THE ELIMINATION OF BONE TISSUE DEFECTS

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Modern trends in medical material science, particularly in the area of import substitution, are leading to the search for alternatives to obtaining biomaterials that are both effective and affordable. One such alternative is the use of silicate bioceramic materials, which have shown to be more bioactive in in vitro and in vivo tests than calcium phosphate ceramics. Ceramics incorporating both calcium phosphate and silicate components also have a synergistic effect. Typically, these composite materials are created using bioglass powders. The application of an aqueous solution of sodium silicate ($\text{Na}_2\text{O} \cdot n\text{SiO}_2$) as a binder allows for the creation of highly biocompatible ceramic materials based on synthetic calcium phosphates (CP). This results in a unique set of properties for the final product.

In this work, we studied a new approach to obtaining a composite bio-compatible ceramic material based on synthetic calcium phosphates and an aqueous solution of sodium silicate, intended for the elimination of bone tissue defects.

Ceramic biomaterials were prepared from high concentration suspensions based on synthetic calcium phosphates: hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, HA), tricalcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$, TCP), and calcium pyrophosphate ($\text{Ca}_2\text{P}_2\text{O}_7$, CPP).

Ceramic materials, after firing at 1000°C , included sodium calcium silicate, $\text{Na}_6\text{Ca}_3\text{Si}_6\text{O}_{18}$, and a small amount of the β -renewite phase, $\beta\text{-NaCaPO}_4$. The relative density of the materials obtained after firing at this temperature was $\approx 28\%$. It has been determined that both the bending and compressive strengths correspond to the strength limit for spongy bone. In vitro tests confirmed biocompatibility.

In the course of the work, a new method for obtaining composite bio-ceramics based on synthetic calcium phosphate and an aqueous solution of sodium silicate has been proposed to eliminate bone tissue defects.

TOPOLOGICAL ANALYSIS OF METAL-ORGANIC FRAMEWORKS FOR DRUG DELIVERY

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Metal-organic frameworks (MOFs) are widely used for drug delivery. An important parameter for the sorption of drugs is the pore size¹ and the size of the channels. In our study, topological analysis of MOFs was carried out to evaluate their applicability for some active molecules used for cancer treatment.

The research was supported by the Strategic Academic Leadership Program of the Southern Federal University ("Priority 2030")

INVESTIGATION OF SORPTION-KINETIC PROPERTIES OF A 5-FU DRUG DELIVERY SYSTEM BASED ON CALCIUM SILICATE

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Drug delivery systems (DDS) represent a new method of drug administration that reduces toxicity and increases the effectiveness of treatment and limits the area of drug administration. This approach is especially relevant during chemotherapy.

One of the most used drugs for chemotherapy is 5-fluorouracil (5-FU). Its use is associated with myelosuppression, hepato-, nephro- and cardiotoxicity, palmar-plantar erythrodisesthesia.

Reducing the toxic effect of 5-FU is possible with the use of targeted drug delivery systems. The approach consists in sorption with a biocompatible matrix of the drug, immersion into the cavity followed by a slow effect of 5-FU on the tumor. By reducing the dose and localization of exposure, it is assumed to minimize the negative consequences¹.

The work involved the synthesis of calcium silicate by various methods (microwave and hydrothermal treatment). The sea urchin shell was also used as a source of calcium. The main characteristics of the obtained DDS are presented in Table 1.

Table 1 – Comparison of the main indicators for the samples

	MV-CaSiO ₃ (sea urchin)	MV-CaSiO ₃	GT-CaSiO ₃
Specific surface area, m ² /g	3,700	6,392	4, 211
Sorption capacity at pH =3, mg/g	0,651	0,750	0,762
The duration of leaching of the drug	11 days	0,17 days	11 days
Amount of desorbed 5-FU	40%	14%	41%

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SYNTHESIS OF POLYMER FORMS OF PHOSPHORUS UNDER THE INFLUENCE OF ACCELERATED ELECTRONS

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Red phosphorus, a polymeric allotropic modification of phosphorus, has a number of industrial applications. [1]. The most widely used high-temperature method for producing red phosphorus is characterized with high duration, heat loss, cumbersome equipment, fire hazard, and in the presence of water vapor is accompanied by the formation of toxic phosphine and phosphoric acids [2].

Previously, the radiation-chemical synthesis of phosphorus-containing polymers under γ - and β -radiation was studied, conversion of white phosphorus up to 87% was achieved, depending on the composition of the reaction medium and the type of ionizing radiation [3–5]. The main disadvantage of these processes is the potential danger of radio-nuclides used as a source of high-energy radiation for humans and the environment. An alternative way to initiate the polymerization of elemental phosphorus may be the irradiation with accelerated electrons [6].

In this work, samples of purified elemental (white) phosphorus in the aqueous medium were irradiated with accelerated electrons using accelerators LINS-02-500 (IPCE RAS) and UELV-10-10-C-70 (CJSC «INTECH»), absorbed dose was 150–4000 kGy, the conversion was 5,4–49,1 %. It should be noticed that the tendency of the process rate slowing down was observed at absorbed doses higher than 2000 kGy. In the future, it is planned to investigate the influence of the reaction medium parameters on the degree of conversion, with the aim to increase it.

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AN INVESTIGATION OF THE STRUCTURAL FEATURES OF NOVEL SYNTHETIC LAYERED SULFIDE-HYDROXIDE OF THE VALLERIITE GROUP

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We present the results of studying the structure of novel synthetic sulfide-hydroxide prepared under hydrothermal conditions in which synthetic valleriites and tochilinites were previously obtained¹. Based on the powder XRD data and the SAED pattern from a single particle, we conclude that the new phase is incommensurate hybrid structure. Like valleriites, it consists of alternating turbostratically disordered 2D layers of LDH- and chalcocite-like sublattices with common “c” cell parameter (fig. 1).

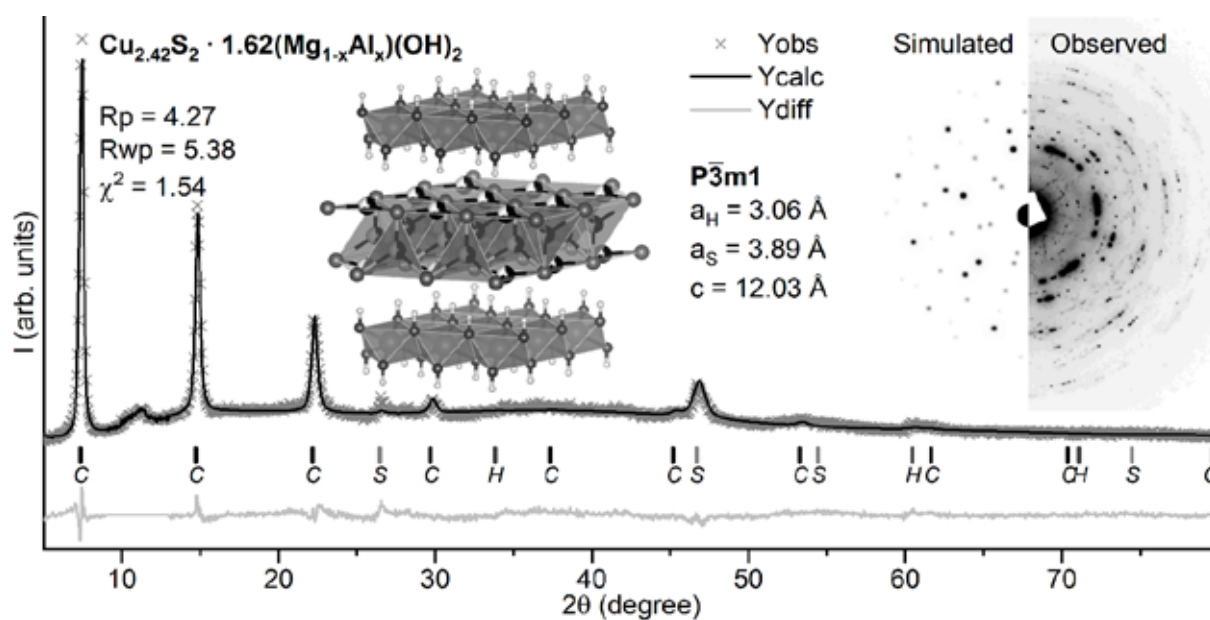


Figure 1. Powder XRD profile, single particle SAED pattern and proposed structure of novel sulfide-hydroxide phase

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AN INVESTIGATION OF CORRELATION EFFECTS IN HIGHLY CONCENTRATED MAGHEMITE NANOPARTICLES HYDROSOLS

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We present the results of studying highly concentrated (up to ~ 30 vol.%) hydrosols of maghemite nanoparticles exhibiting remarkable anomalous aggregation and sedimentation stability. Nanoparticles and sols were characterized by XRD, XPS, TEM, IR and UV-VIS-NIR spectroscopy, DLS and SAXS. Their rheological behavior and magnetic properties were studied as well. An ordering of the particles driven by electrostatic repulsion of their ionic atmospheres was proposed based on the appearance of an oscillations on the SAXS curves which is also accompanied by a significant increase in dynamic viscosity.

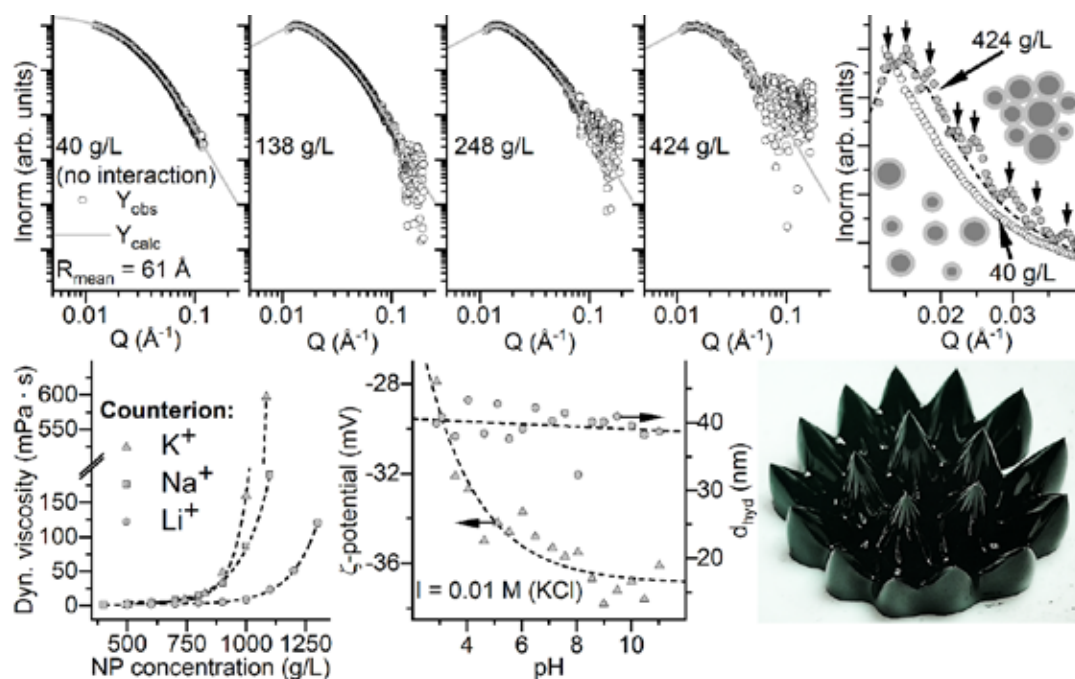


Figure 1. SAXS curves of hydrosols of different concentration, concentration dependences of viscosity for sols with different counterions and the results of DLS measurements for diluted (~ 1 g/L) hydrosol

This research was funded within the state assignment to the Institute of Chemistry and Chemical Technology SB RAS (project FWES-2021-0014).

COMPLEX PROCESSING OF ASH FROM FUEL OIL COMBUSTION WITH VANADIUM AND NICKEL EXTRACTION.

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During oil refining, vanadium and nickel accumulate in fuel oil, the combustion of which produces a significant amount of environmentally hazardous vanadium-containing ashes^{1,2}. This article is devoted to the processing of ash sludge from the Murmansk TPP - material from the high-temperature zone of the boiler unit with the following chemical composition, %: 9,62 V_2O_5 , 2,72 NiO, 45,12 Fe_2O_3 , 5,38 P_2O_5 , 2,53 CaO, 2,44 SiO_2 , 1,89 Al_2O_3 , 1,36 MgO, 1,43 etc., 27,6 calcination losses. It was found that with direct leaching with water, the degree of extraction of V_2O_5 and NiO was 4.4% and 0.6%, respectively, with sulfuric acid - up to 75.0%. Calcination of ash and sludge at 900 °C without additives makes it possible to extract up to 40,8% with water leaching, and 46,3% with sulfuric acid leaching. Nickel is practically not recovered after calcination due to the formation of nickel ferrite. The best results in extracting V_2O_5 were achieved by oxidative roasting with sodium carbonate. It was experimentally established that at a temperature of 900 °C and 24% Na_2CO_3 , the degree of extraction of V_2O_5 into an aqueous solution was 92,0%, sulfuric acid washing increases the extraction to 96.0%. Under these conditions, a precipitate of V_2O_5 with a purity of 98.5% was obtained from an aqueous solution by precipitation of ammonium polyvanadates. The residue after leaching and sulfuric acid washing has the following composition, %: 86.68 Fe_2O_3 , 5,58 NiO, 1,15 K_2O , 1.02 SiO_2 , 0,98 Al_2O_3 , 0,85 V_2O_5 , 0,84 MgO, 0,60 SO_3 , 0,58 MnO, etc. and can be processed in ferronickel production.

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THE EFFECT OF SYNTHESIS CONDITIONS ON THE COLLOID-CHEMICAL PROPERTIES OF MOLYBDENUM-VANADIUM BLUE SOLS WITH A MOLAR RATIO OF [Mo]:[V]=90:10

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Molybdenum-vanadium blues are oxygen-containing compounds in which metals are present in various oxidation states (Mo^{+5} , Mo^{+6} , V^{+4} , V^{+5}). Of particular interest are such compounds in the form of hydrosols - stable dispersions of nanoparticles due to the prospect of their use in the synthesis of catalysts, sensors, membranes, fuel cells, and materials involved in various biochemical reactions.

The aim of this work is to synthesize molybdenum-vanadium blue sols with a composition of $[\text{Mo}]:[\text{V}]=90:10$ and to investigate the effect of synthesis conditions on their main colloid-chemical properties.

The synthesis of molybdenum-vanadium blues was carried out by the reduction of ammonium heptamolybdate and ammonium metavanadate solutions with ascorbic acid in an acidic medium. During the syntheses, the content of the reducing agent ($[\text{R}]/[\text{Mo}+\text{V}]$ from 0.2 to 5.0) and the pH value of the dispersion medium (pH from 1.0 to 2.5) were varied. The obtained samples were characterized using potentiometry, spectrophotometric analysis, and photon correlation spectroscopy.

It was found that aggregative stable molybdenum-vanadium blue sols can be synthesized at a ratio of $[\text{R}]/[\text{Mo}+\text{V}] \leq 1$ within a pH range of 1.5 to 2.2. At pH values of 1.0 and below, coagulation is observed in all samples, while at pH 2.5 and above, particle dissolution (cluster decomposition) is observed. Excessive reduction of Mo and V ions occurs at higher concentrations of the reducing agent ($[\text{R}]/[\text{Mo}+\text{V}] \geq 2$), making it impossible to obtain stable dispersions.

Aggregative stable hydrosols of molybdenum-vanadium blues contain particles/clusters with a predominant hydrodynamic radius of 4 nm. The maximum absorption is at 745 nm, corresponding to toroidal particles of the Mo_{154-x} family. The developed synthesis allows for obtaining dispersions with an initial concentration of 1.0 wt. %, which can be increased up to 20 wt. % if necessary.

SYNTHESIS OF BRANCHED PEG-CONTAINING LIPID

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Cationic liposomes are biocompatible, non-toxic and easy to chemically modify nanoparticles. Therefore, they have found wide application as promising systems for the delivery of therapeutic nucleic acids (NA) in gene therapy. However cationic liposomes undergo rapid clearance due to the influence of the body's immune system, which leads to low transfection efficiency of NA.¹

This problem can be solved by introducing polyethylene glycol (PEG)-containing lipids into the structure of cationic liposomes. Due to the oxygen atoms of PEG directed outward, a shielding hydrate shell is formed around the cationic liposomes, which prevents from adsorption of plasma proteins on their surface and activation of the immune response.

Previously, lipids with linear PEG were used to modify cationic liposomes. The replacement of linear PEG with branched PEG led to the formation of a dense hydrophilic shell. In addition, branched PEG lipids, unlike linear ones, did not cause the immune response of the body upon repeated administration.²

The aim of our work was the synthesis of a branched PEG-containing lipid. For this purpose, diglyceride was selected as the starting compound, which is necessary for incorporation into cationic liposomes. The synthesis included successive stages of activation of diglyceride, the introduction of linear PEG with free amino groups as a spacer, the addition of linkers and, at the final stage, branched PEG.

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THERMODYNAMICS AND KINETICS OF THE ISOTOPIC EXCHANGE REACTION BETWEEN WATER AND CHLOROFORM

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Deuterated solvents are used to determine the structure of organic compounds by NMR spectroscopy as well as standards for mass spectrometry applications.

In this work, aimed at producing deuterated chloroform by isotope exchange in the chloroform – heavy water system, the temperature dependence of the separation factor α and the observed pseudo-first order reaction rate constant k were studied.

Experiments were carried out using an one-time equilibration method at a molar ratio $\text{CHCl}_3 - \text{D}_2\text{O}$ of 1:7 in the presence of sodium hydroxide. The experiments were carried out in 4 parallel operating temperature-controlled glass reactors, equipped with magnetic stirrers, in the temperature range 298 – 323 K. The concentration of deuterium in heavy water was 90 % at. Sampling for kinetic studies was carried out from intermediate reactors; in the last reactor the process was carried out until a quasi-equilibrium concentration of deuterium in chloroform was established. Isotope analysis of chloroform samples was performed using FTIR spectrometry on a Thermo Scientific Nicolet iS10 instrument.

Figure 1 shows the kinetic curves of the isotope exchange reaction at various temperatures.

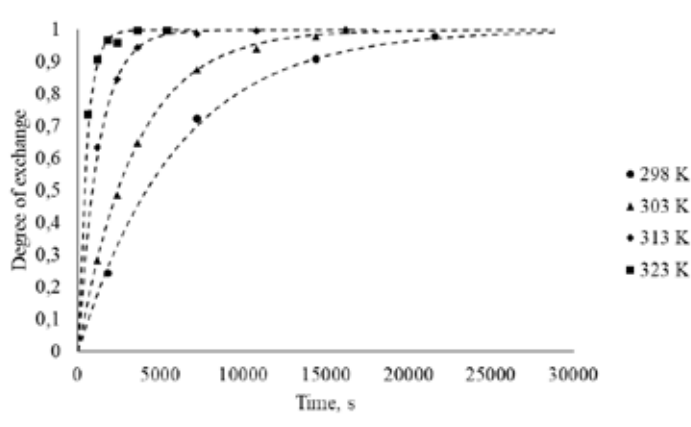


Figure 1. Dependence of the degree of exchange on time at various temperatures

It was found that the value of k with increasing temperature from 298 to 323 K increases from $(1.7 \pm 0.1) \cdot 10^{-4}$ to $(1.9 \pm 0.1) \cdot 10^{-3} \text{ s}^{-1}$. The calculated value of the separation factor at a temperature of 298 K was 1.032 ± 0.004 .

The work is performed in the framework of the development program “Priority-2030” of the Mendeleev University of Chemical Technology of Russia.

THE EFFECT OF SHOCK-COMPRESSED GAS ON HEAT TRANSFER PROCESSES IN THE WELDING GAP IN FRONT OF THE CONTACT POINT DURING EXPLOSION WELDING

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When welding large-sized metal plates by explosion, an area of shock-compressed gas heated to several thousand degrees is formed in the gap between them during the collision process. As a result of intensive heat exchange of the supersonic gas flow with the surfaces of the welded plates, their surface layers are heated even before impact, which can lead to an increase in the number of melts, a change in the parameters of the wave profile and, as a result, to a decrease in the quality of the welded joint.

In this work, the effect of thermal action from shock-compressed gas when filling the welding gap with various media (air, inert gases) was determined using the thermocouple method. It has been established that the composition of the gas medium in the gap does not significantly affect the power of the heat flow from the shock-compressed gas to the surfaces of the welded plates. Thus, the calculated values of the heat flux power in air and helium are significantly different and amount to 0.1 and 0.002 GW/m², respectively. The experimental values of the heat flux in both cases differ by no more than 30-40% and average 0.4 and 0.3 GW/m² for air and helium, respectively. Most likely, this is due to the presence of colliding plates of cumulative origin in the gap of metal particles, the thermal contribution from which is not taken into account in the calculation. Using targets placed in the gap, metal particles of varying degrees of dispersion (micron and submicron size) were found forming a continuous coating with a thickness of up to several tens of microns on the surface of the targets. These particles act as an additional permeable piston moving at a speed greater than the speed of the contact point), which increase the temperature of the shock-compressed gas, the speed of the shock wave, and, ultimately, have a predominant effect on the thermal effect of preheating the plates.

SILICA-BASED AEROGELS WITH TUNABLE PROPERTIES: THE HIGHLY EFFICIENT AMPHOTERIC F-CONTAINING CATALYSTS FOR PREPARATION AND LOOK INSIDE THEIR STRUCTURE

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In recent years, there has been an increased interest in porous materials especially. This is due to the use of such materials in various fields of science, technology and medicine. Aerogels, silica aerogels in particular, have a unique set of properties: high specific surface area and porosity at low density; high rates of heat and sound insulation; optical transparency; low dielectric constant; low Young's modulus; thermal stability, etc.

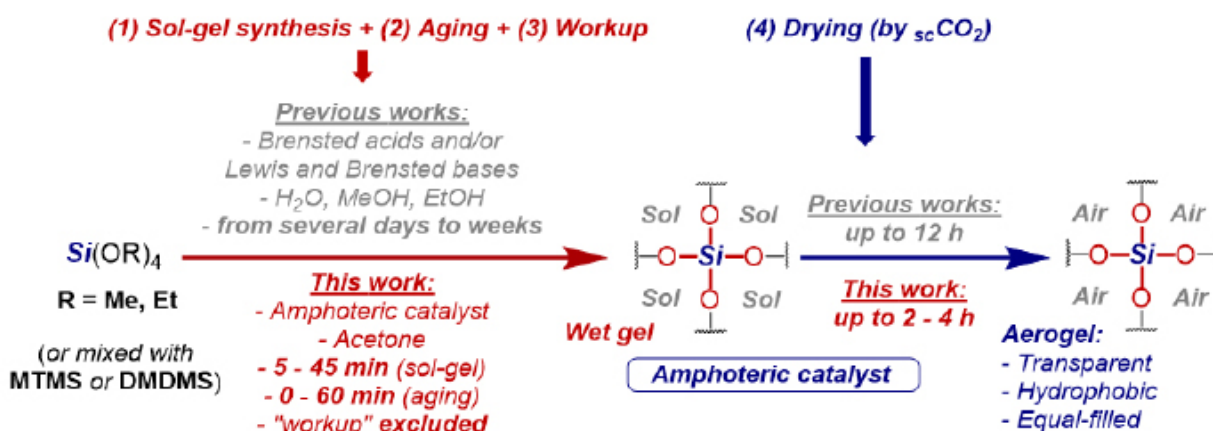


Figure 1. Silica-based aerogels production.

This work presents a solution to fundamental and practically important problems in the production of silica-based aerogels: reducing labor intensity and expensiveness. Based on this, main focus was paid on the sol-gel process (Fig. 1).¹ To obtain aerogels, we chose highly efficient amphoteric F-containing catalysts, which allowed us not only to reduce the stage of formation of a (wet) gel to 5 minutes, but also to completely eliminate stages of "maturation" and gel processing.² This approach makes it possible to quickly obtain both classical opaque and transparent and transparent superhydrophobic silica-based aerogels.

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This work was supported by a grant of the RSF, project № 19-73-10172-II.

THE ELECTRICALLY CONDUCTIVE PROPERTIES OF CERAMICS ZrO_2 -4 MOL. % Y_2O_3 -4 MOL. % Sc_2O_3 DEPENDING ON THE METHOD OF OBTAINING THE INITIAL POWDERS

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The purpose of this work was to determine the electrically conductive properties of ceramics made from powders of the same chemical composition ZrO_2 -4 mol. % Y_2O_3 -4 mol. % Sc_2O_3 , but obtained in different ways, and therefore having different properties. Ceramics were made from powder No. 1, obtained by reverse ammonia co-deposition followed by cryogranulation in liquid nitrogen, and powder No. 2 (nanostructured), obtained by nitrate-organic synthesis, annealed subsequently at 900 ° C. For this purpose, the powders were cold pressed at 245 MPa, and then the samples were sintered at 1650 ° C. The electrical resistance of the samples was measured using a two-probe alternating current method at a frequency of 20 kHz in the range of 873-1173 K, and the electrical conductivity and activation energy were calculated. The samples were then kept in an oven. The first 3000 hours at 650 ° C, the next 1000 hours at 950 ° C. After every thousand hours, the same measurements and calculations were performed. The measurement results are shown in Figure 1.

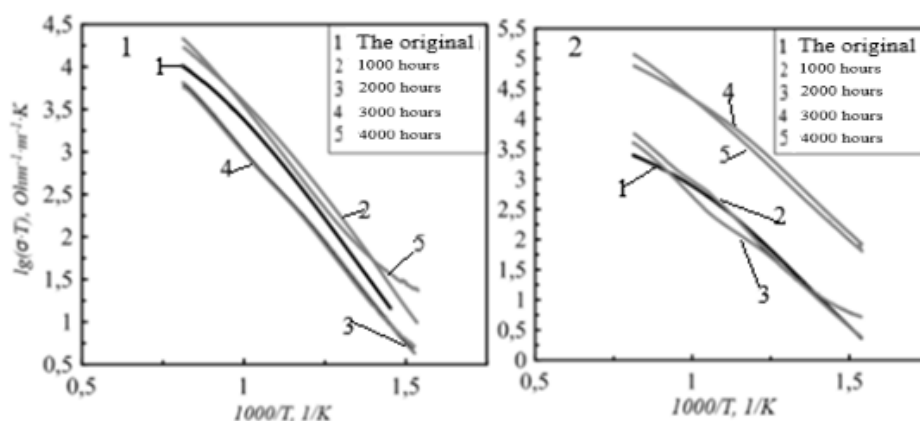


Figure 1. Temperature dependences of the electrical conductivity of ceramics before and after high-temperature exposure: 1 – sample No. 1; 2 - sample No. 2

The results showed that ceramics made from nanostructured powder No. 2 did not undergo degradation: its electrical conductivity increased by 30 and 40 times after 3000 and 4000 hours, respectively.

THE EFFECT OF THE PRODUCTION METHOD ON THE PROPERTIES OF POWDERS OF THE SAME COMPOSITION OF ZrO_2 –4 MOL. % Y_2O_3 –4 MOL. % Sc_2O_3

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The goal of this work was to obtain powders of the same chemical composition ZrO_2 –4 mol. % Y_2O_3 –4 mol. % Sc_2O_3 in different ways, in order to further evaluate the effect of the properties of powders, which depend on the production method, on the electrically conductive properties of ceramics made from these powders.

Powder No. 1 was obtained by reverse ammonia co-precipitation followed by cryogranulation in a liquid nitrogen medium. The method of nitrate-organic synthesis was used for powder No. 2. Both powders were annealed at 900 °C, No. 1 – for 1 hour, No. 2 – for 5 hours.

In powder No. 1, the structure consisted of 95 and 5% of the high-temperature cubic and monoclinic phases of zirconium dioxide, respectively, in powder No. 2 - only of the high-temperature cubic phase. Both powders were characterized by strong agglomeration. Powder No. 1 consisted of agglomerates consisting of particles with a size of ~100-300 nm (Fig. 1, a). In powder No. 2, the particles forming agglomerates were even smaller – about 20-50 nm (Fig.1, b).

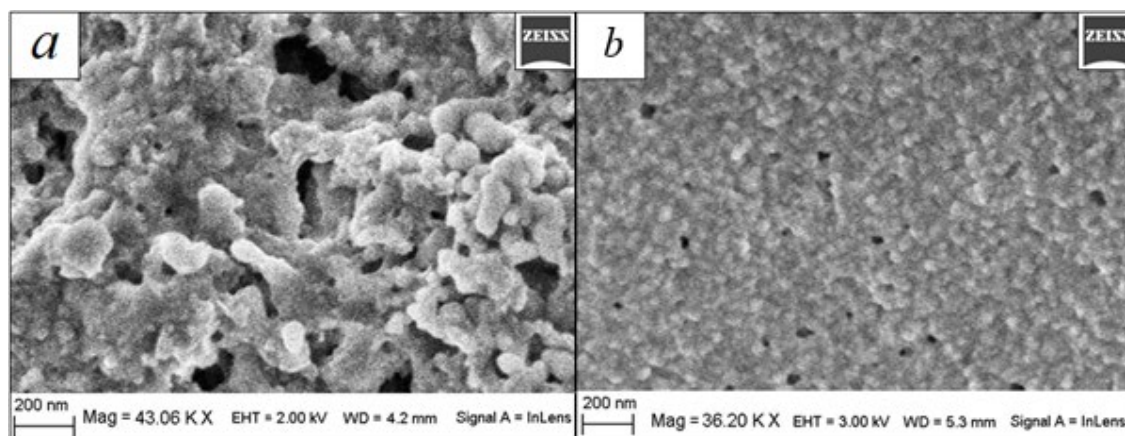


Figure 1. SEM image of powders ZrO_2 –4 mol. % Y_2O_3 –4 mol. % Sc_2O_3 : a – obtained by ammonia co-precipitation followed by cryogranulation; b - obtained by nitrate organic synthesis

Subsequently, the powders were meant to produce ceramics and determine its electrically conductive properties.

THE TECHNOLOGY OF PROLONGED NITROGEN AND COMPLEX FERTILIZERS USING WASTE FROM VARIOUS INDUSTRIES AND EVALUATING THEIR AGROCHEMICAL EFFICIENCY

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The main potential benefits of slow-acting nitrogen fertilizers are: more efficient use of nitrogen, availability of nutrients throughout the growing season, reduction of eutrophication of reservoirs, etc. The main types of prolonged fertilizers are urea-formaldehyde fertilizers (CFCs) and encapsulated fertilizers coated with various insoluble compounds ¹⁻³. CFCs are mainly used to fertilize lawn grasses and are added to many nutrient media.

The essence of our proposed technology of prolonged fertilizers is the «sealing» of nitrogen and potassium compounds $[\text{NH}_4\text{NO}_3, (\text{NH}_2)_2\text{CO}, \text{K}_2\text{SO}_4, \text{KHSO}_4]$ with «Sorel cement» $[\text{nMg}(\text{OH})_2 \cdot \text{Mg}(\text{NO}_3, \text{SO}_4) \cdot \text{mH}_2\text{O}]$, the components of which are batteries ^{4,5}. The main sources of magnesium oxide and salts are caustic magnesite – « $\text{MgO} + \text{MgCO}_3$ » and waste acid mixtures – « $\text{HNO}_3 + \text{H}_2\text{SO}_4$ » (waste from the production of refractories and cellulose nitrate).

Changing the ratio of «fertilizer:Sorel cement» it is possible to reduce the rate of dissolution of granules in accordance with the duration of the growing season (the rate of dissolution of granules is 10-100 times less, the strength of granules is 2-3 times higher, the pH value is 8-10).

Agrochemical tests have shown that in vegetation experiments the yield increase of the main crops (wheat, barley) reaches 10-20 %, and feed (Sudanese grass, rapeseed) – 20-30 % (in field experiments in the Republic of Tatarstan, an increase in the wheat harvest – 15 %).

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STUDY OF SIZE AND SPECTRAL CHARACTERISTICS OF SILVER NANOPARTICLE COMPLEXES WITH THE ANTIBIOTIC DAUNOMYCIN AND ERYTHROMYCIN AND THE BIOPOLYMER DEXTRANE

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One of the approaches to increasing the effectiveness of the antibiotics daunamycin (DM) and erythromycin (EM) and reducing their toxicity is the complexation of antibiotics with silver nanoparticles (AgNPs) and the biocompatible polymer dextran (Dex) as a stabilizer.

Ag NPs. were obtained as a result of the reduction reaction of silver nitrate with sodium borohydride. Dextran with MW of 15000, 40000, 70000 and 110000 was used as stabilizers for Ag NPs. It was found that these antibiotics by themselves do not stabilize AgNPs.

The concentrations of the components were: NPs-Ag – 0.005 wt.%, polymer – 0.1 wt.%, antibiotic – 0.005 wt.%.

Complexes of dextran-stabilized AgNPs with antibiotics were prepared in two ways:

1st method: the synthesis reaction of silver NPs was carried out in the presence of a mixture of dextran and antibiotic;

method 2: the synthesis reaction of silver NPs was carried out in the presence of dextran, and the antibiotic was added the next day after the synthesis of Ag NPs.

The sedimentation and aggregation stability of aqueous dispersions of AgNPs stabilized with dextran of different molecular weights was studied. The use of Dex silver NPs of various molecular weights in the range $(15-110) \times 10^3$ as a stabilizer was practically not accompanied by a change in the position of the SPR absorption band in the region $\lambda \sim 400$ nm.

Measurements of the hydrodynamic radius (R_h) of (NP_{Ag}+Dex) by the DLS method showed that the sizes of NPs decreased by half (from $R_h=15$ nm for $M_{Dex}=15 \times 10^3$ to 7 – 8 nm) as the molecular weight of the stabilizer increased and approached the size of “pure” Dex.

The dependences of the hydrodynamic sizes on the MW of Dex for Ag:Dex:EM complexes synthesized by methods 1 and 2 are similar, i.e. the presence of EM did not significantly affect the process of stabilization of Ag NPs by Dex macromolecules. The dependence $R_h=f(MMDex)$ for the system with DM repeated the dependence for the system with EM (method 2), which indicates the similarity of the stabilization mechanisms in these cases.

NANOCOMPLEXES OF ANTHRACYCLINE ANTIBIOTICS DAUNOMYCIN AND DOXORUBICIN WITH SELENIUM NANOPARTICLES AND POLYVINYL PYRROLIDONE

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One of the approaches to modifying antibiotics is to obtain complexes based on antitumor antibiotics, nanoparticles of biogenic elements and biocompatible polymers. Selenium (Se) is especially interesting because it itself has antitumor activity. Unfortunately, Se nanoparticles are hydrophobic and do not form stable aqueous solutions. It was shown that PVP is an effective stabilizer of Se NPs in aqueous solution.

Se nanoparticles were synthesized by the reaction between selenic (H_2SeO_3) and ascorbic ($\text{C}_6\text{H}_8\text{O}_6$) acids.

The resulting nanoparticles were sedimentationally unstable and precipitated after 5-10 hours. To obtain a nanocomplex with DM or DOX, a synthesis method was developed with preliminary stabilization of selenium nanoparticles with PVP, followed by the introduction of an antibiotic, at atmospheric pressure and a temperature of 200°C.

It was found that the OH group present in the molecular structure of DOX did not affect the sizes of (PVP-Se)-DOX ternary nanocomplexes compared to (PVP-Se)-DM nanocomplexes. In this case, nanocomplexes were formed of a fairly small size: with Rg from 40 to 60 nm and Rh from 20 to 70 nm.

The presence of an OH group in the aglycone of the DOX molecule, which promotes hydrophilization of this part of the molecule, led to the formation of (PVP-Se)-DOX nanocomplexes with a looser, leakable shell compared to (PVP-Se)-DM nanocomplexes. Moreover, the width of the shell of (PVP-Se)-DOX nanocomplexes increased with increasing Se concentration.

The data obtained can serve as the basis for further development of a method for the synthesis of nanocomplexes in order to create drugs based on anthracycline antibiotics modified by nanoparticles, which have low toxicity compared to the original antibiotics, while maintaining their biological activity.

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SPECTRAL PROPERTIES OF CHLORINATED TIN PORPHYRINATE IMMOBILISED ON SILVER NANOPARTICLES

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Metallic nanoparticles (NPs) have unique physicochemical and optical properties, which makes them attractive objects for a wide range of applications in various fields of science and technology. For example, metallic nanoparticles have high surface activity and are able to catalyse reactions, modify the optical properties of materials, and can be used in sensors, biomedicine and other fields. Nanomaterials have high specific surface area, making them efficient adsorbents and platforms with unique properties¹.

Porphyrins are macroheterocyclic compounds which are capable of forming complexes with metals. In the present work, a tin complex with tetraphenylporphyrin having two chloride extraligands (SnCl_2TPP) was chosen. The aim of the work was to establish the regularities of interaction of silver NPs with a diameter of 20-30 nm with SnCl_2TPP by resonance light scattering, which allowed us to describe the spectral and dimensional characteristics of porphyrin-modified nanoparticles. Electron absorption spectroscopy, spectrofluorimetry and electron microscopy were also used to investigate the interaction. The electronic absorption spectra of the hybrid nanoparticles show a band shift compared to the bands of individual nanoparticles and pure porphyrin, while the formation of SnCl_2TPP molecular aggregates is not observed.

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SPECTRAL PROPERTIES OF HYBRID COMPLEXES BASED ON HEXAMOLYBDENUM AMMONIUM TETRAPYRROLES AND HEXAMOLYBDENOMETALLATES

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Porphyrins are a class of tetrapyrrole compounds, many of which occur in nature, such as chlorophyll, corrin in vitamin B₁₂ and haem in haemoglobin and myoglobin. Porphyrins are involved in a multitude of biological processes and are promising compounds for medical applications¹.

The presence of a number of interaction and binding moieties in the molecules of porphyrins and their metal complexes, such as unshared electron pairs of heteroatoms, electron vacancies of the central metal cation, and functional groups of peripheral substituents, provide ample opportunities for the formation of hybrid structures involving other molecules, such as heteropolymetallates.

In this work, the interaction of hemin and metal complexes (M = Zn, SnCl₂, 2H) of tetraphenylporphyrin derivatives with heteropoly compounds in aqueous media was comparatively studied. The formation of hybrid organic-inorganic structures in the case of ammonium hexamolybdenometallates was observed by electron absorption spectroscopy. Comparison of the spectra of individual compounds and their mixtures shows that the combined presence of organic and inorganic components in solution leads to the formation of hybrid structures with a stoichiometric composition of 1:1 and a binding constant of 10⁴-10⁶ l/mol.

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PHOTOCHEMICAL PROPERTIES OF HYBRID STRUCTURES BASED ON PORPHYRINS AND HETEROPOLYCOMPOUNDS

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The interaction of hemin (Fe (III) complex with protoporphyrin IX, FePP) and the Zn (II) complex of tetra(4-pyridyl)porphyrin (ZnTPP) with hexamolibdenonicate anions (sodium hexamolybdenonicate crystalline hydrate $\text{Na}_4[\text{Ni}(\text{OH})_6\text{Mo}_6\text{O}_{18}]\cdot 8\text{H}_2\text{O}$, HMN) in an aqueous-organic medium was investigated using optical absorption and fluorescence methods. N,N-dimethylformamide (DMF) was used as an organic solvent.

The stability of the resulting hybrid systems was assessed based on the binding constants, as well as the coordinating ability of the organic and inorganic components of the system.

Studies carried out in this research field will significantly expand the range of applications of hybrid organo-inorganic systems based on porphyrins and heteropolycompounds due to their stabilization in aqueous environments.

The data obtained allow us to consider these hybrid complexes as promising materials when creating systems for biomedical applications.

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SPECTRAL PROPERTIES OF METAL (Al, Zn) PHTHALOCYANINE – OXYGEN-FREE GRAPHENE COMPLEXES

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Spectral properties of hybrid systems based on AlCl₃- and Zn-phthalocyanines and suspension of oxygen-free graphene in an aqueous-organic medium were studied using electronic absorption spectroscopy and spectrofluorimetry methods. N,N-dimethylformamide (DMF) was used as the organic solvent. It has been shown that the presence of oxygen-free graphene in the systems prevents the aggregation of phthalocyanines and contributes to their stabilization in monomeric form.

A mechanism of phthalocyanines and graphene interaction through a cyclic complex due to Coulomb attraction of *sp*²-hybridized electron orbitals of carbon atoms of graphene and protonated DMF nitrogen atoms is proposed.

The stability of the resulting hybrid systems as well as the binding capacity of the components of the systems has been evaluated.

The results make it possible to consider these hybrid complexes as promising materials when creating platforms for vector drug delivery and early diagnosis.

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SILICON CARBIDE CORE FIBERS

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Silicon carbide core fibers are a unique reinforcing filler in modern composite materials. High-strength silicon carbide core fibers are widely used as reinforcing fillers for composite materials, which, in turn, are used as critical parts for special equipment. The prospects of silicon carbide fibers use for composite materials are explained by their stability in aggressive and oxidizing environments at high temperatures. Moreover, a distinctive feature of materials based on silicon carbide is their low density (from 3.0 to 3.2 g/cm³) compared to metal alloys, which reduces the weight of individual parts by more than 3 times.

Silicon carbide fibers were prepared by researchers of GNIChTEOS using the CVD method from a mixture of alkylchlorosilanes and hydrogen on carbon (SiC/C) and tungsten (SiC/W) substrates.

SiC/W fibers with a deposited layer of pyrolytic carbon were prepared. The diameter of the fibers was from 140 to 144 microns, the tensile strength was up to 3500 MPa¹. The fibers were analyzed by SEM with EDS. It was shown that the fiber has an almost stoichiometric composition (C/Si ≈ 1).

SiC/C fibers with a layer of pyrolytic carbon deposited on them were also prepared. The diameter of the fibers was from 140 to 144 microns, the tensile strength was up to 3000 MPa². The fibers were studied by SEM with EDS. The SiC/C fiber also had an almost stoichiometric composition (C/Si ≈ 1).

The resulting SiC/W and SiC/C fibers were studied by X-ray diffraction. The main phase of the sample was similar to cubic β-SiC, and the coherent scattering region was on the order of 15 nm.

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FEATURES OF THE STRUCTURE FORMATION OF CORROSION-RESISTANT STEELS OF CHROMIUM-NICKEL ALLOY COMPOSITION IN ADDITIVE MANUFACTURING

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Selective laser melting (SLM) and direct metal deposition (DMD) are potential alternatives for the production of components and assemblies in the power generation and marine industries. These additive manufacturing techniques offer several advantages over traditional casting and machining methods, including: The speed of manufacturing of parts with complex geometry, high material utilization rate achieved due to reduced machining costs, reducing the number of welded connections, bimetal production.

Additive manufacturing techniques are relevant for the production of structural components of reactors, in the field of shipbuilding, laser powder synthesis can be used to manufacture propellers, ship fittings, drill pipes, rods, pump parts, and other critical components.

The paper presents the findings from a study on the impact of DMD and SLM parameters on the microstructure and properties of three types of steel: austenitic stainless steel grades 08Cr18Ni10Ti, 04Cr20Ni6MoV and 08Mn14NiSi. These steels exhibit excellent corrosion resistance and can therefore be employed in marine environments, as well as under high-stress conditions. The nitrogen-containing steel and martensitic 08Mn14NiSi grade demonstrate exceptional strength and durability.

Depending on the modes of fusion, the macro- and microstructure, phase composition, density, and mechanical properties of additive steels were studied. It was shown that the density of the printed samples could be controlled by the fusion parameters and achieved values comparable to those of steel produced by casting and deformation. It has been established that features of the dendritic and grain structures with nanoscale carbides and oxides contribute to an increased level of strength in additive steels when compared to traditional production methods.

KINETICS OF PROCESSES ON ELECTRODES BASED ON LANTHANUM NICKELITES DOPED WITH CALCIUM. REASONS FOR LONG-TERM STABILITY AND DEGRADATION OVER TIME.

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This work is devoted to considering the effect of doping La_2NiO_4 (LNO) Ca (LCNO) in an amount of 0 – 15 mol. % on its electrochemical properties for 1500 hours. The rate-determining stages were identified using the Equivalent circuit method (ECM) and analysis of the Distribution of Relaxation Times (DRT) functions.

It has been established that substitution at the lanthanum position leads to a deterioration in the electrochemical activity of the electrodes, which is possibly due to the loss of interstitial oxygen, as well as the segregation of Ca to the surface of the particles. The relationship between surface and volume diffusion has been revealed. Undoped LNO shows long-term stability in contrast to Ca-doped electrodes. The reason for this behavior, as mentioned above, is the segregation of calcium on the oxide surface, with the subsequent formation of carbonates and blocking of the adsorption centers, which is clearly confirmed by changes in relaxation times (surface exchange rate) and interface resistance. Methods for optimizing electrodes have been proposed that make it possible to obtain electrodes with a reduced sintering temperatures, possessing low in-plane resistance, stable over time. The use of composite electrodes can significantly reduce the polarization resistance due to the effect of surface exchange between different phases (spillover effect).

This work was partly done using facilities of the shared access center “Composition of compounds” IHTE, UB RAS.

PREPARATION AND PROPERTIES OF HYDROGENATED BUTADIENE-NITRILE RUBBER

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Selective hydrogenation of butadiene-nitrile rubbers (NBR) is an urgent task facing the domestic science and industry. Hydrogenated butadiene-nitrile rubbers (HNBR) obtained in this way have better physical and mechanical properties and aging resistance than NBR and are used in such key industries as automotive, aerospace.

This work is devoted to the study of the process of obtaining HNBR by homogeneous catalytic hydrogenation in solution, as well as the structure and properties of rubbers based on them. Rhodium complex catalysts have high efficiency and high selectivity towards carbon-carbon double bonds in HNBR, but the presence of the catalyst in the final product can accelerate the thermo-oxidative aging of such elastomers. In this regard, solving the problem of efficient catalyst removal is also a goal of this work.

The report presents the results of hydrogenation of different grades of NBR carried out in a high-pressure autoclave under different initial conditions: temperature varied within 80-130 °C, pressure - 3.6-5.6 MPa, rubber concentration in 2-methyltetrahydrofuran solution 2 -10 wt. %.

The catalyst was removed from the HNBR using various methods including washing with ethanol, and interaction with various chelating agents. The efficiency was evaluated by X-ray fluorescence analysis.

The residual content of double bonds in the rubber was determined by IR -spectroscopy methods according to ISO 14558:2016(E) and iodine number according to ASTM D5902:05(2023).

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SYNTHESIS OF MOLYBDENUM CARBIDE NANOPOWDERS USING ACETONE AND HEXANE AS A CARBON SOURCE

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In the past decades, transition metal carbides and nitrides have been intensively studied as a possible substitute for noble metals in catalysts¹. Among them, molybdenum carbide is recognized as one of the most promising materials. It exhibits catalytic activity in many reactions and often has higher resistance to sulfur and nitrogen than noble metals. One of the most common methods to produce nanosized molybdenum carbide powder are temperature-programmed reactions (TPR). Their disadvantage is the need to use compressed flammable explosive gases. The possibility of synthesis of tantalum carbide and niobium carbide by carburizing powders of these metals with products of pyrolysis of organic fluids (OL), for example, toluene and acetone was shown earlier^{2,3}. In relation to carbide synthesis by the TPR method, the method using OL as a carbon source is simpler and safer.

The purpose of this work is to investigate the possibility of obtaining nanosized molybdenum carbide powders using acetone and hexane as a carbon source.

Powders of molybdenum carbide Mo_2C with hexagonal crystal structure $P63/mmc$ were obtained in the temperature range of 600-850 °C using acetone and hexane vapors as a carbon source, carried to the reaction zone by argon. The specific surface of the powders is at the level of 12-29 m²/g. The average sizes of the carbide crystallites determined by XRD are in the range of 8-25 nm. Adsorption curves of molybdenum carbide powders correspond to type IV according to the International Union of Pure and Applied Chemistry (IUPAC) classification. They are characterized by the presence of a hysteresis loop and are characteristic of materials with mesoporous structure.

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CREATING ULTRA-LIGHT WEIGHT COMPOSITE MATERIALS

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The creation of ultra-light composite materials (CM) is a priority direction in modern materials science, since lightweight materials can reduce the weight of products and the burden on the environment. The physicochemical properties of highly oriented fibers made of ultra-high molecular weight polyethylene (UHMWPE) per unit weight exceed all fibers and metals known today. The UHMWPE molecule with saturated chemical bonds has a low surface energy (33 mJ/m²), which inhibits the interaction of the fibers with polymer matrices (PM) during the production of CM. A bundle of nanocrystalline UHMWPE-fiber contains from 900 to 2000 or more filaments (monofilaments). Due to the small diameter of the filaments, the fiber has a huge interfacial surface, the main part of which is located inside the fiber. In this regard, strengthening the interfacial interaction between the fiber and matrix is one of the main tasks when creating CM.

The fiber was activated by non-equilibrium low-energy plasma and used to strengthen CM polyethylene plastic. Fiber activation allows one to increase the strength of the connection between the fiber and the matrix by a factor of 3, and to improve wetting and impregnation of the fiber/matrix interface. The transition from physical to chemical interaction, as well as its influence on the properties of CM, has been experimentally established. The criteria for evaluating the plasma treatment of fibers were the capillarity characteristics of UHMWPE-fibers, the tensile properties of micro-plastics, and the shear characteristics of layered and wound ring-shaped CM samples.

It has been established that after plasma treatment of non-woven material made of Dyneema@SK-75UHMWPE-fibers, the composite bending strength was increased by a factor of 1.65 (from 265 to 436 MPa). The composite shear strength was increased by the factor of 1.7 (from 19 to 33 MPa). The properties of more than 50 composite materials have been determined¹.

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POLYHALOGENIDE COMPLEXES OF THE COMPOSITION $\text{Cat}_n\{[\text{M}_x\text{Cl}_y](\text{I}_m)\}$: SYNTHESIS, STRUCTURE AND PROPERTIES

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Halide complexes have physical properties that are interesting for potential applications. One of the most promising areas is solar energy, the development of a new direction of which began just over a decade ago by studying the photovoltaic properties of lead-methylammonium iodide. The efficiency of such devices gradually reached 25%, which is comparable to the performance of industrial silicon-based devices. A large number of studies around the world are devoted to the search for new halide complexes, including other elements (tin, bismuth, antimony).

A similar trend towards an annual increase in the number of publications can be traced for articles on halogen bonding – non-covalent interaction involving halogen atoms, the definition of which was adopted by IUPAC relatively recently, in 2013. This interaction is related to the ability of halide complexes to form polyhalide compounds containing polyhalide fragments in their structure. The inclusion of polyhalide fragments in the structure, which are most often involved in non-covalent interactions, leads to an increase in the dimension of the anionic part, which radically changes the physical and chemical properties of compounds.

Until recently, compounds containing polyiodide fragments and chlorometallate anions were not known (composition $\text{Cat}_n\{[\text{M}_x\text{Cl}_y](\text{I}_m)\}$). This work is devoted to the synthesis and investigation of the physical and chemical properties of new polyhalide complexes of p-elements.

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IMPACT OF THERMAL HEATING ON THE CORROSION-ELECTROCHEMICAL PROPERTIES OF NEW STEEL VNS53-M

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The object of this study is the experimental high-nitrogen steel VNS53-M, modified with niobium and vanadium. High-nitrogen steels occupy a strong position in the industrial market and belong to the class of corrosion-resistant steels. However, the susceptibility of this type of steel to localized corrosion is a known problem.¹ High corrosion resistance of this class of steels can be achieved by grinding inclusions, which have a significant effect on the formation of pitting, or by choosing a directed heat treatment mode.²

The widely used stainless steel AISI 321 and the original steel VNS53 without modified additives were taken as objects of comparison. Since the steels under study, among other things, are used as elements of pipeline fittings operated, including at elevated temperatures, good strength, thermal stability and corrosion resistance of this material are important. It is of interest to study the relationship between thermal heating and the mechanical and corrosion properties of these steel grades. It was revealed that in the tested electrolytes after heat treatment there is no significant change in the corrosion resistance of steels.

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S-DOPED Zn-SUBSTITUTED BISMUTH NIOBATES: SYNTHESIS, OPTICAL AND DIELECTRIC PROPERTIES OF PYROCHLORES

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In this work, a series of Li- and Na-doped compositions of Zn-substituted bismuth niobates were synthesized by nitrate-organic precursors combustion followed by high-temperature sintering up to 1000 °C, and phase analysis was carried out using X-ray analysis and scanning electron microscopy. It has been established that the compositions are bismuth deficient relative to the original $\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$ matrix: by 7 % in the compositions $\text{Bi}_{1.4}M_{0.25}\text{Zn}_{0.65}\text{Nb}_{1.5}\text{O}_{7-\delta}$ ($M = \text{Li, Na}$) and by 14% in the compositions $\text{Bi}_{1.3}M_{0.4}\text{Zn}_{0.5}\text{Nb}_{1.5}\text{O}_{7-\delta}$. According to a FullProf analysis of XRD patterns using the Rietveld method, the distribution of Li^+ and Na^+ cations in the A sites, and Zn^{2+} cations in the B sites in the pyrochlore structure $A_2B_2O_6O'$, was established. As for many bismuth-based pyrochlores, a displacement of the $A(96g)$ and $O'(32e)$ cations relative to their ideal sites was observed¹⁻². Based on DSC data, the melting temperature of samples in air varies in the range of 1120-1180 °C and decreases with increasing dopant content. The resulting compounds are wide-gap semiconductors ($E_g^{\text{dir}} = 3.12\text{-}3.22$ eV). The dielectric properties of the compounds were studied using impedance spectroscopy (impedance analyzer E7-28, silver electrodes). The real part of the dielectric constant ϵ' varies in the range 120-190 (25 °C, 1 MHz) with the temperature coefficient of capacitance $\text{TCC} = -545\text{-}(-800)$ ppm/°C (25-280 °C). The dielectric tangent loss is 0.0015-0.0030 at 25 °C and 1 MHz. The compounds obtained in this work are promising as high-frequency dielectric capacitors up to 280 °C.

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SCREEN-PRINTED ELECTRODES MODIFIED WITH POLY(AMINOPHENYLBORONIC ACID) FOR LACTATE DETECTION

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Polyaminophenylboronic acid (poly(3-APBA)) can be used in enzyme-free lactate sensors¹.

The electrochemical characteristics of planar electrodes based on carbon inks of different manufacturers (Delta and Gwent) were investigated. The electroactive surface area and electrochemical charge transfer rate constants for electrodes were determined by cyclic voltammetry at different sweep rates. The polymerization of 3-aminophenylboronic acid on planar electrodes as well as on a glassy carbon electrode was carried out. It is shown that modification of electrodes based on carbon ink Delta allows to obtain a polymer with high conductivity and improve electrochemical characteristics of the electrodes. Raman spectra and impedance spectra were recorded for the polymer-modified electrodes. The binding constants (K_{app}) of lactate with the polymer were determined by impedance spectroscopy (Table 1).

Table 1. Range of lactate binding constants with poly(3-APBA)

Electrode	Range of K_{app} , M ⁻¹
Planar, paste Gwent	100-200
Planar, paste Delta	900-1200
Glassy carbon	30-50

Thus, by varying the carbon paste material, it is possible to achieve an increase in the sensitivity of the impedimetric lactate sensor.

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DEVELOPMENT OF PHOTOCATALYTICALLY ACTIVE COMPOSITE NANOPOWDERS $\text{TiO}_2\text{-Fe@SiO}_2$

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TiO_2 nanopowders (NPs) possess photocatalytic activity (PCA). Presence of the both rutile and anatase phases is necessary to increase PCA in NPs^{1,2}. To expand the range of the TiO_2 absorption spectrum and increase its PCA, doping with various elements, including Fe, was used. It was found that significant contribution to the PCA increase was made by the SiO_2 shell formed on the surface of NPs anatase (from 65 to 90%)³. In this regard, the purpose of this work was the synthesis of anatase and rutile NPs, both doped with iron and modified with a SiO_2 shell, and the study of their phase composition and PCA. NPs TiO_2 doped with Fe was obtained by co-precipitation from aqueous solutions of TiCl_4 and FeCl_3 , followed by heat treatment at 500 and 1000 °C. The obtained NPs $\text{TiO}_2\text{-Fe}$ were treated in silica, as a result of which a SiO_2 shell was formed on their surface. The obtained NPs $\text{TiO}_2\text{-Fe@SiO}_2$ were studied by X-ray powder diffraction, IR Fourier spectroscopy, scanning electron microscopy with microprobe X-ray spectral analysis. PCA was assessed by the degree of degradation of the methylene blue solution. The results of the study showed that during heat treatment at 500 °C, anatase NPs were obtained. In this case, either Fe entered the anatase structure and did not crystallize as a separate phase (FeO_x) or we obtained small quantities of non-crystalline FeO_x . The phase composition of $\text{TiO}_2\text{-Fe}$ NPs, heat-treated at 1000 °C, corresponded to a mixture of rutile and hematite. For anatase NPs doped with Fe (1-7 at.%), PCA increased by more than 2 times (from 16 to 35%). For rutile NPs, on the contrary, the alloying of Fe (1-4 at.%) reduced PCA by ~4 times (from 100 to 24%). The additional application of a SiO_2 shell on the surface of Fe-doped NPs for anatase further increased the PCA (up to 70-80%), and in the case of rutile, on the contrary, further reduced the PCA (from 24 to 3-16%). Thus, modification of the NPs surface, coupled with doping, is an effective way to control the PCA of NPs TiO_2 .

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STRUCTURE AND PHYSICOCHEMICAL PROPERTIES OF SOLID INORGANIC ACIDS CONTAINING Sb(+5) AND Nb(+5)

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Due to their high thermal stability and ability to retain water molecules up to 400°C, solid inorganic acids containing Nb(+5) and Sb(+5) ions have prospects for use as components of hydrogen-air fuel cell membranes¹⁻³. One way to modify the proton conductivity of these acids is to create substitutional solid solutions on the basis of these acids.

In this regard, the aim of this work was the synthesis of substitutional solid solutions based on niobic acid (NA) and polyantimony acid (PAA), the study of their structure and the determination of the composition with the highest conductivity value.

According to X-ray phase analysis (Rigaku “Ultima IV”), solid solutions with a pyrochlore type structure (sp. gr. symm. Fd3m) are formed on the basis of PAA. The extreme solid solution based on PAA contains 34 at. % Nb(+5). NA samples are X-ray amorphous. Calcination at 500°C leads to the formation of a crystalline structure of NA (sp. gr. symm. Im3). Solid solutions based on NA remain X-ray amorphous even when heated to 500 °C.

The substitutional solid solution based on PAA with 34% Nb(+5) has the highest proton conductivity. At T=25°C, RH=58%: $\sigma = 1.6 \cdot 10^{-2}$ S/m. It is likely that the appearance of $[\text{NbO}_3]^-$ octahedra in a pyrochlore structure leads to a change in the symmetry of hydrogen bonding, which affects proton transport.

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SINGLE-STAGE SYNTHESIS OF TANTALUM CARBIDE CERAMICS

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Tantalum carbide is one of the most refractory materials, which defines its use in mechanical engineering, metallurgy, mining and space industry.¹ Such ceramics are produced by sintering powders, so the technology is energy consuming and limits the shape of products. The oxidative constructing approach makes it possible to obtain ceramic materials by single-stage oxidation of metals.²

The single-stage synthesis of tantalum carbide was carried out on an experimental setup providing resistive heating of samples in the form of rolled ribbon by passing an electric current in an atmosphere of a mixture of argon and ethylene. The synthesis of tantalum carbide was carried out by polythermal heating to 2100°C with annealing for 70 minutes. The temperature of the sample was monitored with a LumaSense IMPACT IS 50-LO pyrometer.

The SEM images of the surface layer and the results of its local elemental analysis revealed the polycrystalline structure of TaC with a grain size reaching 10-15 μm . The SEM images of the material bulk allowed to assume the presence of three carbide phases in the bulk of the material, the composition of which consistently changes towards carbon enrichment (from the bulk to the surface).

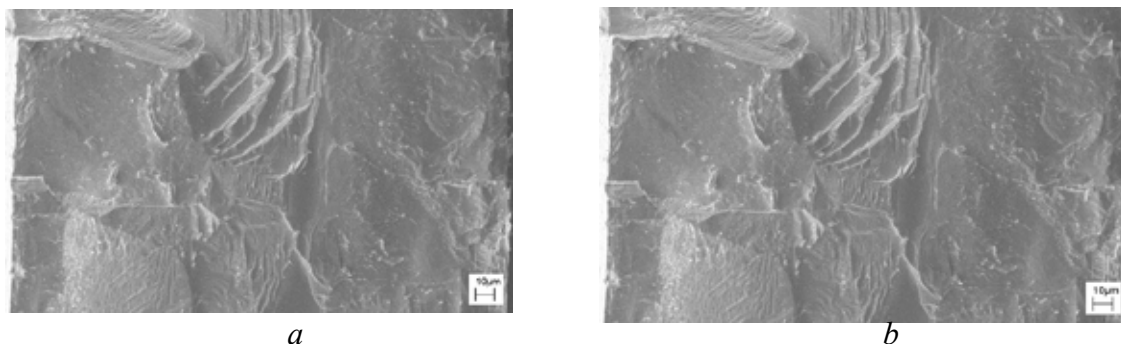


Figure 1. SEM images of produced tantalum carbide: *a* – surface layer, *b* – bulk of the material.

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CHANGING THERMOELECTRIC EFFECTS IN THE PROCESS OF NITRIDIZATION OF THE METAL PAIR Zr-V

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Ceramic nitride samples of a given composition and shape were synthesized by controlled nitridization of Zr-V metal pairs. The kinetic and voltage dependences of the interaction of Zr-V metal pairs with nitrogen have been established. The nitridization process is characterized by different mechanisms for different parts of the pair. In individual metals, the formation of ceramics close to the stoichiometric composition occurs through the formation of three and two-layer gradient structures. Nitridization of the junction region containing a solid solution of Zr-V is determined by the chemical affinity of zirconium and vanadium to nitrogen.

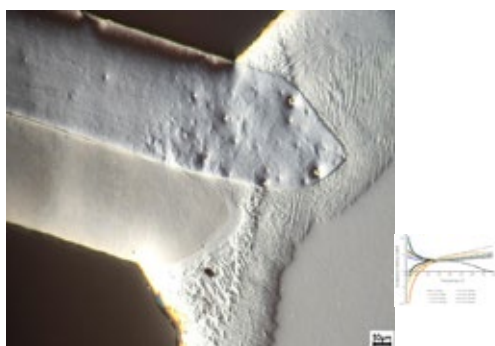


Figure 1 – Optical image of the surface of the metal junction strip in differential interference relief contrast.

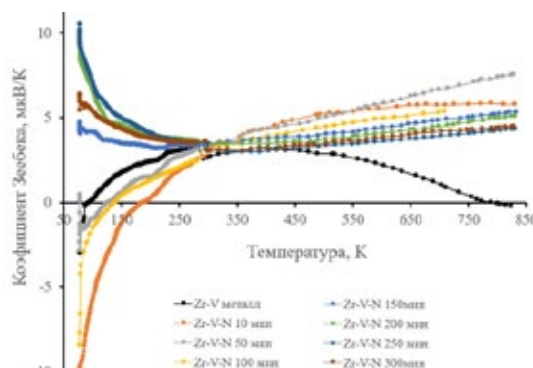


Figure 2 – The difference in the value of the Seebeck coefficient from the temperature for cermet and ceramic Zr-V-N different values of nitridization time.

It was found that the nature of the Seebeck coefficient changes to the opposite for systems nitridized for 150-300 minutes relative to a metallic system. This is due to the presence of a metallic residue or solid nitrogen solution in the individual zirconium metal.

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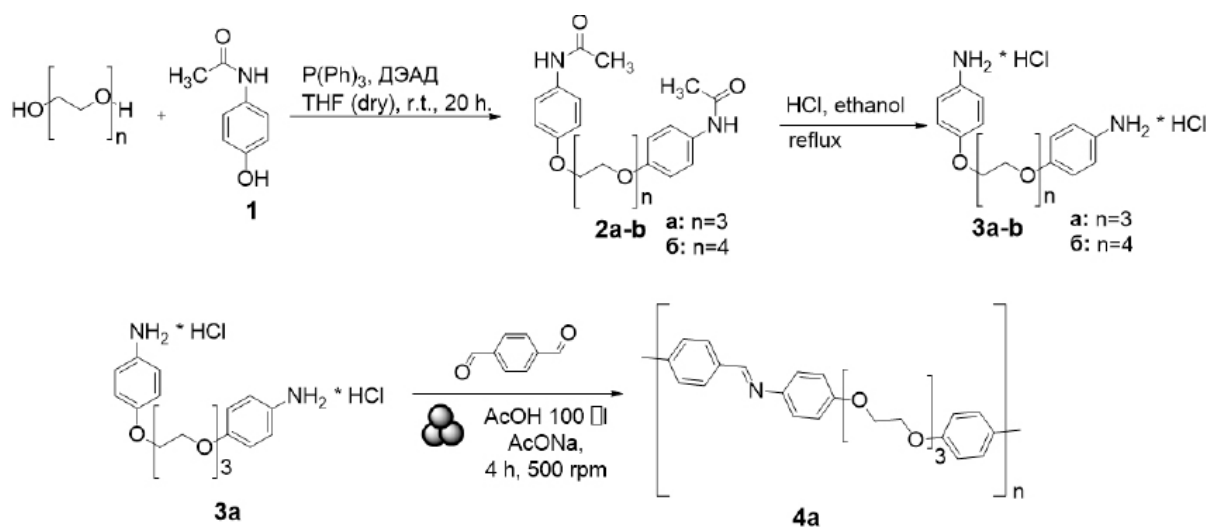
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DEVELOPMENT OF METHODS FOR MECHANOSYNTHESIS
OF POLYAZOMETHINES BASED ON BIS-ARYL-
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Due to the development of the pharmaceutical industry, the problem of disposal of expired and/or substandard pharmaceutical substances is relevant. One of the methods for solving this problem is the transformation of such medicinal substances into useful products of fine organic synthesis. This paper presents a method for possible disposal of the drug substance “paracetamol”. The main method for obtaining bis-aryl-substituted ethylene glycol podands was the interaction of tri- and tetraethylene glycol with paracetamol according to the Mitsunobu reaction mechanism. The resulting podands **2a-b** may be capable of detecting metal cations.

The polycondensation reaction of podand **3a** with terephthalic aldehyde under mechanical synthesis conditions made it possible to successfully obtain polymer **4a**. The sensory properties of the resulting ligand **4a** are being studied.



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OBTAINING MATERIALS OF “TI-FE” SYSTEM WITH INCREASED HYDROGEN CAPACITY BY EXPLOSIVE PRESSING AND SUBSEQUENT SINTERING OF MIXTURES OF TITANIUM AND IRON POWDERS

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Powder mixtures of Fe and Ti with the content of the latter exceeding the stoichiometric content for TiFe intermetallide (50 at.%) were used to obtain the materials. The synthesis was carried out using explosive pressing and subsequent sintering at 1100°C. During the sintering process, the initial components of the pressings reacted with each other and the sintered materials had a structure consisting of TiFe and Ti₂Fe intermetallides with insignificant amount of β-Ti. At the same time, the accompanying introduction impurities (O, N and C) were bound into oxycarbonitrides (Figure 1).

The increase in Ti content from 57.3 to 67.95 at.% allowed to increase Ti₂Fe content from 17.4 to 73.3 vol.% with β-Ti content not exceeding 13.5 vol.%, which in accordance with the data on hydrogen solubility in phases means the possibility of increasing the hydrogen capacity of the material from 108.0 to 171.2 kg/m³.

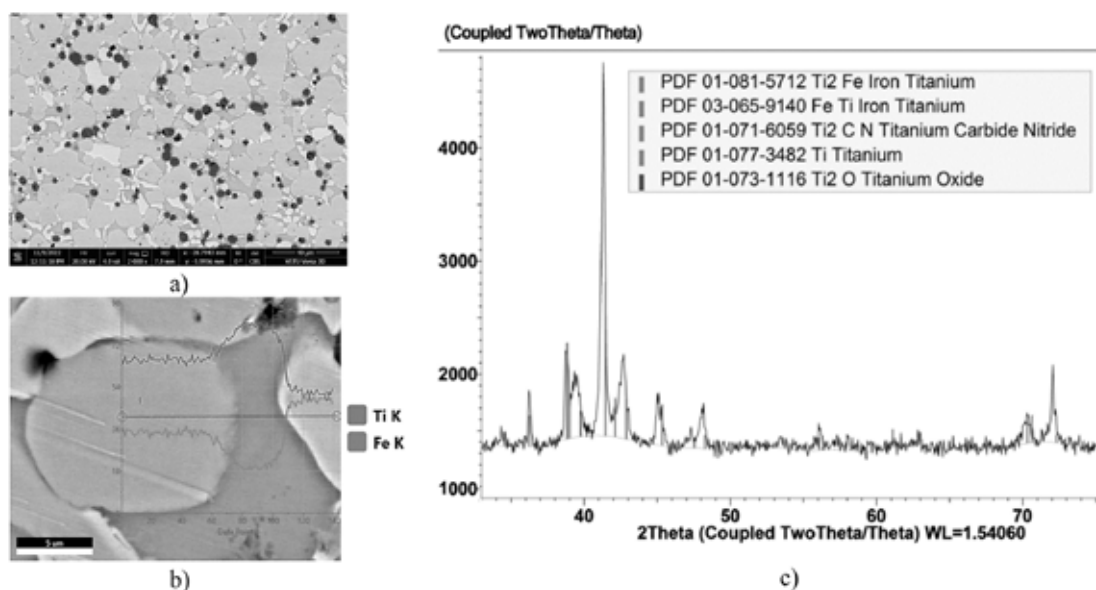


Figure 1: Structure (a), phase composition (c) and distribution of elements between phases (b) in Ti-Fe system materials obtained by explosive pressing and reaction sintering.

PREPARATION OF METAL-CONTAINING COMPOSITES BASED ON THERMALLY EXPANDED GRAPHITE USING A BLOCK COPOLYMER IN AQUEOUS ORGANIC MEDIA

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In recent years, the production of inorganic particles characterized by uniformity in size and structure has remained an urgent task. Micelle-like structures formed by block copolymer molecules in selective solvents are used as nanoreactors to produce such particles by reducing metals from their salts.

In this work, a block copolymer based on vinyl acetate and N-vinylpyrrolidone synthesized by the mechanism of controlled radical polymerization with reversible chain transfer¹ was used to stabilize sols of reduced silver², copper and nickel in aqueous organic media, followed by the deposition of nanoscale particles on the surface of thermally expanded graphite.

Photocatalytic activity in oxidation reactions of organic dyes has been established for silver- and copper-containing composites, ferromagnetic properties for nickel-containing composites, which makes it possible to use the obtained materials in water treatment processes.

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PHOTOANODES BASED ON TiO_2 NANOTUBE ARRAYS FOR FLEXIBLE SOLAR CELLS

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The development of flexible solar cells (SC) is an urgent task, since the use of polymer substrates expands the range of application of such devices, compared to silicon SC¹. However, there are some limitations in the process of creating flexible SC, such as low thermal stability of polymer substrates, which prevents obtaining a crystalline functional semiconductor layer. For example, crystallization of TiO_2 to the anatase phase occurs at 450°C, which exceeds the melting point limits of polymers used in flexible devices².

The research proposed a solution - transferring already crystallized membranes of TiO_2 nanotube arrays onto polymer substrates without further thermal treatment. The obtained functional photoanode layers are resistant to deformation, the generated photocurrent is 4.5 mA/cm² (AM 1.5), and the efficiency is ~ 3.2%, indicating that they can be used in the design of flexible SC.

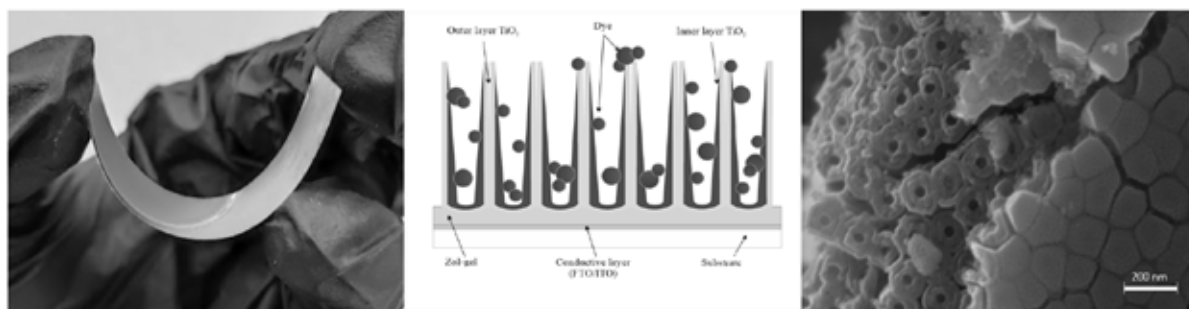


Figure 1: Flexible photoanode based on TiO_2 array membrane; schematic of the sensitized photoanode; SEM image of the obtained structure

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SYNTHESIS, ATTESTATION AND CONDUCTIVITY OF BIMEVOX-BASED COMPLEXLY SUBSTITUTED COMPOUNDS

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One of the important trends of research in the field of materials chemistry is the modernization of well-known compositions in order to improve their properties, in particular, improve the characteristics and reduce the cost of production of solid electrolytes. Doped bismuth vanadates are promising compositions for SOFC electrolytes.

Doped bismuth vanadates with general formula $\text{Bi}_4\text{V}_{1.8}\text{M}_{0.2}\text{O}_{11-\delta}$ (where M = Ca, Mg, Cu, Ni in various proportions, including high-entropy version) were obtained by the solid-phase synthesis. Certification of powdered samples was carried out by X-ray analysis. Monophasic compounds are crystallize in tetragonal system (space group $I4/mmm$). High-entropy compositions $\text{Bi}_4\text{V}_{1.8}\text{Mg}_{0.05}\text{Ca}_{0.05}\text{Cu}_{0.05}\text{Ni}_{0.05}\text{O}_{11-\delta}$ and $\text{Bi}_4\text{V}_{2-y}\text{Ca}_{0.25y}\text{Cu}_{0.25y}\text{Ni}_{0.25y}\text{Zn}_{0.25y}\text{O}_{11-\delta}$ were obtained for the first time. Investigation of the samples using by Raman spectroscopy confirmed the formation of solid solutions of the BIMEVOX type in the series under study and the presence of tetrahedral and octahedral surroundings of vanadium by oxygen atoms in the structure. Elemental composition of the samples was determined by electron microscopy, its correspondence to the nominal formulas was revealed, and the distribution of elements over the surface and cleavage of the samples was uniform.

The transport characteristics of obtained $\text{Bi}_4\text{V}_{1.8}\text{M}_{0.2}\text{O}_{11-\delta}$ materials were investigated by impedance spectroscopy as a function of temperature in the range 1073-473 K in cooling mode. Impedance parameters were estimated, equivalent cell circuits were selected for different temperature regions. Temperature dependences of the total electrical conductivity of the samples were plotted. The dependences have a form typical for BIMEVOX with a change in slope and corresponding to transitions of $\gamma \leftrightarrow \gamma'$ modifications. Temperature coefficients of electrical conductivity of the samples were calculated.

As a result of the study, a data array was obtained. It makes it possible to evaluate the effect of multicomponent substitution on the properties of materials using the example of substituted bismuth vanadates.

A NEW APPROACH TO THE TREATMENT OF EARLY DENTAL CARIES BY CREATING BIODEGRADABLE PLATES WITH ACTIVE COMPONENTS

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Due to the high prevalence and cost of caries treatment, there is a growing interest in the use of more effective and minimally invasive dental treatments. Hydroxyapatite (HA), well established in biomedicine, is often used as a remineralising component. Studies show that HA can act as a source of phosphate and calcium ions to remineralise enamel and dentin. The use of enzymes is a promising method to control cariesogenic biofilms in the oral cavity. The low resistance of bacteria to the action of enzymes is a great advantage of this approach. In this regard, the aim of the present work is to obtain new dental composite materials of prolonged action based on HA, enzyme-destroyers and biodegradable polymers for the treatment of early caries.

Biomaterials in the form of plates were prepared by mixing gelatin, synthesised HA powder and selected enzymes in aqueous solution in a given ratio. The choice of gelatin as a polymer matrix was due to its high biodegradation rate and excellent biocompatibility with the body. Glucoamylase, dextranase, lysozyme, bromelain and papain were chosen as enzymes due to their ability to cleave polysaccharide molecules and effectively control microbial biofilm. After uniform mixing, the suspensions were poured into moulds, frozen and subjected to lyophilic drying at -85 °C for 9 hours. The structural and morphological characteristics of the obtained biomaterials were analysed by SEM using EDS analysis system. The absorption capacity and degradation kinetics were measured in PBS medium at 37 °C. The antibacterial properties were studied against undesirable microorganisms inhabiting the human oral cavity and causing caries formation. In the course of work, new biomaterials in the form of plates were obtained, which are active against pathogenic microflora of the oral cavity and have a mineralising effect in the processes of restoration of damaged enamel and dentin.

HIGH ENTROPY EQUIATOMIC ALLOY CoCrFeNi: SYNTHESIS, STRUCTURE AND PROPERTIES

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The CoCrFeNi system is a single-phase concentrated solid solution alloy and served as the basis for the creation of the Cantor-CoCrFeNiMn alloy¹. Interest in the study of alloys based on CoCrFeNi is associated with their structural features, namely the formation of a high-temperature stable fcc single-phase or fcc + bcc two-phase solid solution depending on the additions of Al and Si. Cu, etc., as well as excellent mechanical and corrosion properties^{2,3,4}.

In this work, the key thermophysical properties required for the successful design and use of equiatomic CoCrFeNi alloy in thermophysical applications were measured experimentally, and the results were compared with literature values previously obtained for commercial Ni–Cr alloys and equiatomic CoCrFeNi alloy. In particular, the thermal diffusivity, thermal expansion coefficient, and specific heat capacity of cast and homogenized equiatomic CoCrFeNi alloy were measured over a temperature range allowing thermal conductivity to be calculated up to 1173 K. The thermal diffusivity and thermal diffusivity of CoCrFeNi alloys were found to deviate from monotonic behavior in the temperature range from 773 to 1100 K. Such a deviation from monotonic behavior was previously observed only in the temperature curves of the CTE and heat capacity of the equiatomic CoCrFeNi alloy. Nonlinear behavior is primarily the result of short-range order/disorder phenomena for homogenized samples, and for initial samples, additionally, non-equilibrium solidification of the sample under arc melting conditions.

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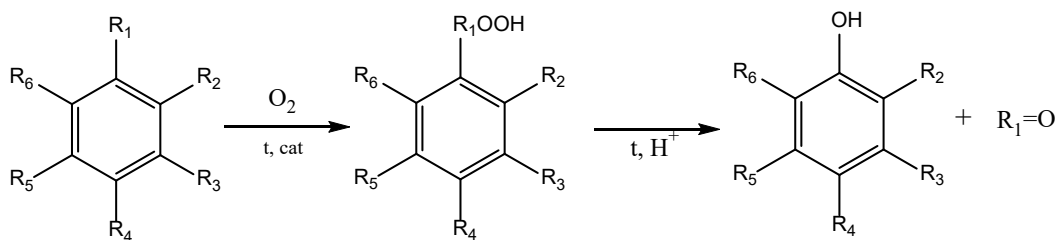
DEVELOPMENT OF A METHOD FOR PRODUCING PHENOL AND ITS ALKYL DERIVATIVES TOGETHER WITH ALIPHATIC AND ALICYCLIC KETONES

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The development of technology for large-scale petrochemical production is one of the most important tasks of modern technology of organic substances, and the development of combined syntheses as part of it allows us to comprehensively solve not only the problem of the synthesis itself, but also its economic and environmental components, which play a decisive role in the competitiveness of the product in the modern rapidly developing world. Such technologies include the synthesis of various substances based on the hydroperoxide oxidation of alkyl aromatic hydrocarbons.

The hydroperoxide approach to the production of oxygen-containing compounds has been around for about 80 years¹. The cumene method for producing phenol and acetone and the joint synthesis of styrene and propylene oxide ("Halcon process") have been studied in detail and widely implemented in industry. This important direction for obtaining valuable oxygen-containing products of organic synthesis can be expanded through the use of other alkylarenes and their hydroperoxides:



where R_1 – *i*-Pr, *sec*-Bu, Cy, Et; R_2, R_3, R_5, R_6 – none, Me; R_4 – none, Me, *t*-Bu.

In this regard, scientific and applied aspects of the production of phenol, cresols, xylenols and para-tert-butylphenol together with aliphatic and alicyclic ketones based on hydroperoxide aerobic oxidation of the corresponding alkylarenes in the presence of phthalimide catalysts have been developed. The regularities of the main stages of the proposed methods have been studied.

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POROUS NANOSTRUCTURED MATERIALS BASED ON NICKEL HYDROSILICATE NANOSCROLLS

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Synthetic nickel hydrosilicate nanotubes $\text{Ni}_3\text{Si}_2\text{O}_5(\text{OH})_4$ can be used as catalysts¹ and sorbents² due to their developed surface and high surface energy. In addition, hydrosilicate nanoparticles have high thermal stability³, which makes it possible to use nanotubes as reinforcing additives in thermally stable nanocomposites.

The formation of porous materials from nickel hydrosilicate nanoscrolls by compressing samples into tablets with subsequent heat treatment allows expanding the area of possible applications of synthetic hydrosilicate. Compression of the sample can affect the magnitude of its ζ -potential. Thermal treatment of nickel hydrosilicate can significantly change the ζ -potential, which gives an opportunity to influence the adsorption activity of the material.

Table 1. Effective particle diameter and ζ -potential data

Firing temperature of $\text{Ni}_3\text{Si}_2\text{O}_5(\text{OH})_4$ nanotube	Effective diameter of agglomerates, nm	ζ -potential, mV
Nanotubes without firing	349	-5.57
100 °C	846	0.31
350 °C	736	-1.94
500 °C	1641	-96.45
605 °C	467	0.05

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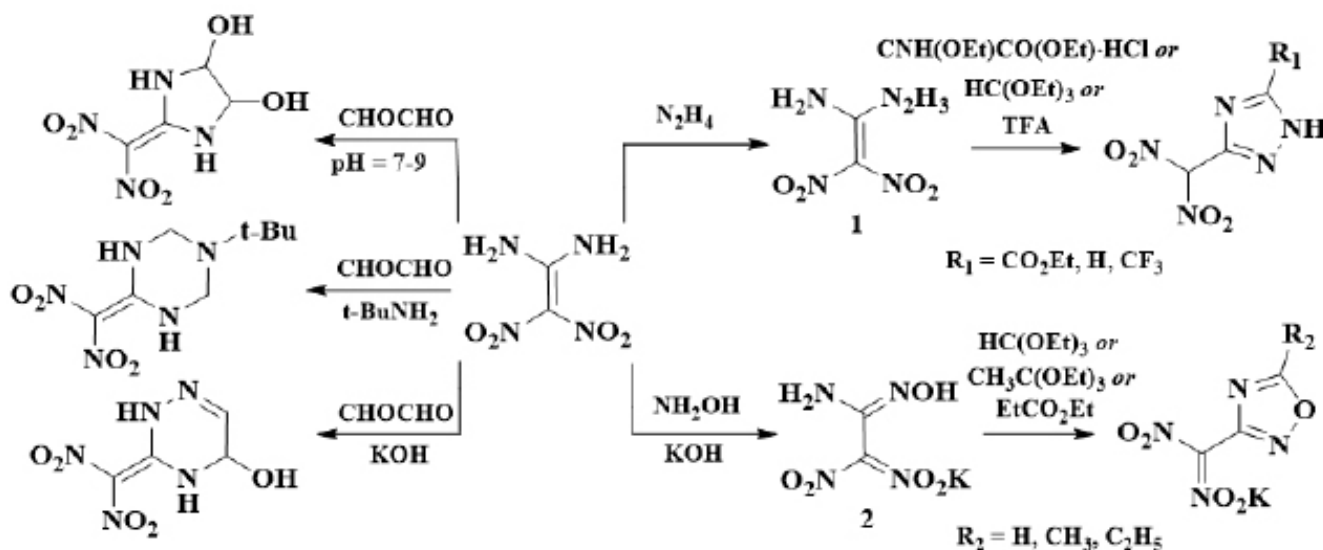
1,1-DIAMINO-2,2-DINITROETHENE AND ITS DERIVATIVES ARE USEFUL SYNTHONES FOR PREPARATION OF HETEROCYCLIC SYSTEMS CONTAINING A DINITROMETHYL GROUP

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1,1-diamino-2,2-dinitroethene (DADNE, FOX-7) is a promising low-sensitivity explosive that is produced on a semi-industrial scale in a number of countries, including Russia.

In recent years, the interest of researchers in high-energy materials has been focused on the study of FOX-7 and its hydrazino- (1) and hydroxyamino (2) derivatives reactivity. A significant number of heterocyclic systems have been synthesized by both Russian and foreign authors, including di- and triazoles, di- and triazines, and oxadiazoles¹⁻⁴, which contain a dinitromethyl group in the side chain (Scheme 1).



Scheme 1. Synthesis of heterocyclic systems containing a dinitromethyl group

The dinitromethyl group, due to its relative lability, is not widely regarded as an explosiphorous group. It provides a gateway for dinitromethyl fragment transformation, which is part of the heterocyclic system, into trinitromethyl and fluorodinitromethyl groups³.

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OXIDIZED FRACTIONS OF APPLE PECTIN AND THEIR INTERACTION WITH 4- AND 5-AMINOSALICYLIC ACIDS

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Apple pectin (YAP) has the ability to reduce cholesterol in the blood, remove heavy metals from the body, exhibit an anti-ulcer effect, etc. In this paper, it is proposed to use an oxidized fraction of apple pectin to immobilize drugs in order to increase their effectiveness, increase bioavailability, reduce toxicity and prolong action.

In the framework of this work, the kinetics of ozonated oxidation of YAP has been studied. Mathematical modeling of the process under study was carried out using the HimKinOptima software package.¹ The rate constants of the key stages were calculated and the kinetic curves of the participants in the oxidative process were obtained, which made it possible to select conditions for the production of an oxidized fraction of a nuclear fuel with a given molecular weight.

Studies aimed at improving the characteristics of biologically active compounds by complexation with polymer and oligomeric matrices have long been conducted on the basis of our department.²⁻³ The interaction of the oxidized fraction of YAP with 4- and 5-aminosalicylic acids has been studied spectrophotometrically. The composition, constants and thermodynamic parameters of complexation have been determined. Based on the data obtained, a method for synthesizing complexes was developed, a prototype was developed and its pharmacological activity was studied.

It was found that the complex of 5-aminosalicylic acid with an oxidized fraction of apple pectin exhibits higher anti-ulcer activity compared to the starting substances.⁴

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FUNCTIONAL ORGANOSILICONE LIGANDS AND SYNTHESIS OF METAL-ORGANIC FRAMEWORKS BASED ON THEM

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The chemistry of metal-organic frameworks (MOFs) is a dynamically developing field, one of the tasks of which is the production of porous materials with wide potential applications - from gas storage and separation to drug delivery and catalysis. MOFs are built on the basis of polyfunctional organic ligands (usually carboxylates and azolates) and metal units, which are metal ions or clusters. Despite the fact that their synthesis, as a rule, is carried out under severe solvothermal conditions, the hydrolytic and thermal stability of such compounds is often not satisfactory for their industrial and domestic use.

One of the ways to obtain hydrolytically stable MOFs is to include a hydrophobic fragment in the ligand, which in turn can have a negative effect on thermal stability. However, the use of ligands based on a siloxane backbone makes it possible to obtain hydrophobic and at the same time heat-resistant MOFs. Recent advances in the functionalization of organosilicon compounds¹ open the way to the preparation of polyfunctional siloxane ligands, including those based on cyclosiloxanes.² The latter have greater structural rigidity and are a more suitable basis for the synthesis of MOFs compared to acyclic siloxanes.

As part of this work, a number of stereoregular polyfunctional cyclotetrasiloxanes and MOFs based on them were obtained, and their crystal structure, thermal and solvolytic stability were studied.

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NEW TYPE OF DIAMOND COMPOSITES WITH LUMINESCENT AND MAGNETIC PROPERTIES BASED ON PARTICLES EMBEDDED IN DIAMOND

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Record values of hardness and thermal conductivity, combined with high chemical resistance, provide permanent interest in the development of diamond materials. The properties of diamond can be modified by incorporating heteroatoms such as N, B, P, Si, Ge, Sn, etc. into its crystal lattice.

The work proposes a method for the synthesis of a new type of diamond film composite, which consists of growing particles of various chemical compositions into the volume of diamond during its growth by deposition from hydrogen-methane microwave plasma. As a result, the conditions for the growth of particles into diamond were determined, and a description of the ongoing processes was proposed^{1,2}.

When using europium as a luminescent ion in the form of EuF_3 , $\text{SrF}_2:\text{Eu}$, $\beta\text{-NaGdF}_4:\text{Eu}$, the reduction of europium ($3+ \rightarrow 2+$) was recorded at typical diamond synthesis temperatures of 550-700°C with the probable formation of metal hydrides on the surfaces of overgrown particles³⁻⁵. At overgrowth temperatures of 800-1000°C, the valence state of europium 2+ was not detected, since the probable corresponding hydrides undergo decomposition. The luminescence spectra of composite samples after growth at 800-1000°C differ sharply from the spectra of the initial substances and composites at growth temperatures of 550-700°C. The luminescence band of europium $^5\text{D}_0 - ^7\text{F}_2$ was greatly enhanced relative to the others bands. For it, compliance with the rule of additivity of intensity on the number of overgrown particles was revealed, as well as a decrease in the width at half-maximum of the luminescence band (less than 1 nm).

The compositions and conditions for the growth of $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}$ and $(\text{Gd},\text{Sc})_3\text{Al}_5\text{O}_{12}:\text{Ce}$ particles into diamond were determined⁶⁻⁹. The synthesized composites demonstrate intense broadband luminescence of cerium in the visible spectral range with similar observance of the rule of additivity of intensity on the number of overgrown particles. By growing particles into single-crystal diamond, a transparent composite was obtained, which was used for the first time as a synchrotron radiation visualizer.

By growing iron oxide nanoparticles, magnetic composite diamonds were synthesized. According to Mössbauer

spectroscopy, it was determined that the iron integrated into the diamond is in a high-pressure modification. This indicates that the substance inside the diamond is under pressure and is a static analogue of a “diamond anvil”.

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BIO-INSPIRED SYNTHESIS OF ZINC SULFIDE NANOPARTICLES

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The biosynthesis of nanoparticles using plant extracts and microbial factories is a relevant topic. Earlier studies have reported on the biosynthesis of ZnS nanoparticles using microorganisms and plants.¹ It has been observed that the properties of these biosynthesized nanoparticles compare favorably with those of chemically synthesized nanoparticles, offering advantages in terms of ease of operation, lower costs, and an eco-friendly approach.²

ZnS nanoparticles were synthesized using two different methods: on sprouted *Cucumis sativus* seeds and in a microfluidic chip that mimics the microstructure of the root of the *Cucumis sativus*. The resulting nanoparticles were then analyzed using X-ray diffraction, fluorescence spectroscopy, infrared spectroscopy, and transmission electron microscopy.

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PHOTOELECTRODES BASED ON CLUSTER COMPLEXES

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Octahedral cluster complexes of composition $[\{M_6Q_8\}L_6]$ ($M = \text{Re}, \text{Mo}$; $Q = \text{halogen or chalcogen}$, $L = \text{halogen, CN, etc.}$) are widely used to design functional materials^{1,2,3} due to their physicochemical properties, such as bright luminescence in the red and near-infrared regions, X-ray contrast and reversible electrochemical transitions in a narrow potential window, accompanied by a significant change in their optical properties. These properties can be widely varied by changing the ligands (Q and X) and the nature of the metal in the cluster core ($\{M_6Q_8\}$).

It was previously shown that the molybdenum cluster complex of the composition $\text{Cs}_2[\{\text{Mo}_6\text{I}_8\}\text{I}_6]$ deposited on a semiconductor substrate of fluorine-doped tin oxide (FTO) belongs to a rare class of ambipolar materials, which allows the development of simple devices with a reduced number of layers and interfaces.⁴ The $[\{M_6Q_8\}L_6]$ cluster complexes have similar structure and properties. Thus, cluster semiconductor materials with tunable composition-dependent properties can be obtained.

In this work, photoelectrodes based on compounds with $\{\text{Re}_6\text{Q}_8\}$ and $\{\text{Re}_4\text{Mo}_2\text{Q}_8\}$ ($Q = \text{S, Se}$) cluster cores and a semiconducting FTO substrate were obtained for the first time. It is found that, depending on the film composition, the electrodes can exhibit ambipolar behavior or properties of p-type semiconductors. The presence of semiconductor properties opens up possibilities for their integration into photocatalytic and photovoltaic systems.

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THERMAL AND SUPRAMOLECULAR PROPERTIES OF OLIGOPEPTIDES

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Currently, a variety of biocompatible nanostructures that have wide biomedical applications are obtained based on oligopeptides using thermal treatment methods. At the same time, there is practically no information in the literature on critical temperatures above which the processes of self-organization of oligopeptides turn into chemical reactions, in addition, the thermal properties of clathrates of oligopeptides with organic compounds remain practically unstudied.

In this regard, in this work, we studied the thermal properties of a number of aliphatic and aromatic dipeptides in the solid phase, as well as trileucine clathrates with organic compounds. The start temperatures of dipeptide cyclization reactions in the solid phase were determined. It was found that as the size of dipeptide molecules increases, in general, the temperature at which cyclization begins decreases. A kinetic study of these reactions was carried out within the framework of non-isothermal kinetics. Memory of trileucine crystals to previously bound guests was discovered, manifested as thermal effects on the differential scanning calorimetry curve in the absence of mass loss. The difference in self-assembly between linear and cyclic dipeptides was visualized using atomic force microscopy.

The results obtained may be useful for the development of methods for producing nanomaterials based on oligopeptides at elevated temperatures, methods for the synthesis of 2,5-diketopiperazine derivatives, as well as for molecular recognition of vapors of organic compounds.

The study was supported by the Russian Science Foundation grant No. 24-23-00473.

BIOCIDAL PROPERTIES OF PREPREGS BASED ON TERPENOID RAW MATERIALS

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The problem of damage to materials by microorganisms (biodamage) in the modern world is relevant for various industries. Biodamage to wood, that is included in production, relates to the fact that cellulose is an excellent organic substrate, food for various groups of microorganisms, primarily fungi.

The ski industry is developing rapidly and wooden skis have been replaced by plastic skis, one of their components being a wooden wedge that is susceptible to microorganisms. Modern skis are a multilayer composite of wood and plastic, interconnected by prepreg, consisting of reinforcing fiber and epoxy binder. Secondary terpenoid products are promising anhydride-type hardeners. At the same time, the availability of the original turpentine, the absence of complex operations in the process of their production, and high reactivity make them a valuable chemical raw material [1].

The object of the study was a wooden wedge in the following variations: wooden wedge, wooden wedge with binder residues, wooden wedge with prepreg. The biostability of the samples was studied using the "agar block" method. Blocks of nutrient medium with a continuous lawn of pure test culture were applied in the center to the surface of the test samples placed in Petri dishes. Petri dishes were incubated in a thermostat at 30°C for 28 days.

It has been proven that the use of chemically modified terpenoid products as a hardener for epoxy prepreg binders can protect a wooden wedge from biodamage.

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AN EFFECTIVE METHOD FOR SYNTHESIS OF N(2)-ARYL-1,2,3-TRIAZOL-4-CARBOXYLATES

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Compounds containing a 1,2,3-triazole fragment are known to possess antimicrobial, antiviral, antiproliferative and other activities.

In this work, a method for the preparation of N(2)-aryl-1,2,3-triazoles was proposed, which contain a carboxyl group in their structure, increasing the solubility of the resulting compounds, as well as fluorine atoms, which increase affinity for biological systems, and also facilitate the infiltration of substances through cell membranes.

The method for the synthesis of target compounds consists of two subsequent stages. On the first one, hydrazine **1** reacts with nitrosoacetoacetic ester to form intermediates **2a-b**, which are cyclized in the presence of copper sulfate. Further addition of hydrochloric acid to the reaction leads to hydrolysis and the production of target molecules in yields of 45-67%.

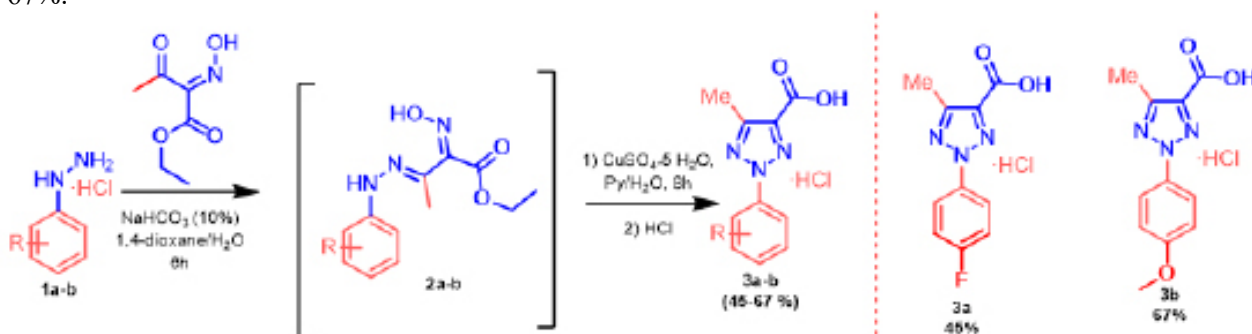


Figure 1. Method for the synthesis of N(2)-aryl-1,2,3-triazole-4-carboxylates

Toxicity studies on HEK-239 cells showed IC_{50} values in the range from 600 to 1024 μ M, which indicates the low cytotoxicity of these molecules.

The study was supported by the Russian Science Foundation grant No. 23-63-10011, <https://rscf.ru/project/23-63-10011/>.

LOW-ALLOY HIGH-SPEED STEEL BASED ON COMPOSITE MATERIAL IN IRON MATRIX DISPERSION-HARDENED WITH NANO- AND MICRO-ENTROPY CERAMICS

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Fast-cutting steels due to the high carbon content do not have high wear-resistant properties, which is associated with the burnout of carbon from the steel surface, in view of which there is a special interest in the creation of metal composites with low carbon content with similar or better strength properties.

The original technological method of obtaining composite material based on iron matrix with strengthening additive based on powder of high hardness equimolar medium-entropy ceramics (MEC) (W,Ti,Ta,Cr)C is presented. The Fe-n(W,Ti,Ta,Cr)C composite (where n = 0.2, 0.5 and 1.0 at.%) was fabricated by a combination of mechanical activation (MA) and spark plasma sintering (SPS) methods followed by air quenching.

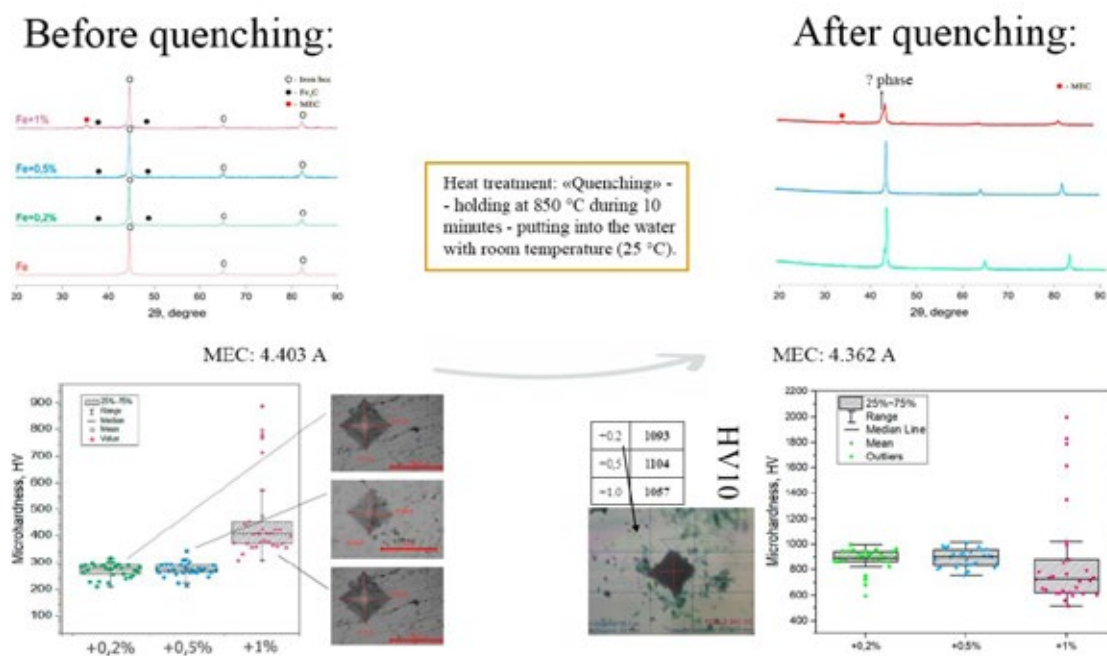


Figure 1. Strength and structural characteristics of the obtained composites.

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BIOCERAMICS OF COMPLEX CHEMICAL COMPOSITION BASED ON STABILIZED GLASERITE-LIKE PHASES

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Being in the field of biomedical materials development the regenerative approach is considered to be a promising direction; instead of filling the defect with a biocompatible implant it is focused on accelerating the processes of integration, implant dissolution with its gradual replacement by the native bone tissue *de novo*; this is facilitated by the osteoinductive properties of the material acting as a porous framework. The inclusion of additional macro- and microelements besides the basic ones (calcium, phosphorus, oxygen) in composition of the bioceramic matrix allows for a) stabilization polymorphic modifications with an optimal level of resorption, b) delivery of bioactive elements into the body, thereby specifically activating processes are associated with bone tissue regeneration.

The osteoconductive functions of the material referred to as aiding the ingrowth of bone tissue into the volume of the implant, formation of a blood vessel network, support of cell adhesion and proliferation, are provided due to the architecture of interconnected macropores created by stereolithographic 3D printing.

Thus, osteoconductive implants with specific macroporous architecture created with the use of 3D printing technologies are proposed, based on materials of the type of high-entropy ceramics of compositions $\text{Ca}_{7-(a+b+c+d)}\text{Mg}_a\text{Sr}_b\text{Na}_c\text{K}_d(\text{PO}_4)_{2+c+d}(\text{SiO}_4)_{2-(c+d+e)}(\text{GeO}_4)_e$ incorporating osteoinductive elements. Each element of the complex composition of the proposed material serves a well-defined purpose. By rapid cooling from 1500 °C high-temperature polymorphs of glaserite-like structures of nagelschmidtite and carnotite are stabilized. The effectiveness of stabilization increases with the complexity of the elemental composition. In the systems $\text{CaMPO}_4 - \text{Ca}_2\text{XO}_4$ ($M = \text{Na, K; X} = \text{Si, Ge}$) expanding fields of solid solutions with glaserite structure are observed. Ceramics based on high-temperature glaserites show improved dissolution dynamics in model environments compared to traditional calcium phosphate ceramics, making them prospective materials for resorbable bone implants.

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LASER ENGINEERING OF MXENES ON FLEXIBLE SUBSTRATES

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MXenes are widely implemented in optoelectronics, sensors, and energy storage devices due to their high metallic electrical conductivity, transparency in thin films, and significant surface area. One limitation MXenes face is their poor adhesion to the substrates as they are very fragile. Solving this would significantly promote the development of flexible interconnects. Building upon our previous insights into fabricating flexible nanomaterial-based sensors using lasing,¹ we anticipate that laser processing will overcome this challenge, maintaining excellent MXenes properties. In this work we irradiate $\text{Ti}_3\text{C}_2\text{T}_x$ on polydimethylsiloxane (PDMS) and polyethylene terephthalate (PET).

Processing in an inert atmosphere indeed leads to stable and robust $\text{Ti}_3\text{C}_2\text{T}_x$ structures partially integrated into PET (PET content after the laser raised by 12%), which remained electrically conductive even after sonication. Moreover, unexpectedly, direct laser processing of MXenes on air resulted in carbonization and a promise for flexible MXenes/polymer composites, while using relatively high powers. This work explored extensive characterization of laser processing configurations to fabricate flexible and robust MXenes-based composites, with the potential applications ranging from wearables to water purification systems.

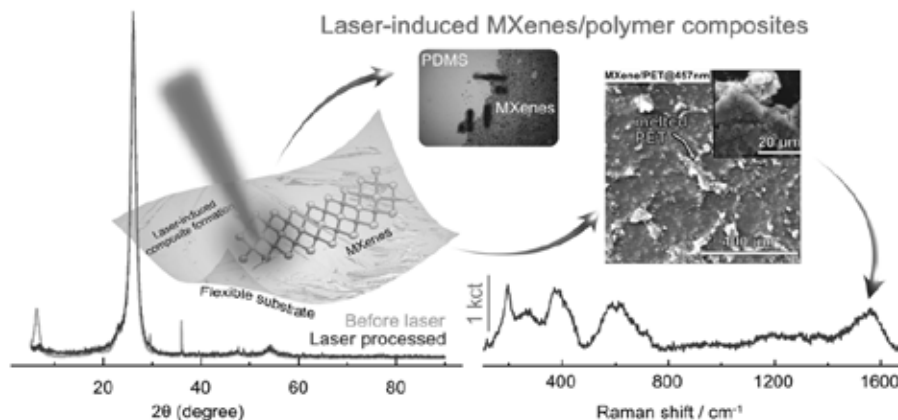


Figure 1. The concept of laser-induced MXenes/polymer composites and their characterization

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MAGNETIC PROPERTIES OF MATERIALS BASED ON PYROCHLORE-STRUCTURED COMPOUNDS OF VARIABLE COMPOSITION IN THE $\text{Bi}_2\text{O}_3\text{--Fe}_2\text{O}_3\text{--WO}_3$ SYSTEM

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Among the currently actively developing high-tech technologies, a fairly young and promising direction should be noted – spintronics. The sustainable development of spintronics requires the creation of new functional materials that have the ability to “tune” their magnetic characteristics, in particular, the parameters of spin-spin interaction, by varying the chemical composition, as well as the morphological and dimensional parameters of the particles and crystallites of their constituent oxide compounds. Pyrochlore-structured complex oxides of variable composition, having a large isomorphic capacity, are promising candidates for creating a wide range of functional materials based on them, in particular, having unique magnetic characteristics. The aim of the work is to determine the nature of the magnetic behavior of new materials based on pyrochlore-structured compounds in the $\text{Bi}_2\text{O}_3\text{--Fe}_2\text{O}_3\text{--WO}_3$ system over a wide temperature range (from 1.8 to 300 K), depending on the degree of magnetic dilution of the compound composition.

The synthesis of powdered materials was carried out by the hydrothermal method, and the composition of pyrochlore-structured compounds was within the atomic ratios of $0.16 < \text{Fe}/\text{W}, \text{at.} < 0.52$, i.e. the degree of its magnetic dilution varied.

It was established that materials based on the obtained compounds are paramagnetic with predominantly antiferromagnetic spin-spin interaction and belong to the class of geometrically frustrated magnets. The dependences of the spin glass state transition temperature, the Curie-Weiss temperature and the frustration parameter, as well as the residual magnetization and coercive force at 2 K on the degree of magnetic dilution of the compound composition were determined.

The work was financially supported by the Russian Science Foundation, project No. 24-13-00445.

HIGH CAPACITY ALLOYING ANODE MATERIALS FOR SODIUM-ION BATTERIES

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Today, SIB - sodium-ion batteries are a more attractive alternative to lithium-ion batteries from an economic point of view. Some of the metals and semimetals, such as Sn, Pb, Bi, Sb, etc., with the mechanism of alloying with sodium to form Na_xM , can be a good alternative to non-graphitizable carbon due to the low operating potential relative to Na^+/Na (0.2 - 0.8 V), on average, high specific capacity (from 385 to 850 mAh/g). In addition, metals are characterized by: high electrical conductivity, ductility and elasticity, which allows them to be used in their pure form without the addition of an electrically conductive additive or a binding polymer.¹⁻⁴

In our work, we demonstrate that a key factor in the cycling stability of metal anodes is the electrolyte. For this purpose, films of Bi, Pb and Sn were obtained on copper foil by electrodeposition. The electrodes were cycled in a half-cell with sodium and in a full system with $\text{NaVPO}_4\text{F}/\text{C}$ -based cathode material for hundreds of cycles, retaining a significant portion of the original capacity.⁵

It was shown for the first time that the most preferable morphology of the metal layer is a dense metal layer due to the achievement of theoretically possible specific characteristics. In addition, it was shown for the first time that electroplated coatings based on bismuth and lead can be used as anode materials with almost complete reversible conversion of the active material. The electrochemical properties of such anode materials will be discussed in detail in the report.

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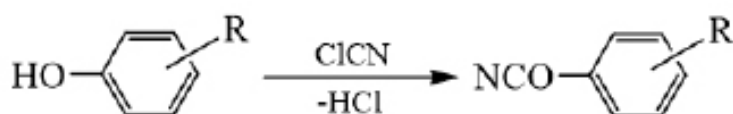
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CYANE ESTERS OF PHENOLS AND HEAT RESISTANT HIGH STRENGTH PLASTICS

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The preparation of the cyano esters of mono- and bisphenols is mainly reduced to the interaction of phenols with cyan chloride in the presence of hydrogen chloride acceptors. Tertiary amines and alkalis are used as an acceptor of hydrogen chloride.



The process of obtaining the cyanic esters of phenols using trialkylamines is not very suitable for industrial production, since in this case a large amount of wastewater is formed.

Using only alkalis as acceptors complicates the synthesis due to the need to obtain solid cyanates of alkali metals that do not contain water.

In this regard, a method is proposed for the preparation of cyanic esters, combining both production options. When using catalytic amounts of trialkylamine in the process of synthesis of cyanates of phenols, it is possible to use aqueous solutions of alkalis. The method of obtaining is more universal. Both phenol monocyanate esters and bisphenol dicyanate esters were obtained.

A characteristic feature of the monocyanate esters of phenols is their low storage stability; they are easily trimerized to form substituted triazines. Therefore, studies have been conducted to improve the stability of monocyanates. The obtained samples after stabilization are not trimerized for more than 6 months.

At present, the parameters of cyanation are being refined, scientific and technical documentation is being developed for pilot batches of cyanates.

Cyanate ethers have been used as monomers to produce heat-resistant polymers. Based on them, heat-resistant, high-strength plastics were obtained¹.

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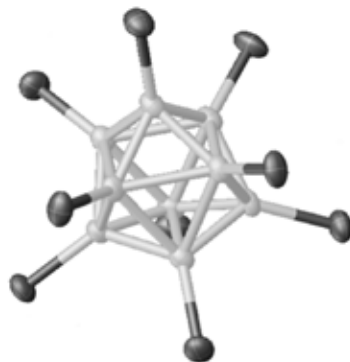
STUDYING THE COORDINATING ABILITY OF PERHALOGENATED ANION $[B_9Cl_9]^{2-}$

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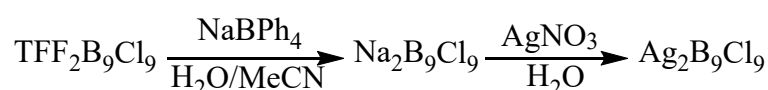
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Perhalogenated boron cluster anions are weakly coordinating anions and can act as stabilizers of reactive cations, for example, Et_3Si^+ , Et_2Al^+ and carbocations.¹ Derivatives of the nonahydro-*closo*-nonaborate anion of the form $[B_9X_9]^{2-}$ (where X = Cl, Br, I), which were obtained back in 1980,² can be considered as such stabilizers, but their properties are currently poorly studied.

In this work, salts of the $[B_9Cl_9]^{2-}$ anion were obtained using a well-known procedure² and its structure was established for the first-time using X-ray diffraction analysis of a single crystal. It was established that the structure of the anion is similar to the structure of the $[B_9Br_9]^{2-}$ anion, and is a triangular prism with three vertices on the side faces.



A method for the synthesis of silver salts of the resulting anion has been proposed and their coordinating properties in various solvents have been studied using the methods of X-ray diffraction analysis and IR spectroscopy.



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The work was carried out within the framework of the state assignment of the IGIC RAS.

NOVEL PHOSPHIDE-PLATINIDES WITH COMPLEX ARCHITECTURES IN Eu-Pt-Cu-P AND Ca-Pt-Cu-P SYSTEMS

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The chemistry of pnictogens not only is one of the most complex, but also one of the most fascinating. Both the elements themselves and their compounds show a great variety of compositions, structures, and physical properties. The chemistry of phosphides is of particular interest, since to date they represent a relatively unexplored class of inorganic compounds. This work is devoted to the directed search, synthesis and study of the structural features of new metal-rich quaternary phosphide-platinides in the Eu-Pt-Cu-P and Ca-Pt-Cu-P systems.

Using the high-temperature ampoule synthesis from the elements, with the use of metal fluxes such as lead and bismuth, several new phosphide-platinides in the R-Pt-Cu-P (R = Ca, Eu) systems were obtained. Thus, we have obtained the crystals of the $\text{Eu}_2\text{Pt}_6\text{Cu}_2\text{P}_{2.98(5)}$ compound, belonging to a rather rare structure type $\text{Eu}_2\text{Pt}_7\text{AlP}_{2.95}$ (space group $I4/mmm$), the structure of which is a result of linear intergrowth of AuCu_3 and CaBe_2Ge_2 type blocks. The compound obtained has unique structural feature: rather than only centering platinum-based cuboctahedra in the binary block, as in the prototype, copper atoms in this compound completely replace one of the platinum positions in the structure, occupying the entire equatorial plane of the cuboctahedra. Thus, in this phosphide-platinide, AuCu_3 -type blocks are replaced by AuCu -type blocks.

Also in the R-Pt-Cu-P (R = Ca, Eu) systems new complex quaternary phosphide-platinides, crystallizing in a new structure type, hexagonal cell with large metrics (space group $P\bar{6}2m$), were obtained: $\text{Ca}_6\text{Pt}_{17}\text{Cu}_4\text{P}_9$ и $\text{Eu}_2\text{Pt}_4\text{Cu}_3\text{P}_3$ ($\text{Eu}_6\text{Pt}_{12}\text{Cu}_9\text{P}_9$). The structural motif in these two compounds is the same. They are constructed from a framework formed by platinum, copper and phosphorus atoms, with cavities containing europium and calcium atoms, respectively. However, these phosphide-platinides have different Pt:Cu ratios, which leads to differences in the framework formed by these atoms.

This work was supported by Russian Science Foundation (grant No. 23-23-00263).

EFFECT OF PREPARATION CONDITIONS OF EXFOLIATED GRAPHITE ON SORPTION CAPACITY AND WATER WETTABILITY

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Exfoliated graphite (EG) is a porous carbon material, which combines the advantages of both inorganic and polymeric sorbents for oil sorption from the water surface ¹. EG preparation process includes the oxidation and intercalation of graphite with Bronsted acids, water washing and flash thermal treatment. The structure of the initial graphite intercalation compound (GIC) has a significant influence on the structure of exfoliated graphite and its sorption properties: sorption capacity and selectivity of water/octane sorption. The aim of the research was identifying the relationship between the structure of EG obtained from 1-4 stage GICs and the sorption capacity and selectivity of water/octane. The influence of the GIC stage number on the EG sorption and surface properties is studied. EG obtained from 1st stage GIC at 1000 °C is characterized by a higher sorption capacity toward octane than EG from 4th stage GIC. The selectivity of octane/water sorption reduces when decreasing the GIC stage number from 4 to 1. The high water sorption can be explained by a higher surface area of EG and the presence of remaining oxygen groups on the edges of graphite crystallites in the EG structure. The EG structure was investigated by XRD, SEM, nitrogen adsorption-desorption method, FTIR and Raman spectroscopy.

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INTERFACIAL SYNTHESIS, CHARACTERIZATION AND ANALYTICAL APPLICATIONS OF FUNCTIONALIZED MAGNETIC NANOPARTICLES

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Interfacial synthesis is poorly studied and is not a “classical” liquid-phase method. The processes of nucleation and particle growth occur on a nonplanar surface in a microemulsion or a flat surface of the interface between two immiscible liquids. The variety of materials for creating dispersed systems and careful study of the reaction medium parameters make it possible to obtain various nanoparticles, films and 3D-materials.

This work presents a method for the synthesis of magnetic nanoparticles (MNPs) in a biphasic aqueous-polymer system with the addition of functionalizing agents - ionic liquids (ILs) and deep eutectic solvents (DESS). The reaction medium's optimal parameters, including PEG molecular weight and precursor concentration, were determined using response surface methodology. Static analysis was carried out and the regularities of the nanoparticle size variation were determined. The morphology and structure of the MNPs $\text{Fe}_3\text{O}_4@\text{PEG}@\text{IL}$ и $\text{Fe}_3\text{O}_4@\text{PEG}@\text{DES}$ were characterized using SEM, PEM, TGA, XRD, and IR spectroscopy. The magnetometry determined the superparamagnetic structure and residual magnetization of the MNPs.

The report presents comparative data on the sorption properties of the functionalized MNPs towards various bio-organic compounds and metal ions depending on the composition of nanoparticles and conditions of their synthesis. The report also provides examples of the use of synthesized MNPs in separation and purification technologies.¹⁻³

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ATOMIC LAYER DEPOSITION OF ALUMINUM-MOLYBDENUM OXIDE FILMS: WATER AND WATERLESS PROCESSES

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Aluminum-molybdenum mixed oxides $Al_xMo_yO_z$, their nanolaminates $Al_2O_3-MoO_x$, aluminum molybdate ($Al_2(MoO_4)_3$) can be use as solid-phase electrolytes, catalysts, photovoltaic cells, dry lubricants, etc.

In this work, thin film atomic layer deposition (ALD) of $Al_xMo_yO_z$ was carried out using water as a co-reactant and without (waterless processes). The $Al_xMo_yO_z$ ALD using H_2O was carried out in combination with trimethylaluminum ($Al(CH_3)_3$, TMA) and molybdenum dichloride dioxide (MoO_2Cl_2)¹. The waterless process was conducted using TMA and MoO_2Cl_2 only². The ALD processes were studied from 120 to 180 °C using *in situ* quartz crystal microbalance (QCM) and *ex situ* using number of spectroscopic techniques such as XRR, XPS and ellipsometry.

The QCM showed film linear growth with number of ALD cycles and self-limiting surface reactions of the precursors. The film growth rate determined by XRR varied from 3.5 to 5.5 Å/supercycle and the density from 3.4 to 3.7 g/cm³ depending on the surface chemistry used. The obtained films had an amorphous structure. XPS data showed that the films contained some amount of carbon and chlorine impurities (2-4 at.%), and Mo had oxidation states of +6, +5 and +4. These data suggested that TMA chemically reduces molybdenum to the lower oxidation states and surface chemistry modification is needed to retain original +6 oxidation.

This research also showed that $Al_xMo_yO_z$ thin films can be deposited using oxi groups on molybdenum precursor as an oxygen source.

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The work was carried out with the financial support of the Ministry of Science and Higher Education of the Russian Federation, State Assignment FZNZ-2020-0002.

INCREASING THE HYDROPHILICITY OF N-ACYL-SUBSTITUTED AMINO ACID ESTERS DUE TO COMPLEXATION WITH BIOMETALS FOR THE CREATION OF ANTIVIRAL DRUGS

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Pyrazine-2-carboxylic acid derivatives are used as pharmaceutical molecules for the treatment of various diseases. The idea of the proposed work is to study new derivatives of pyrazine-2-carboxylic acid with amino acid esters as antiviral agents. Pyrazine-2-carboxylic acid derivatives with amino acid esters containing an aromatic or aliphatic side group (Ser-OMe, Thr-OMe, His-OMe, Trp-OMe) have been successfully synthesized. In biological experiments *in vitro*, the target compounds were used as complexes with iron(II) chloride, which are formed *in situ* at a ratio of Fe : L = 1 : 2 to form clear, colorless aqueous solutions. The antiviral activity of the compounds against influenza A/H1N1 and SARS-CoV-2 viruses was studied *in vitro*. Using MDCK cell culture, it was shown that only one of the presented amino acid derivatives with 2-pyrazinecarboxylic acid (namely, Trp-OMe) has the ability to suppress the replication of the pandemic strain of influenza A virus. The cytotoxicity of the compounds was about 190 μ mol for a monolayer of Vero-E6 cells and about 247 μ mol for MDCK cells, i.e. these compounds are moderately toxic. The proposed method of attaching functional groups to molecules of heterocyclic carboxylic acids and creating chelate compounds based on these ligands makes it possible to obtain bioavailable forms of antiviral drugs.

The proposed compounds of amino acids with heterocyclic carboxylic acids, due to their significant activity and low toxicity, can be considered as a model for the creation of new antiviral drugs based on them.

The work was supported by the Russian Science Foundation, grant no. 23-23-00142 (Russia).

INVESTIGATION OF THE PERMEABILITY OF PAINT COATINGS FILLED WITH BASALT PRODUCTION WASTE

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Recently, waste from various industries has been increasingly used as part of protective coatings, which makes it possible to reduce the cost of the composition and profit from the secondary sale of raw materials.¹ The use of such materials in paint and varnish compositions not only contributes to environmental protection, but can also contribute to improving the characteristics of the paintwork and giving it special properties.²

In this work, the effect of a mineral filler, which is a pulverized waste product of basalt production, on the permeability of polyurethane and epoxy coatings was investigated. Previously, the effect of another filler of a similar nature on the permeability of polyurethane and epoxy coatings was investigated. The results of the study showed the influence of basalt filler on the curing processes, leading to an increase in the degree of curing and a decrease in the permeability of coatings. The purpose of this work was to confirm the results obtained by examining another basalt filler.

First of all, it is necessary to determine whether the introduction of basalt filler into the composition of coatings leads to a deterioration in its properties and the properties of coatings based on it. For this purpose, the physico-mechanical characteristics of paint material and paint coating were studied: the degree of grinding, hardness, impact strength and adhesion. The conducted studies have shown that the introduction of basalt filler into the composition of compositions does not entail a deterioration in their properties. To determine the diffusion coefficient, which characterizes the permeability of paint coating, the method of permeability of free coating films based on experimental compositions was used. The results obtained allowed us to conclude that the introduction of basalt filler affects the permeability of the paintwork, often reducing it.

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DEFECT CHEMISTRY AND THERMODYNAMICS OF MIXED CONDUCTING PEROVSKITE-TYPE OXIDES $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$

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Mixed ionic- and electronic-conducting perovskite-type oxides are the state-of-the-art materials for high-temperature solid-state electrochemical devices such as solid oxide fuel cells (SOFCs), oxygen membranes and sensors. The oxides $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ have received a lot of attention as promising materials for such applications. They are capable of oxygen exchange with surrounding atmosphere. This results in strong dependence of their oxygen content on temperature (T) and oxygen partial pressure ($p\text{O}_2$) as well as in strong variation of other properties including the thermodynamic ones. As a result, the detailed understanding of the defect chemistry of these materials is of high importance for understanding their properties. However, these data for $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ oxides are very restricted to date. Therefore, the main aim of this work was to perform detailed study of the relationship between the thermodynamics of defects in $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ oxides and their various properties such as oxygen nonstoichiometry, oxidation enthalpy, heat capacity, total conductivity, Seebeck coefficient etc.

Powder samples of $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ ($x = 0.3\text{--}0.7$) were synthesized using the standard ceramic and spray-pyrolysis techniques. Phase-purity of the samples was confirmed by X-ray diffraction (XRD) with 7000S diffractometer (Shimadzu, Japan) in $\text{Cu K}\alpha$ radiation.

Oxygen nonstoichiometry, total conductivity, Seebeck coefficient, oxidation enthalpy, enthalpy increments and thermal and chemical expansion of perovskite-type oxides $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ ($x = 0.3\text{--}0.7$) were studied as functions of oxygen partial pressure $10^{-5} < p\text{O}_2/\text{atm} < 1$ and temperature $600 < T/^\circ\text{C} < 1050$. The extensive defect chemical modelling was carried out. As a result, the dominating defect species were identified, and thermodynamic functions of the corresponding defect reactions were determined. This allowed obtaining the self-consistent set of parameters describing the variation of various measured properties of $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ oxides with T and $p\text{O}_2$.

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SYNTHESIS OF POROUS SILICON OXIDE MATERIALS AND THEIR ROLE IN IMPORT-SUBSTITUTE TECHNOLOGIES

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Porous materials based on silicon oxide (silica gel, SiO_2) play an important role in many industries. Silica is not only a sorbent and desiccant in the gas and petrochemical industries, but also a support for catalysts, a filler for functional composite nanomaterials, as well as a sorbent widely used in everyday life. Russian manufacturers cover only part of the needs of the domestic market. Therefore, many sectors of the economy are in urgent need of imported grades of SiO_2 because of the sanctions pressure. The development of domestic technologies for producing SiO_2 with characteristics that are not inferior to imported analogues is in great demand.

A technology for producing SiO_2 for toothpastes and cosmetics is being developed (market volume is more than 3,000 tons per year). The role of SiO_2 in toothpastes is to provide the paste with the necessary viscous consistency and cleansing (abrasive) properties. The technology of silica production is based on the precipitation of liquid glass (sodium silicate $\text{Na}_2\text{O} \cdot n\text{SiO}_2$) with mineral acids. Fine control of the deposition regime and subsequent treatments makes it possible to obtain dispersed SiO_2 with the required chemical purity and functional properties.

An even larger sector of the market is SiO_2 tire fillers. Adding SiO_2 to tires (20-40%) allows to increase the environmental class of tires and improve exploitation characteristics, such as grip on wet asphalt and winter roads. The requirements for this type of SiO_2 are also very high, since it is necessary that it be evenly distributed in the rubber, chemically bond with it, and provide the necessary mechanical properties.

Thus, the development of technologies for producing SiO_2 materials is in great demand for the domestic market. Only cooperation of scientific and scientific-educational organizations with enterprises in the real sector of the economy with direct government support can ensure relatively rapid access of developed technologies to industrial implementation.

The work was carried out with financial support from the Development Program of Tomsk State University (Priority-2030).

COMPLEX COMPOUNDS OF LANTHANIDES WITH CROWN ETHERS BASED ON BORON CLUSTER ANIONS

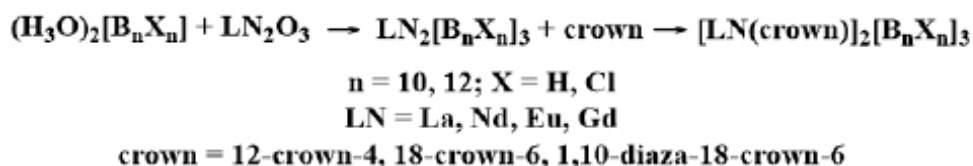
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Due to a unique set of properties such as optical, luminescent, fluorescent, magnetic properties, these compounds have a wide range of applications, for example, in medicine, such as effective contrast agents for MRI enhancement, for cell visualization or drug detection in foodstuffs¹. Among the coordination compounds, complexes with crown ethers are of particular interest. Such compounds are single-molecule magnets, which makes them promising candidates for applications in high-density information storage systems, quantum computing and molecular electronics^{2,3}.

In the present work the synthesis of new complex compounds of lanthanides with crown ethers on the basis of higher polyhedral boron anions has been carried out. The obtained compounds were characterized by modern physicochemical methods of analysis.



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The work was carried out within the framework of the state building of the N.S. Kurnakov Institute of General and Inorganic Chemistry in the field of fundamental scientific research.

EFFECT OF TELLURIUM ON THE CORROSION OF STRUCTURAL MATERIALS HASTELLOY B-3 AND VDM ALLOY 59 IN FLiNaK-BASED MELTS

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Tellurium is one of the typical fission products including processes of actinides burning in a molten salt reactor. The tellurium interaction with components of metallic construction materials causes the intergranular degradation of alloys along grain boundaries (tellurium cracking). This leads to changes in the alloys structure and decline of their mechanical properties.

In the present study the corrosion tests of nickel-molybdenum Hastelloy B-3 alloy samples in molten FLiNaK-UF₄-NdF₃-CeF₃-Te at 550 and 650 °C with different mass ratios salt:tellurium were performed to investigate the influence of tellurium on the stability of structural materials. The similar purpose was aimed when experiments on corrosion of chromium-nickel-molybdenum VDM Alloy 59 were carried out in FLiNaK-UF₄ and FLiNaK-UF₄-Te at 650 °C when the mass ratio salt:tellurium was equal to 1:20. All the experiments were performed during 100 h contact of samples with molten salts under high-purity argon atmosphere when the decreases of samples weight were measured. The quenched melt is also analysed by X-ray fluorescence spectral method. The calculated corrosion rates are summarised in Table 1 and 2. The obtained data clearly indicate on the course of tellurium on the corrosion processes in fused salts.

Table 1. Corrosion rates of Hastelloy B-3 alloy in FLiNaK-UF₄-NdF₃-CeF₃-Te system with various tellurium content at 650 °C after 100h exposure time

Mass ratio Te : salt	Corrosion rate, mm/year	
	Gravimetric method	Analytical method
1:10000	< 0,01	0,03
1:1000	0,28	0,14
1:100	1,69	1,49

Table 2. Results of the investigation on corrosion stability of VDM Alloy 59 alloy after the 100 h exposition in fluoride melts at 650 °C

Salt	Corrosion rate, mm/year	
	Gravimetric method	Analytical method
FLiNaK - UF ₄	1,33	1,48
(FLiNaK - UF ₄) - Te (20:1)	12,5	4,4

THE EFFECT OF SYNTHESIS CONDITIONS ON THE MORPHOLOGY AND STRUCTURE OF SAMARIUM-BASED NANOMATERIALS

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The development of approaches to the synthesis of nanomaterials with controlled size and shape is one of the key problems of modern science and technology. Nanomaterials based on compounds of rare earth elements with unique properties and high applicability potential are of particular interest. One of these materials is samarium oxide (Sm_2O_3). Samarium oxide based nanomaterials are promising systems for the needs of energy, nanoelectronics and nuclear medicine^{1,2}.

In this study, the influence of homogeneous and heterogeneous deposition parameters (deposition duration, solution temperature and reagent concentration) on the morphology and crystal structure of samarium-based nanomaterials was studied. In the homogeneous precipitation case, a urea hydrolysis reaction was used to change the pH of aqueous solutions of $\text{Sm}(\text{NO}_3)_3$. For heterogeneous precipitation, pH correction was performed by a concentrated NH_4 solution.

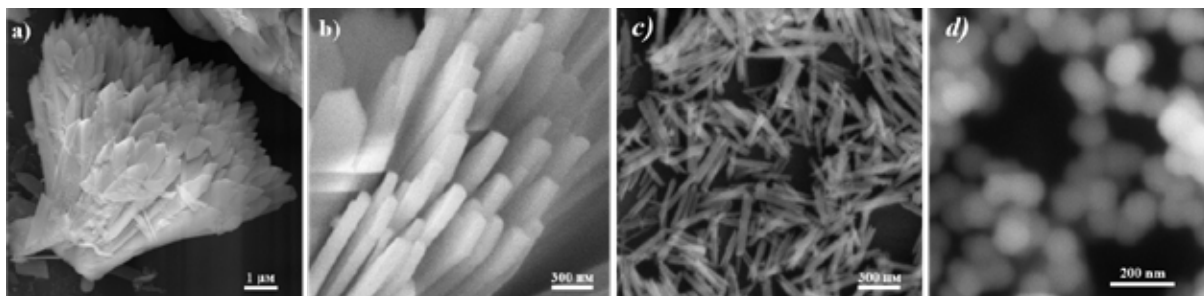


Figure 1. Morphology of the obtained nanomaterials: a), b) Sm_2O_3 microparticle consisting of an array of needle-like nanoparticles; c), d) Sm_2O_3 nanosheet and spherical nanoparticles

Using the methods of scanning electron microscopy and X-ray diffraction, it was confirmed that a change in the synthesis conditions leads to a change in the morphology (Fig. 1) and the structure of the powders.

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The work was carried out with the financial support of the Ministry of Science and Higher Education of the Russian Federation (project FZNS -2023-0012)

INDUCTION FLOW LEVITATION AS A NEW APPROACH FOR OBTAINING HIGH-PURITY MONODISPERSE NANOPARTICLES OF MONOMETALLIC SYSTEMS, “CORE-SHELL” STRUCTURES, INTERMETALLIC COMPOUNDS AND THEIR APPLICATION

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Induction flow levitation is a very promising method for producing micro- and nano-sized particles, which is still being developed, but real prospects for its application are already visible both for the scientific sphere and for industry. The main advantages of inductive flow levitation (IFL) are non-contact heating in a wide range of pressures and temperatures, with the ability to carry out synthesis in various gas environments with different thermal conductivities. The low operating temperature of the medium itself makes it possible to create large temperature gradients in the area of formation of nano-sized particles and aerosols.

The IPL method has been used to obtain a wide range of nanoparticles with the ability to control structural and surface characteristics, which is confirmed by articles in high-ranking journals. This installation produced Al, Au, Ag, Ba, Ga, Ti, Ni, Fe, Cu, Mg, Zn, Si and some of their oxides. Experimental studies have also been carried out on the production of core-shell structures, semiconductors, and substances for microelectronics (tungsten hexafluoride, monosilane, monogermane).

Over several years of work, this development has demonstrated itself as one of the best technologies for producing a wide range of nanoparticles for applied problems. Nanoparticles obtained at our installation are already used in industry: in the production of conductive adhesives; as CO₂ conversion catalysts; tungsten hexafluoride for microelectronics.

The work was carried out with financial support from the Ministry of Science and Higher Education of the Russian Federation within the framework of scientific project No. FSWR-2022-0008 and the Russian Science Foundation, project 20-79-10097.

TRANSPORT PROPERTIES OF COMPOSITES BASED ON ALKALI METAL NITRITES AND HETEROGENEOUS ADDITIVES (NANODIAMONDS, MgO , Al_2O_3)

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The search for new electrolytes for electrochemical devices is an urgent problem in solid state ionics¹. By switching to composite solid electrolytes of the “ionic salt-heterogeneous additive” type, it is possible to influence the characteristics of electrolytes by varying the composition and concentration of the inert additive (highly dispersed oxides, nanodiamonds). It is preferable to use alkali metal salts as ionic salts, due to their possible practical use. Alkali metal nitrites attract attention due to their relatively high ionic conductivity and satisfactory thermal properties². The following requirements are imposed on oxide additives: large specific surface area, chemical and thermal stability. Ion transfer in such systems occurs across interphase boundaries¹.

This work proposes to conduct a comparative study of the influence of highly dispersed oxide additives (Al_2O_3 , MgO) and nanodiamonds on the transport properties of alkali metal nitrites. The resulting composites were studied using a complex of physicochemical research methods (XRD, DSC and electrochemical impedance spectroscopy).

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SYNTHESIS AND FUNCTIONALIZATION OF CHITOSAN-CONTAINING MAGNETIC NANOPARTICLES FOR ENZYME IMMOBILIZATION

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Immobilization of the enzyme on the magnetotransplanted particles allows preserving a significant part of the activity of the free form of the enzyme, while the synthesized biocatalyst can be completely separated from the reaction mixture with the help of a magnet and used again practically without loss of activity. A carrier based on mesoporous magnetite nanoparticles (more than 60% of pores with a diameter of 10-20 nm) was synthesized, the surface and pores of which are functionalized with chitosan and sodium tripolyphosphate. The immobilization efficiency was tested for glucose oxidase, an enzyme of the oxidoreductase class that oxidizes D-glucose to D-glucono- δ -lactone in the presence of hydrogen peroxide. Prior to support, the carboxyl groups of the enzyme were activated with carbodiimide and N-hydroxysuccinimide.

The magnetic properties of the support were reduced by no more than 15% after the components were applied to the magnetite and remained unchanged when the biocatalyst was reused. IR-Fourier spectroscopy, X-ray photoelectron spectroscopy, low-temperature nitrogen adsorption and electron microscopy have proven successful modification of the carrier surface with a thin layer of chitosan and immobilization of the enzyme on it, as well as the presence of target functional groups on the carrier surface.

It has been experimentally determined that immobilization of glucose oxidase on chitosan-containing magnetic nanoparticles increases the resistance of the enzyme to inhibitory effects (pH, temperature, concentrations of substrates and reaction products) by 15-20% compared to the free form of the enzyme. When repeatedly used in the D-glucose oxidation reaction, the synthesized biocatalyst lost no more than 21% of the initial activity over 10 consecutive cycles.

The synthesized biocatalyst can be used to produce gluconic acid and determine the concentration of D-glucose in biological fluids.

This research is funded by the Ministry of Science and Higher Education of the Russian Federation, grant number 075-15-2022-1232.

SYNTHESIS AND PHOTOPHYSICAL PROPERTIES OF PENTAFLUOROPHENYLATED 5-THIENYL-2H-IMIDAZOLES

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Photoactive compounds find their application in various fields of science and technology, ranging from molecular electronics to medicine. Of greatest interest in the preparation of such molecules are compounds containing various heterocycles in their structure.

The synthesis of target compounds consists of 5 subsequent stages. On the first stage, the starting 2-acetylthiophene **1** reacts with isopropylnitrite **2** and sodium ethoxide to form oxime **3** with a yield of 75%. Cyclization of the resulting substrate occurs in the presence of ammonium acetate, acetic acid and ammonium acetate to obtain 2H-imidazole **4**. The reaction of nucleophilic hydrogen substitution (S_NH) leads to pentafluorophenylated derivative **5** in 85% yield. Subsequent bromination and Suzuki-Miyaura reaction gives series of target fluorophores **7a-e** in 70–90% yields.

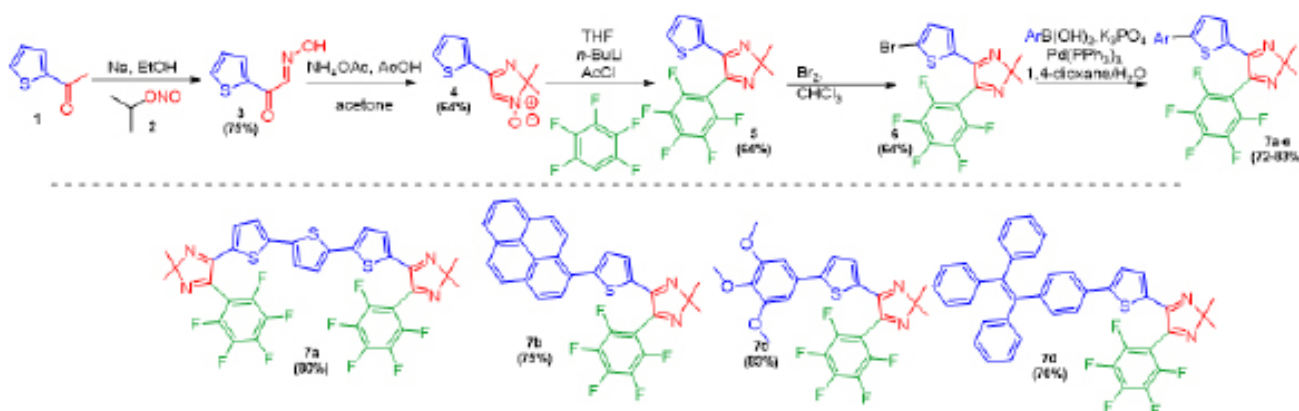


Figure 1. Synthesis of 2H-imidazole derivatives containing pentafluorophenyl and thiophene moieties

The resulting fluorophores are characterized by absorption in the region of 320–410 nm and emission with maxima at 490–600 nm, which corresponds to the green-red range of the visible spectrum. Quantum yields for these fluorophores are in range from 10 to 70%.

The investigation was supported by the Russian Science Foundation grant No. 20-73-10077, <https://rscf.ru/en/project/20-73-10077/>.

AMORPHOUS ALLOY SYSTEM Sc-Gd-Co-Al

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The experimental search for concentration ranges of verification in three-component systems requires the study of several thousands of compositions, whereas for four or more alloy's components the task becomes impracticable at all. To reduce material costs, it is vital to develop reliable theoretical methods for predicting glass formation regions in multicomponent metal systems.

A new model for predicting the composition of amorphous metallic glasses is applied to the Sc-Gd-Co-Al system. The proposed model parameters $\Theta(x-y)(x)$, $\Theta(x-y)(y)$ make it possible to predict the location of glass-forming compositions by finding the minimum of the P_{HSS} parameter multiplication by the geometric coefficient $\Gamma(x)$, $\Gamma(y)$.

The alloy with the composition $\text{Sc}_{33}\text{Gd}_{32}\text{Co}_{19}\text{Al}_{16}$ was successfully predicted and then successfully prepared as rods with a diameter of 3 mm. According to the results of X-ray diffraction and thermal analysis, the sample $\text{Sc}_{33}\text{Gd}_{32}\text{Co}_{19}\text{Al}_{16}$ is an amorphous material with the lowest value of the crystallinity index 4%.

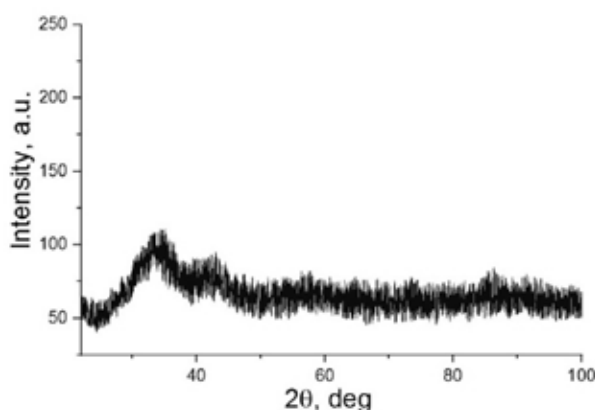


Fig. 1. XRD pattern for $\text{Sc}_{33}\text{Gd}_{32}\text{Co}_{19}\text{Al}_{16}$ glassy rod with a diameter of 3 mm

The proposed approach can be used as a predictive model for determining glass-forming compositions in various quaternary metal systems.

This work was supported by the Russian Science Foundation, grant 23-23-00100.

FORMATION THERMODYNAMICS OF PEROVSKITE-LIKE LEAD HALIDE SOLID SOLUTIONS

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Nowadays, ternary APbX_3 halides (where A — metal or organic ammonia cation, X — halide anion), which are crystallized in the structure of classic CaTiO_3 perovskite, are the relatively huge class of compounds that have lots of potential scientific and technological applications. The main problem that prevents commercialization of devices based on that materials is the insufficient level of their long-term stability due to quite rapid degradation of the perovskite-like materials at the operating conditions. Usage of the various solid solutions (which sometimes are called ‘mixed halide perovskites’) in the such devices instead of pure halide perovskites in general leads to the significant increase of the device long-term stability. However, the exact nature of the observed apparent ‘stabilization’ (thermodynamic or kinetic one) is not quite clear.

That work is devoted to the experimental study of formation thermodynamics of $\text{CsPb}(\text{Cl}_{1-x}\text{Br}_x)_3$ and $\text{CH}_3\text{NH}_3\text{Pb}(\text{Cl}_{1-x}\text{Br}_x)_3$ perovskite-like solid solutions. By the way of solution calorimetry the solution enthalpies of the pure ternary lead halides and the corresponding solid solutions were obtained, the compositional dependencies of mixing enthalpies were calculated and analysed. The significant differences in the observed dependencies are shown: for the $\text{CH}_3\text{NH}_3\text{Pb}(\text{Cl}_{1-x}\text{Br}_x)_3$ solid solutions the mixing enthalpy dependence is clearly positive in the whole range of compositions, possessing, however, the complex non-monotonic nature; for the $\text{CsPb}(\text{Cl}_{1-x}\text{Br}_x)_3$ ones the mixing enthalpies take small, near-zero values. For both systems the Debye temperatures were estimated on the basis of the results of X-ray powder diffraction analysis and the compositional dependencies of vibrational mixing entropy were calculated. The compositional dependencies of the Gibbs free energy of mixing were calculated for both systems on the basis of experimental mixing enthalpies and estimated total mixing entropies. The obtained results show that both solid solution systems are thermodynamically stable in the whole range of compositions.

The research was supported by RSF (project No. 24-23-00492)

DEVELOPMENT OF NEW APPROACHES TO THE SYNTHESIS OF DIMERIC POLYCATIONIC AMPHIPHILES WITH A REDOX-SENSITIVE GROUP

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At present, gene therapy, a new area of personalized medicine, is actively developing. This is a highly effective method of treating many diseases, including genetic ones, based on the delivery of therapeutic nucleic acids (TNA) into the cells. Non-viral systems such as cationic liposomes are the safest systems for delivering TNA into cells. Their main component is the cationic amphiphile. It can be various of nature, but the most efficient are dimeric polycationic amphiphiles (DPCA)¹. They consist of four structural units: polycationic domain, spacer, linker, hydrophobic domain. For better release of TNA into the cells, a redox-sensitive group, such as a disulfide group, can be introduced into the structure of the amphiphile. However, the dependence of transfection efficiency on the location of this group in the molecule has not been fully revealed.

In this work, various approaches to the synthesis of disulfide DPCAs have been studied. The synthesis strategy involved the obtaining of large blocks containing a hydrophobic or polycationic domain, their condensation and removing of protective groups. For introducing the disulfide group a cystamine molecule was used. The structure of all compounds has been confirmed by physico-chemical analysis methods.

Overall, we have developed approaches to the synthesis of disulfide DPCAs, which allow us to obtain a library of such compounds to study the effect of the location of a redox-sensitive group in the structure of DPCAs on the efficiency of TNA delivery by cationic liposomes.

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This study was supported by the Ministry of Education and Science of Russia, project № 0706-2023-0004.

PHOTOMEMRISTIVE STRUCTURES BASED ON MODIFIED GRAPHENE OXIDE AND CARBON NANOPARTICLES

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For compact storage and fast autonomous processing of large volumes of visual information, photomemristors based on 2D materials^{1,2}, including graphene oxide (GO), are being actively studied. This work is devoted to studying the possibility of modifying graphene oxide using carbon nanoparticles (CNPs) to control the photosensitivity of memristive structures and create photomemristors for an extended range of wavelengths³.

GO films were prepared by depositing its sol on the surface of an oxidized silicon substrate. After which the GO film was reduced under hydrothermal conditions. CNPs were synthesized by thermal decomposition of aqueous solutions of spermine and citric acid, and after dialysis purification they were applied to the surface of a reduced modified GO film⁴. Measurements of the current-voltage characteristics of the fabricated structures when irradiated with light of different wavelengths showed characteristic changes in memristive behavior. The results obtained indicate the possibility of using these structures to process a photosignal in memory.

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The work was carried out with the financial support of the Russian Science Foundation, project 23-49-00159.

A STUDY OF THE TRANSITION METALS REDOX ACTIVITY IN Prussian Blue ANALOGS AS CATHODE MATERIALS FOR POTASSIUM-ION BATTERIES

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Among electrochemical energy storage systems, metal-ion batteries are the most high-power, versatile, and long-life devices. In stationary storage equipment, the operational costs of lithium-ion batteries are significant. This problem attracts research interest in post-lithium-ion systems, including those based on potassium¹. Among cathode materials for potassium-ion batteries, Prussian Blues analogues (PBAs) with the formula $K_2M^I[M^2(CN)_6] \cdot nH_2O$ (M^I – 3d transition metal, $n \geq 0$) are promising solution with wide variety of composition and tuning of redox reactions. The aim of this work is to study the mechanism of redox activity in PBAs with the compositions $K_2Mn_{1-x}M^I[M^2(CN)_6] \cdot nH_2O$ (M^I – inner-sphere cations Fe, Co, Mg, M^2 – outer-sphere cations Fe, Mn, $x=0-1$, $n \geq 0$).

Series of single-phase samples of hexacyanoferrates and hexacyanomanganates were synthesized and studied. According to electron and X-ray diffraction investigation in hexacyanoferrates, it was found that with increasing cobalt content with more than 50 at.%, the crystal structure changes from monoclinic to cubic². During an iron content increasing, in both hexacyanoferrates and hexacyanomanganates, a decrease in the unit cell volume without changing the monoclinic system was identified. The magnetic, electronic and electrochemical properties of the obtained compounds were studied, as well as the evolution of the electronic structure of transition metals in the PBAs in *ex situ* and *operando* modes during dis/charge by X-ray absorption spectroscopy. Finally, a correlation between the composition and their electronic and electrochemical properties of materials was identified. The results will be discussed in detail in this report.

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SYNTHESIS AND PHOTOPHYSICAL PROPERTIES OF LUMINOPHORES BASED ON *ORTHO*-CARBORANE

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Carboranes are compounds consisting of carbon and boron atoms located at the vertices of polyhedra with triangular edge. The most numerous are *closo*-carboranes distinguished by thermal and chemical stability, unique spatial, structural, and electronic organization. Due to their unique physical and chemical properties, many compounds based on them have found their applications as light-emitting diodes, organic transistors, chemosensors, and other molecular electronics materials.

In the several works of our scientific group, methods for the preparation of π -conjugated and heterocyclic photoactive systems based on *ortho*-carborane have been developed. The developed compounds are characterized by absorption in the region from 300 to 400 nm, emission up to 700 nm, quantum yields up to 99%, ability to form aggregates (AIE & AIEE), as well as rigidochromism effect.

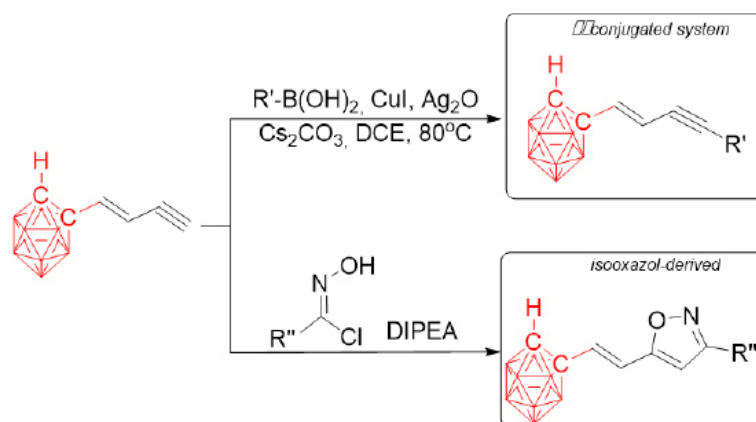


Figure 1. Luminescent π -conjugated and heterocyclic systems based on *ortho*-carborane

Thus, the obtained *ortho*-carboranyl phosphors can be used in the design of OLED, chemosensors, and other functional elements of molecular electronics.

The research was supported by a grant from the Russian Science Foundation № 24-13-20023, <https://rscf.ru/en/project/24-13-20023/>.

VIRTUAL MODEL OF MUTUAL DIFFUSION PROCESSES IN MULTICOMPONENT SYSTEMS

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The development of the theory of mutual diffusion processes in multicomponent systems experiences significant difficulties due to the impossibility of experimentally determining the main fundamental parameters - partial diffusion coefficients (PDC) of atoms. The effect of “upward diffusion” in diffusion pairs of multicomponent systems has not yet received an unambiguous description. All these difficulties can be overcome by creating a virtual model of the mutual diffusion process, which is based on the mechanism of random walks of atoms and partial diffusion coefficients of components. Such a model is presented in this work.

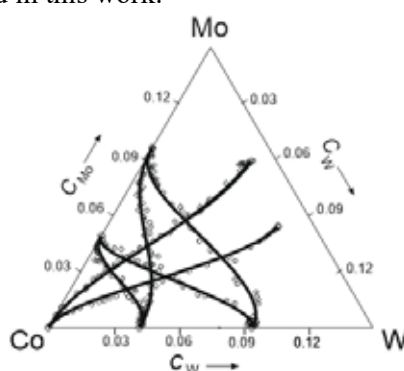


Figure 1. Comparison of modeled and experimental diffusion paths in diffusion pairs of the Co-Mo-W system after annealing for 120 hours at 1100 K. Partial diffusion coefficients:

$$D_{Co} = 2.25 \cdot 10^{-15} (\text{m}^2/\text{s}), D_{Mo} = 1 \cdot 10^{-15} (\text{m}^2/\text{s}), D_W = 0.43 \cdot 10^{-15} (\text{m}^2/\text{s}).$$

To assess the performance of the model in real systems, we used the values of the PCD of cobalt, molybdenum and tungsten in the cobalt corner of the Co-Mo-W system at 1375 K, which were first calculated by the authors of this study using Darken's equations based on experimental data from work¹. The obtained PCD values were used for subsequent modeling of experimental diffusion paths using a virtual model of mutual diffusion. Good agreement between experimental results and theoretical calculations was established (Figure 1).

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DETERMINATION OF FUNDAMENTAL PARAMETERS OF MULTICOMPONENT SYSTEMS – PARTIAL DIFFUSION COEFFICIENTS OF COMPONENTS – USING DARKEN'S EQUATIONS

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Using the Darken hypothesis, an analysis of the processes of mutual diffusion in an N-component diffusion pair was carried out and for each component the Darken equation was obtained - the equation for the connection of N partial diffusion coefficients (PDC) D_N with the mutual diffusion coefficient \tilde{D} , determined experimentally. In the diffusion zone of the three-component system A+B+C, one of three cases can be observed for any plane (Table 1).

Table 1. Types of Darken equations in ternary systems, depending on the direction of partial flows of components

1. $J_A = J_B + J_C$	$\tilde{D}_A = D_A \cdot (1 - C_A) + D_B \cdot C_A \cdot \partial C_B / \partial C_A + D_C \cdot C_A \cdot \partial C_C / \partial C_A$ $\tilde{D}_B = D_B \cdot (1 - C_B) + D_A \cdot C_B \cdot \partial C_A / \partial C_B - D_C \cdot C_B \cdot \partial C_C / \partial C_B$ $\tilde{D}_C = D_C \cdot (1 - C_C) + D_A \cdot C_C \cdot \partial C_A / \partial C_C - D_B \cdot C_C \cdot \partial C_B / \partial C_C$
2. $J_B = J_A + J_C$	$\tilde{D}_A = D_A \cdot (1 - C_A) + D_B \cdot C_A \cdot \partial C_B / \partial C_A - D_C \cdot C_A \cdot \partial C_C / \partial C_A$ $\tilde{D}_B = D_B \cdot (1 - C_B) + D_A \cdot C_B \cdot \partial C_A / \partial C_B + D_C \cdot C_B \cdot \partial C_C / \partial C_B$ $\tilde{D}_C = D_C \cdot (1 - C_C) - D_A \cdot C_C \cdot \partial C_A / \partial C_C + D_B \cdot C_C \cdot \partial C_B / \partial C_C$
3. $J_C = J_A + J_B$	$\tilde{D}_A = D_A \cdot (1 - C_A) - D_B \cdot C_A \cdot \partial C_B / \partial C_A + D_C \cdot C_A \cdot \partial C_C / \partial C_A$ $\tilde{D}_B = D_B \cdot (1 - C_B) - D_A \cdot C_B \cdot \partial C_A / \partial C_B + D_C \cdot C_B \cdot \partial C_C / \partial C_B$ $\tilde{D}_C = D_C \cdot (1 - C_C) + D_A \cdot C_C \cdot \Delta C_A / \Delta C_C + D_B \cdot C_C \cdot \partial C_B / \partial C_C$

Determined that:

1. Coefficient of mutual diffusion \tilde{D} , determined by the Matano-Boltzmann method from experimental concentration curves, is an auxiliary parameter, has no physical meaning and can take both positive and negative values.
2. A technique has been developed for determining the coefficients of mutual diffusion \tilde{D} on samples with the effect of "uphill" diffusion.
3. The resulting system of Darken equations for any plane in the diffusion zone coincides with the Onsager system of equations.

The adequacy of the obtained equations to diffusion processes was tested both on model and real systems, where the PDC of components in real systems are experimentally determined for the first time.

LIGNOCELLULOSE BIOMASS AS A SOURCE OF HARD CARBON FOR METAL-ION BATTERIES

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In the role of energy storage and supply systems, sodium-ion batteries (SIBs) can be used as a promising alternative to lithium-ion batteries (LIBs). Non-graphitizable carbon, which is used as an anode material for metal-ion batteries, is attracting significant attention due to the possibility of obtaining it from inexpensive renewable sources, such as various biomass materials. One such source could be lignin, which is a major component of wood (15-40%) [1].

This study is dedicated to investigating the properties of non-graphitizable carbon based on lignin, its electrochemical characteristics, and the search for optimal synthesis conditions to improve performance in lithium and sodium-ion batteries. Commercial sodium lignosulfonate and kraft-lignin were used as starting materials, which are abundant waste products in the pulp and paper industry. Non-graphitizable carbon was obtained through several methods: direct annealing in an inert atmosphere at 1300°C, annealing after reprecipitation with subsequent drying, and with prior cation exchange of sodium for protons in lignosulfonate.

Based on the results of electrochemical tests in the sodium-ion half-cell, it can be seen that the coulombic efficiency of the redissolved sample and the sample washed from sodium reaches 85% in the first cycle, and 74% in the sample obtained by direct annealing. The discharge capacity of the samples is in the range of 250–300 mAh/g. During redissolution, there is a change in particle size and porosity, which leads to a change in surface area from 13 m²/g to 6 m²/g. It can be concluded that it is the change in morphology during redissolution that affects the change in coulombic efficiency, and the sodium content has a lesser effect on electrochemical characteristics.

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GAS SENSITIVE MATERIALS BASED ON SEMICONDUCTOR NANOCRYSTALLINE INDIUM AND BISMUTH VANADATES

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Gas sensors are of great practical importance. Semiconductor gas sensors have the advantages of high sensitivity to trace concentrations of noxious gases, stability, low cost and ease of operation. The main problem of semiconductor gas sensors is the lack of selectivity in gas determination. At the moment, gas sensitivity of many semiconductor mixed-metal oxides remains unstudied. The purpose of this work is to determine the influence of composition and structure on the gas sensitivity of mixed-metal oxides using the example of InVO_4 and BiVO_4 , in comparison with simple oxides In_2O_3 and V_2O_5 , and to determine the interaction mechanism between materials and target gases.

The In_2O_3 and BiVO_4 -CP samples were obtained by the precipitation method, and the V_2O_5 , InVO_4 and BiVO_4 -HT samples were obtained by the hydrothermal method. According to the X-ray diffraction results, the choice of synthesis method determines the crystal structure of BiVO_4 : the BiVO_4 -CP sample is predominantly a tetragonal dreyerite phase, and BiVO_4 -HT is a monoclinic clinobisvanite phase.

Gas sensors based on the materials were prepared, and gas sensitivity measurements were carried out for various reducing gases and NO_2 in dry and humid environments. It was shown that the sensor based on InVO_4 has high selectivity to NO_2 , and BiVO_4 has high selectivity to H_2S .

Using in situ IR spectroscopy, the mechanism of interaction of vanadates with target gases was revealed. It has been shown that InVO_4 has a great gas sensitivity to NO_2 due to the large number of oxygen vacancies in the structure, and the synergistic effect of bismuth cations and vanadate anions determines the adsorption and oxidation of H_2S on the surface of BiVO_4 .

USE OF MINERAL RAW MATERIALS FROM THE ARCTIC ZONE OF THE RUSSIAN FEDERATION FOR SYNTHESIS OF HIGHLY EFFECTIVE PHOSPHATE SORBENTS

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Inorganic, in particular, phosphate sorbents are capable of forming mineral-like compounds that are well compatible with matrices for radionuclide disposal¹, which gives them an advantage over hybrid materials. The aim of this work is to develop methods for synthesis of new composite sorbents based on titanium and magnesium phosphates, and to study the properties of the final products. Such materials include several phosphate phases, so their effectiveness is higher than of the individual components - due to the synergism effect².

Titanium salt, a semi-product from the processing of sphene (technogenic waste from the enrichment of apatite-nepheline ores from the Khibiny deposit) was used as a source of titanium. Serpentine – the main component of overburden rocks of various deposits of the Kola Peninsula, Karelia and the Urals (part of the Arctic zone of the Russian Federation), currently unclaimed and going to dumps – was chosen as the source of magnesium.

Physicochemical studies of the phase formation of titanium and magnesium phosphates and the kinetics study of the serpentine decomposition under various conditions have been carried out. Based on these studies general principles and methodological approaches to the targeted synthesis of new composite materials based on titanium and magnesium phosphates using industrial wastes have been developed.

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PREPARATION AND CONVERSION OF 4-METHYLENE-1,3-DIOXACYCLOALKANES

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Cyclic derivatives of acetone and other ketones - substituted 2,2-dialkyl-1,3-dioxolane - are formed in a number of biotechnological processes and are widely used in the production of biofuels and pharmaceutical materials^{1,2}.

The condensation of epichlorohydrin with ketones in quantitative yield leads to the formation of 4-chloromethyl-1,3-dioxolanes, the dehydrogenation of which can yield the corresponding 4-methylene-1,3-dioxolanes^{3,4}.

These compounds are of significant interest due to their double bond reactivity and acetal function. As a result of their dichlorocarbonation, we obtained spirocyclic structures containing a gem-dichlorocyclopropane and cycloacetal fragment.

In the presence of CF_3COOH , alcohols and phenols are added to the double bond of 4-methylene-1,3-dioxolanes to form 4-alkyl(aryl) derivatives. When interacting with pharmacophoric diols and bis-phenol, mono- and bisadducts were isolated from the reaction mixture.

Biomedical tests have shown that cyclic acetals exhibit antimicrobial activity, which depends on the hydrophilic-hydrophobic balance.

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The work was carried out within the framework of the state task «Development and creation of small-scale products and reagents (corrosion and scale inhibitors, antioxidants, biocides, additives, etc.) for petrochemical processes and purification of aquatic environments from pollution, replacing imported substances and materials. Theoretical and experimental approaches».

ADSORPTION OF POLYOXOMETALATE COMPLEXES MO AND W ON SURFACES OF DIFFERENT NATURE

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Polyoxometalate complexes (POM) of molybdenum and tungsten are giant polyanions, the size of which can range from 1 to 5 nm [1]. One of the promising directions is their use as precursors for the synthesis of molybdenum- and tungsten-containing supported catalysts. By choosing a specific synthesis strategy, it is possible to obtain a highly dispersed catalyst both based on carbides and based on molybdenum and tungsten oxides. An important role in liquid-phase deposition of a precursor is played by the properties of the support, in particular, the nature of its surface. Analysis of the adsorption of polyoxometalate complexes on surfaces of various natures is one of the opportunities to assess the nature of the interaction, which, in turn, is necessary to control the properties of the supported catalyst.

The purpose of this work was to quantify the adsorption of molybdenum and molybdenum tungsten blue (POM) nanoparticles on the surface of alumina and carbon nanotubes (CNTs).

Dispersions of molybdenum and molybdenum-tungsten blues were obtained by the reduction of molybdate and tungstate ions in an acidic medium using ascorbic acid. Molybdenum-tungsten blues have been synthesized with different [Mo]:[W] molar ratios, namely 95:5; 90:10; 80:20; 50:50. Gibbs adsorption of nanoparticles was used as a quantitative characteristic; their equilibrium concentration in a dispersion medium was determined using optical spectroscopy.

Analysis of the obtained adsorption isotherms using the Langmuir and Freundlich equations made it possible to estimate the monolayer capacity and adsorption equilibrium constants. It was found that the quantitative parameters of adsorption are influenced by both the nature of the surface of the support/adsorbent (Al_2O_3 and CNTs) and the pH value of the dispersion medium of molybdenum and molybdenum-tungsten blues.

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COORDINATION COMPOUNDS OF BIOMETALS AS PRECURSORS FOR OBTAINING SUBSTANCES AND MATERIALS WITH SPECIFIED PROPERTIES

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The possibility of using metal coordination compounds, both in solid form and those formed *in situ*, to obtain substances and materials with desired properties has been demonstrated.

During the thermal reduction of copper(II) coordination compounds $[\text{Cu}(\text{N}_2\text{H}_4)_3][\text{B}_{10}\text{H}_{10}]\cdot n\text{H}_2\text{O}$ or $[\text{Cu}(\text{NH}_3)_4][\text{B}_{10}\text{H}_{10}]\cdot n\text{H}_2\text{O}$ in an argon atmosphere at 900°C, a boron-containing copper composite identical in composition was obtained. Based on X-ray powder diffraction data and a study of the morphology of the composite, it was established that the sample obtained is a boron-nitride matrix doped with cubic copper nanoparticles, the average particle size being 81 and 52 nm. A study of the conductivity of the coating obtained from annealed samples showed an increase in electrical conductivity with increasing temperature, characteristic of semiconductors.

The possibility of using zinc(II) salts to increase the solubility in water of hydrophobic inhibitors of replication of RNA viruses has been demonstrated. Carbocyclic derivatives of N-acylated esters of L-amino acids with aromatic carboxylic acids were studied as antiviral low-molecular agents. It has been found that hydrophobic organic compounds in the cationic zinc(II) complex formed *in situ* in an aqueous solution with the addition of zinc(II) chloride are capable of suppressing the replication of a strain of influenza A virus resistant to adamantane drugs, while zinc(II) chloride at the concentration used does not have an antiviral or toxic effect in *in vitro* experiments.

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SYNTHESIS OF SELF-DISPERSING MOLYBDENUM-VANADIUM BLUE XEROGELS OF VARIOUS COMPOSITIONS

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The ability to synthesis highly concentrated initial dispersions and to store them without losing their essential properties, in particular, without losing aggregative stability, is of great importance for the implementation of sol-gel synthesis of various materials. It is known that it is possible to synthesize such hydrosols of certain compounds (AlOOH , ZrO_2 , CeO_2 , molybdenum blue dispersions) that, after drying, allow the production of xerogels capable of spontaneous redispersion and the formation of stable hydrosols of the required concentration. This ability opens up wide possibilities for practical application of the above-mentioned dispersions.

The aim of this study was to obtain xerogels from dispersions of molybdenum-vanadium blue of different compositions and to investigate their ability for spontaneous redispersion.

Molybdenum-vanadium blue dispersions with a molar ratio $[\text{Mo}]:[\text{V}] = 20:80, 50:50, 80:20, 90:10$ were prepared by the reduction of Mo^{+6} and V^{+5} salts with ascorbic acid in an acidic medium. Xerogels were prepared by drying the dispersions at various temperatures (ranging from 25°C to 200°C). They were then redispersed in water at $\text{pH} = 2$. The xerogels were analyzed using thermogravimetric analysis and IR spectroscopy, while the sols obtained by redispersing the xerogels were analyzed using spectrophotometry and photon correlation spectroscopy.

It has been found that upon redispersion of xerogels obtained by drying at temperatures ranging from 25°C to 150°C , stable dispersions of molybdenum-vanadium blue are formed independently of the particle composition (within the investigated range). The hydrodynamic particle radius in the resulting hydrosols is 4 nm and corresponds to the particle sizes in the initial hydrosols. When the drying temperature is increased to 200°C , xerogels lose the ability for redispersion. Data from thermogravimetric analysis and IR spectroscopy indicate that an increase in drying temperature to 200°C leads to irreversible dehydration and destruction of molybdenum-vanadium clusters.

GROWTH OF NANOWHISKERS ON THE SURFACE OF OXIDISED Al AND THEIR INFLUENCE ON THE STRENGTHENING OF Al-MATRIX COMPOSITE

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Dispersed strengthening is one of the main mechanisms for improving the thermomechanical properties of metals. The highest strength characteristics of metal-matrix composites (MMCs) can be obtained by using dispersed particles in the form of nanosheets or nanotubes. However, nanoparticles (NPs), due to their high surface energy, are prone to agglomeration, which leads to a decrease in the mechanical properties of MMCs. To address this problem, this thesis considers a new concept, i.e., the formation of NPs directly on the surface of Al particles. In particular, the formation of nanowhiskers on the surface of Al particles due to the interaction of LiNO_3 with the Al_2O_3 layer is studied.

Al powder was oxidized in air at 500-600 °C for 15-180 min. After the formation of Al_2O_3 surface layer of different thicknesses, the powders were wetted with aqueous LiNO_3 solution, dried and heat treated in argon atmosphere. Heat treatment temperatures in the range of 700-1200 °C and heat treatment times of 30 and 60 min were studied.

The thickness of the Al_2O_3 layer after oxidation was determined by the powder weight gain, as well as by the increase in the oxygen content determined by energy dispersive X-ray spectroscopy. The morphology of the obtained nanowhiskers was studied using scanning and transmission electron microscopy, including high-resolution microscopy. The nanowhiskers were found to form at 1000 °C on the surface of Al_2O_3 layer at 600 °C for 180 min. MMCs was obtained from the material containing 0.9 wt.% of nanowhiskers by spark plasma sintering. It was found that at 25 °C, the tensile strength of MMCs increased by 67% and the Vickers hardness increased by 64%.

The work was performed within the framework of the State Assignment FSME-2023-0004.

INFLUENCE OF MECHANOCHEMICAL SYNTHESIS PARAMETERS ON CRYSTALLINITY OF HIGH-ENTROPY LAYERED DOUBLE HYDROXIDES

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Research in the field of high-entropy materials is expanding significantly, and at present, not only high-entropy alloys, but also oxides¹, sulfides², carbides³, etc. are being extensively studied. Promising materials in the high-entropy field are layered double hydroxides (LDHs). LDH is a class of natural and synthetic materials characterized by wide ranges of variation in both cationic and anionic compositions, which contributes to the formation and development of specific electrical, magnetic, catalytic, and sorption properties.

LDH samples of the MgCoNi/AlYFe composition were synthesized using mechanochemical approach without an additional aging step. Planetary ball mill with a stainless-steel reaction vessel was applied. The rotation speed was varied (200, 300, 400 rpm). According to the XRD results, all synthesized materials are characterized by single-phase composition and relatively low crystallinity. However, the intensity of the peaks corresponding to the hydrotalcite structure decreases with increasing the rotation speed of the mill (Fig. 1).

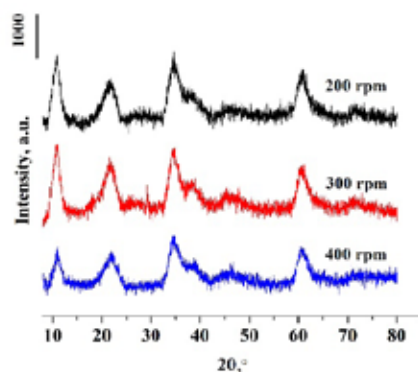


Figure 1. X-ray powder diffraction patterns of LDH samples obtained with different values of rotation speed

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PRASEODYMIUM MAGNESIUM HEXAALUMINATE: SYNTHESIS AND THERMOPHYSICAL PROPERTIES

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The report presents a comparative analysis of synthetic approaches to the production of polycrystalline $\text{PrMgAl}_{11}\text{O}_{19}$, the results of a study of the influence of synthesis conditions on the phase composition and microstructure of the resulting materials, as well as the thermophysical properties of magnesium-praseodymium hexaaluminate.

The main advantages of lanthanide hexaaluminates $\text{LnMgAl}_{11}\text{O}_{19}$ are their high chemical and thermal stability and low thermal conductivity, which makes them promising for use as high-temperature catalysts and thermal barrier coatings. In addition, the possibility of doping with other rare earth elements or transition metals makes $\text{LnMgAl}_{11}\text{O}_{19}$ a potential candidate for use as a luminescent matrix, elements of solid-state lasers, solar panels and white LEDs.

Such properties are determined mainly by the hexagonal (space group $P6_3/mmc$) magnetoplumbite structure of $\text{LnMgAl}_{11}\text{O}_{19}$, which can be represented as two types of blocks alternating along the c axis: spinel blocks, similar in structure to MgAl_2O_4 , and hexagonal blocks consisting of AlO_5 and LnO_{12} polyhedra.

The preparation of lanthanide hexaaluminates $\text{LnMgAl}_{11}\text{O}_{19}$ by solid-phase interaction requires long-term annealing of samples at high temperatures (1600–1700 °C). However, this does not guarantee obtaining a material free of secondary phases. Therefore, alternative synthesis methods have been proposed, such as the citrate sol-gel method or co-precipitation from aqueous solutions of hydroxides followed by annealing of the resulting precursor. The use of “wet” chemistry methods makes it possible to reduce the time of high-temperature heat treatment but can lead to the production of inhomogeneous material due to different decomposition temperatures and the reactivity of metal compounds included in the precursor.

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FERRITE-BASED MATERIALS FOR FUTURE TECHNOLOGIES

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The report presents the results of research related to the creation of a new generation of nanocrystalline powdered materials based on ferrites with reproducible structure-sensitive properties, promising for the creation of electronic devices, the operation of which will be based on the use of electron spin.

To realise these goals, the influence of initial reagents on gel structuring and properties of intermediate and final synthesis products has been investigated by IR, EXAFS- and XANES-spectroscopy, as well as by XRD and SEM. As a result, a universal approach has been developed that allows the preparation of homogeneous materials based on ferrites with different variants of cationic substitutions.

The influence of cationic ratios on the homogeneity region and functional properties of multicomponent oxide compounds has been revealed in the prepared materials. Based on the data obtained, the materials with the highest functional characteristics were identified.

Particular attention is paid to studying the formation of cerium-containing ferrogarnets and the possibility of using them to create stable magnetoplasmonic structures is assessed¹.

A method of obtaining defect-free film structures with volume-like properties, excluding diffusion and interaction of components at the interphase boundary, by non-epitaxial methods has been developed^{2,3}.

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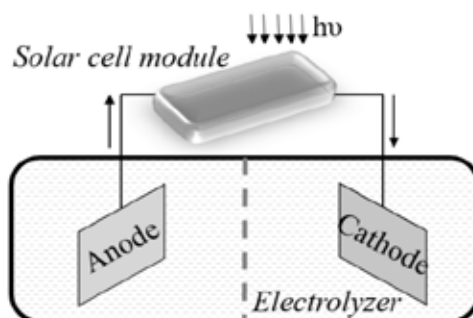
PHOTOVOLTAIC-DRIVEN ELECTROCHEMICAL WATER SPLITTING SYSTEMS FOR GREEN HYDROGEN PRODUCTION

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Nowadays the dependence on fossil fuels and the increase of greenhouse gas emissions make the development of renewable energy sources essential. In this regard, hydrogen production by water electrolysis is considered as a clean energy technology for sustainable development^{1,2}. In addition, when water electrolysis is coupled with a renewable energy source such as solar, zero-carbon green hydrogen can be produced. Due to this photovoltaic-driven water splitting systems, possessing high solar-to-hydrogen efficiencies, are the most promising for green hydrogen production³.



In this study, the development of stable and scalable photovoltaic-driven electrochemical (PV-EC) systems for water splitting, where solar cell module is coupled with an electrolyzer, is presented. Solar cell modules based on perovskite solar cells (PSCs), CIGS or crystalline silica (c-Si) solar cells were constructed and were used in PV-EC systems. The influence of the light intensity on the efficiencies for all systems under investigation was examined. The obtained results revealed that PV-EC system driven by PSC module had shown the best solar-to-hydrogen efficiency under various weather conditions.

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ANTI-CORROSIVE ZIRCONIUM OXIDE COATINGS PRODUCED BY THE SOL-GEL METHOD

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To protect aluminum alloys from corrosion, depending on the grade of the alloy, the design of the product, its purpose, operating conditions and other factors, paint and varnish coatings, conversion coatings, including protective and decorative electrochemical oxidation (anodizing), sol-gel coatings, as well as complex coatings consisting of an oxide film and a paint coating applied onto it¹.

In this work, we investigated the process of applying protective zirconium-containing sol-gel coatings to the surface of the AMg6 aluminum alloy.

The compositions of solutions for the deposition of solo protective zirconium-containing sol-gel coatings were optimized, and the physicochemical and mechanical properties of the deposited coatings, which could become an alternative to chromate coatings, were studied.

It has been established that sol-gel coatings formed in 1% zirconium dioxide sol (67 s) (pH 1.7) and sample pulling speed of 450 mm/min have the greatest protective ability. The subsequent heat treatment of zirconium-containing sol-gel coatings at a temperature of 300 °C leads to an increase in the protective ability from 67 to 120 s. The improvement in protective ability as a result of heat treatment at a given temperature is confirmed by corrosion currents determined using Evans diagrams. Corrosion rate has decreased from $1.4 \cdot 10^{-4}$ to $4.86 \cdot 10^{-5}$ A/cm².

It has been shown that at the optimal rate of sample extraction from the sol, coatings with a thickness of 100-120 nm are formed.

It was shown that three-layer sol-gel coatings (680 s) have the greatest protective ability, which is higher than the protective ability of two-layer (540 s) and single-layer (120 s) coatings.

It has been established that zirconium-containing sol-gel coatings are not inferior to chromate coatings in terms of wear resistance.

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SYNTHESIS OF NANODISPERSED HAFNIUM DIOXIDE SOLS AND ANALYSIS OF PEROXIDASE-LIKE ACTIVITY

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In recent years, a number of examples have shown that inorganic substances in the nanodispersed state can participate in biochemical processes and perform the functions of natural enzymes; such substances have been identified as a separate class of “nanoenzymes”.

HfO₂-based materials absorb X-rays and gamma rays well, opening the possibility of their use as radiosensitizers in nuclear medicine¹. In the context of studying the effects of nanodispersed HfO₂ on the body and potential applications in radiotherapy preparations, it is important to evaluate its enzyme-like properties. The reaction time, the wide particle size distribution and the low stability of the obtained sols make most of the known methods for the synthesis of HfO₂ sols unfavorable.

In the course of this work, by hydrothermal treatment (HT) of hafnium lactate complex with addition of urea at 180°C and 220°C for 2 and 4 days, stable aqueous sols of nanocrystalline hafnium oxide were synthesized. The peroxidase-like activity of the obtained sol towards hydrogen peroxide was investigated by chemiluminescence, using luminol as probe molecule. The measurements were carried out in conditions close to physiological. The synthesis yielded nanocrystalline HfO₂ in monoclinic singularity regardless of the temperature and duration of the synthesis. A stable aqueous sol with ζ -potential = - 29 mV and a particle radius of 17 nm was obtained by washing the HT synthesis product with water. HfO₂ sols show strong luminescence under UV light irradiation and peroxidase-like activity.

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ISOLATION AND PHYSICO-CHEMICAL PROPERTIES OF LOADED EXTRACELLULAR VESICLES

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Extracellular vesicles (EVs) are secreted by all eukaryotic and prokaryotic cells and may be used for intracellular drug delivery ¹. Our research was aimed at preparation of loaded EVs from human embryonic, induced pluripotent and cancer cells. The EVs were isolated from culture media using centrifugation at 9,000 g to remove membrane debris. Subsequent centrifugation of supernatants at 20,000 g allowed us to isolate EVs. Electron microscopy revealed vesicles with internal empty space covered with lipid bilayer of ~7-10 nm and diameters ranged from 10 to 200 nm. Additional filtration using membranes with 0.2 µm pore sizes permitted to remove cellular membranes. Phospholipids forming a complex with ammonium ferrothiocyanate were measured colorimetrically ². Ultraviolet absorption spectroscopy at 280 nm was used to determine protein concentrations in EVs. EVs appeared to remain stable during storage in isotonic phosphate buffer (PBS) at +4C° for several weeks. Membrane lipids of EVs were dissolved in chloroform. After evaporation of the solvent at room temperature and dried thin layer formation the addition of water solutions of fluorescent protein or Au nanoparticles with subsequent sonication resulted in formation of loaded EVs. Structures of the composite loaded EVs were confirmed by fluorescent microscopy and STEM.

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DEVELOPMENT OF THE FUNDAMENTAL BASIS OF A NEW TECHNOLOGICAL PROCESS FOR SYNTHESIS OF NITRIDE CERAMICS BASED ON Zr-Nb SOLID SOLUTION

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Within the framework of the oxidative design approach, the process of complete nitridization of rolled Zr-Nb samples in nitrogen atmosphere at temperatures below, near and above the peritectic reaction temperature has been realized for the first time. The possibility of synthesizing in a single-stage technological process of dense ceramics of a given shape on the basis of mixed nitrides and composites based on them has been experimentally shown.

The kinetic dependences of the processes under consideration have been investigated.

A thermodynamic model of condensed phases in the ternary system Nb-Zr-N at 298 – 3 000 K is proposed.

The interrelation between the structure of the created ceramics and composites based on it and the texture of the initial Zr-Nb solid solution is shown.

Peculiarities of diffusion processes within the framework of high-temperature nitridization of Zr-Nb solid solution throughout the volume of ceramics depending on temperature and time parameters of the process have been revealed.

The hardness distribution along the cross-section of the created ceramics has been studied.

Chemical and thermal stability of the created ceramics based on mixed Zr(Nb)N nitride and composites based on it is shown.

The study was carried out under the grant of the Russian Science Foundation (project No. 20-13-00392).

DEVELOPMENT OF THE FUNDAMENTAL BASIS OF A NEW TECHNOLOGICAL PROCESS FOR SYNTHESIS OF NITRIDE CERAMICS BASED ON Zr-U SOLID SOLUTION

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Within the framework of the oxidative design approach, the process of complete nitridization of rolled Zr-U samples in nitrogen atmosphere at temperatures below, near and above the peritectic reaction temperature has been realized for the first time. The possibility of synthesizing in a single-stage technological process of dense ceramics of a given shape on the basis of mixed nitrides and composites based on them has been experimentally shown.

The kinetic dependences of the processes under consideration have been investigated.

A thermodynamic model of condensed phases in the ternary system U-Zr-N at 298 - 2 800 K is proposed.

The interrelation between the structure of the created ceramics and composites based on it and the texture of the initial Zr-U solid solution is shown.

Peculiarities of diffusion processes within the framework of high-temperature nitridization of Zr-U solid solution throughout the volume of ceramics depending on temperature and time parameters of the process have been revealed.

The hardness distribution along the cross-section of the created ceramics has been studied.

Chemical and thermal stability of the created ceramics based on mixed Zr(U)N nitride and composites based on it is shown.

The study was carried out under the grant of the Russian Science Foundation (project No. 20-13-00392).

DEVELOPMENT OF NEW COMPOSITE MATERIAL: CARBOPYROCERAM-NIOBIUM-NIOBIUM PENTAOXIDE

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Composite materials based on niobium can be used in various fields of science and technology – navigation systems, capacitor construction, thermonuclear energy, microelectronics¹. The demand for niobium and its compounds is due to a combination of high superconducting characteristics that are currently unattainable for other superconductors.

Previously, we obtained superconducting niobium coatings on carbopyroceram² and developed a technological scheme for obtaining carbopyroceram-niobium composite material³. Niobium is an active metal and interacts with air atmosphere and moisture that leads to degradation its superconducting properties.

In order to preserve these properties, it is necessary to perform surface modification of the superconducting coating by creating a protective layer. One of the promising protective coating is niobium pentaoxide, which can be formed as a continuous nanoscale film on niobium. However, optimization of parameters for the formation of niobium pentaoxide coatings is necessary that to achieve the required protective coating properties.

The determination of technological parameters for the oxidation process (current density, electrolyte temperature, molding time) was carried out in this work. The thickness of the protective coatings was measured and their dielectric characteristics were determined.

The formation of a protective niobium pentaoxide layer allows to significantly increase reliability and the resource of the composite material: substrate-superconductor-protective coating.

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SOLUBILITY INCREASING OF CARDIOVASCULAR DRUG TELMISARTAN USING BIOPOLYMERS

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Telmisartan (TMS) is widely used in daily clinical practice in the treatment of patients with arterial hypertension. However, the average bioavailability of this drug, which belongs to the second class of the biopharmaceutical classification system, is 42%, which is due to its low aqueous solubility. The goal of this work was to increase the solubility of the hydrophobic drug telmisartan by using biocompatible polymers: polyvinylpyrrolidone (PVP) and polyethylene glycol (PEG).

To determine the effect of selected polymers on water solubility of telmisartan, phase solubility diagrams of the drug in the presence of various concentrations of PVP and PEG were obtained. It was found that PVP is superior to PEG in its solubilizing effect over the entire temperature range studied. The maximum increase in telmisartan solubility by 123 times at 298 K was achieved with the addition of 6.0 mM polyvinylpyrrolidone. At the same time, the addition of much higher concentrations of polyethylene glycol (26 mM) reduced the hydrophobicity of the drug by only 13 times. The interaction of drugs with polymers is the result of the synergistic action of van der Waals forces, hydrogen bonds and the hydrophobic effect. The obtained TMS phase solubility diagrams are A_L -type curves and indicate the formation of a complex of the drug with the polymers used. Based on the obtained concentration dependences of solubility, the complexation constants were calculated. It should be noted that the slope of the concentration dependences in the system with PVP exceeds 1, which indicates the formation of a second-order complex. Thermodynamic parameters of complexation process were calculated and analyzed. Negative values of enthalpy and Gibbs energy indicate that this process with polymers is spontaneous and exothermic.

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FORMATION OF COMPOSITES WITH ZrB_2 -SiC MATRICES THROUGH INTERMEDIATE PRECERAMIC PREPREGS

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Ceramic matrix composites with refractory and oxidation-resistant matrix reinforced with continuous carbon fibers are widely used as structural materials to create reliable propulsion systems and aircraft experiencing simultaneous exposure to extreme temperatures, mechanical loads and aggressive environment. One of the most promising approaches to the formation of such composites is the method of preceramic prepregs, which has not received due attention and development in the Russian Federation.

The aim of this work is to develop a method of formation of ceramic matrix structural composites with matrices based on SiC and ZrB_2 , reinforced with continuous carbon fibers through intermediate preceramic prepregs.

The developed method consists of infiltration of continuous carbon fiber with preceramic slurry and subsequent formation of flexible preceramic prepregs. Samples formed from the resulting prepregs are hardened in a laboratory autoclave, carbonized in vacuum at 1000°C, and then subjected to liquid-silicon infiltration at temperatures up to 1500°C.

Ceramic matrix composites with ZrB_2 -SiC matrix reinforced with carbon fiber were formed. The morphology, porosity and mechanical properties of the obtained composites have been studied and the rheological properties of a wide range of ZrB_2 -based suspensions have been investigated and their influence on the properties of composites has been established^{1,2}. It has been shown that the developed method of composites formation is simple, variable, highly productive and easily scalable.

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INTERACTION THERMODYNAMICS OF HEXANE WITH CERIUM DIOXIDE

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Cerium dioxide, including those doped with ions of other elements, is widely used in catalysis, biomedicine, sensory technology, alternative energy, etc. Its use as a protective coating against moisture and dust for solar cells is promising. Hydrophobicity of the surface plays an important role in the latter case. At the same time, the literature discusses the possibility of specific sorption of hydrocarbons from the environment that provide this character.¹

In this work, a direct study of the interaction of n-hexane vapors with powdered samples of solid solutions based on cerium dioxide $\text{Ce}_{0.9}\text{Y}_{0.1}\text{O}_2$ (1) and $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9-(3x)/2}\text{F}_{3x}$ ($x = 0.1$) - (2) after six months of storage in air and freshly calcined (3) was carried out. Nanostructured samples were obtained under glycine-nitrate precursor combustion conditions followed by heat treatment. Using the method of gravimetric interval sorption, isotherms of sorbent mass change were obtained and Gibbs energy values of the sorption process (Δg) were calculated. The obtained data indicate the presence of physical sorption, which for sample (1) with $S_{\text{sp.}}$ 27 m²/g could be polymolecular (Δg_{max} -1.4 J/g).

For samples (2), (3) with $S_{\text{sp.}}$ on the order of 12 m²/g, calcination of the sample did not have a strong effect on the progress of the hexane sorption isotherm, only slightly increasing the limit amount of sorbate (from 2 to 3%); Δg_{max} -0.2 and -0.25 J/g. N-butanol vapors were also relatively poorly sorbed: 6.5; 1.5 and 1%, respectively.

The edge angles of wetting the samples with water θ were determined by the Washburn capillary gravimetric method, their value was 74 (1), 88 (2), 89° (3). These parameters for sample (1) did not change much after exposure in hexane and butanol vapors (74 and 78°).

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SYNTHESIS OF NANOSIZED BACTERICIDAL SILVER PARTICLES IN COMBUSTION REACTIONS OF NITRATE-ORGANIC PRECURSORS AND THEIR PROPERTIES

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Silver nanoparticles (Ag-Np's) attract the attention of researchers and practical biomedicine due to their long-known high bactericidal activity. In particular, recently, the possibility of obtaining nanoparticles with different morphology according to different methods has been studied, which in principle can affect their biological activity. Ag-Np's are used in free state and in compositions (bactericidal tissues, implant coatings, etc.). In this regard, a method of burning nitrate-organic precursors in a reaction vessel or directly on a support to obtain a predetermined surface concentration of Ag-Np's is of interest.

Preliminary results of studies on the synthesis of Ag-Np's were obtained, which will be continued together with colleagues from Novosibirsk and Ivanovo. Experiments show that the shape, size of the particles or their aggregates, their bactericidal activity (according to *E. coli*) are markedly influenced by the choice of an organic component (for example, PVA polyvinyl alcohol, PVP polyvinylpyrrolidone, glycine, glycerol, etc.), the method of application on substrates (medical alloy BT6): dipping, spraying, synthesis in the reaction medium itself, etc.

Ag-Np's samples were also obtained on a nanostructured inert inorganic matrix containing hydrated alumina nanoplates (ref. 1), and synthesized in a single cycle with bactericidal particles. These samples, in addition to Ag-Np's (pyrolysis spray with PVP (2), synthesis without organic component (3) - arr. 2, 3) showed promising antibacterial properties. The morphology of some samples is illustrated in Figure 1.

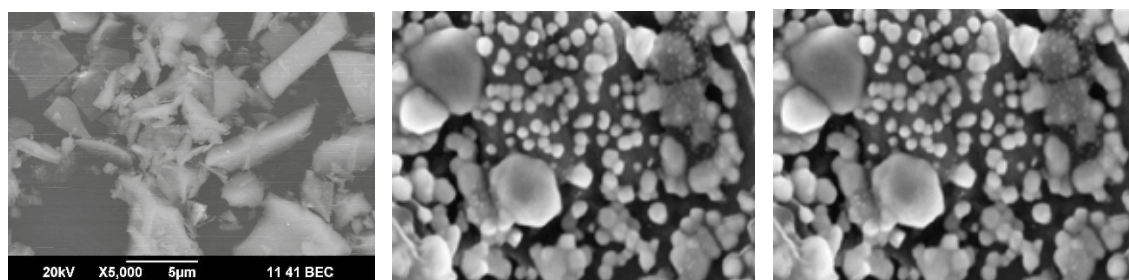


Figure 1. Electron micrographs of samples 1-3.

POLYMERIC COORDINATION COMPOUNDS OF SOME TRANSITION METALS WITH ϵ -CAPROLACTAM AND NICOTINAMIDE

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In recent years, coordination compounds with different structures, including polymeric ones, have been intensively studied. Due to various structures, it is possible to obtain compounds with various physico-chemical properties and use them as functional materials¹.

X-ray structural analysis has established that compounds formed as a result of slow isothermal crystallization of aqueous or aqueous-ethanol solutions obtained by mixing solutions of $\text{MeCl}_2 \cdot n\text{H}_2\text{O}$ ($\text{Me} = \text{Cu}^{2+}, \text{Co}^{2+}, \text{Ni}^{2+}, \text{Cd}^{2+}, \text{Mn}^{2+}$), nicotinamide or ϵ -caprolactam and $\text{Na}_2[\text{Hg}(\text{SCN})_4]$ or $\text{CuSiF}_6 \cdot 6\text{H}_2\text{O}$ and a mixture of ethyl alcohol with ϵ -caprolactam, have polymeric structures.

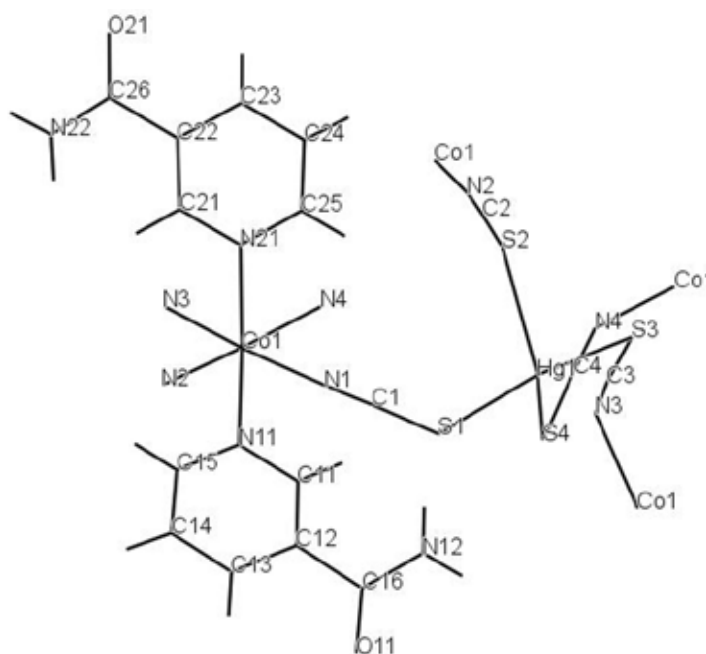


Figure 1. Structure and numbering of atoms in $[\text{CoHg}(\text{C}_6\text{H}_6\text{ON}_2)_2(\text{SCN})_4]$

The authors express their deep gratitude to Pervukhina N.V. and Kuratieva N.V. for assistance in X-ray diffraction studies.

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METHODS OF SYNTHESIS OF Sc-DOPED ZrO_2

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Crystals of partially Sc-stabilized ZrO_2 as well as ceramic materials of similar composition have a wide range of promising applications in engineering and medicine. High ionic conductivity, thermal and chemical resistance, and gas-tightness provide great attention to $\text{ZrO}_2\text{-Sc}_2\text{O}_3$ systems. By introducing ≥ 10 mol% Sc_2O_3 into ZrO_2 , the maximum conductivity of electrolytic membranes and stabilization of the rhombohedral phase are achieved. However, the instability of the transport characteristics of these materials at operating temperatures is due to the presence of a phase transition of the rhombohedral phase to the cubic phase upon heating. One of the possible ways to solve these problems is to stabilize the highly conductive cubic phase by additional co-alloying of $\text{ZrO}_2\text{-Sc}_2\text{O}_3$ solid solutions with other oxides of rare-earth elements. A promising method is to stabilize the phase composition directly during the synthesis of a solid solution with a decrease in the amount of an expensive dopant.

We are developing methods for the synthesis of various oxides using organometallic precursors (precursors) to the changing the chemical and phase composition, structural and morphological properties, setting new and useful properties. The study considers the results of the synthesis of $\text{Zr}_{1-x}\text{Sc}_x\text{O}_2$ by new methods: hydrothermolysis (1), thermolysis in air (2) and ultrasonic aerosol pyrolysis (3) of complex formate $(\text{Zr}_{1-x}\text{Sc}_x)_2\text{O}(\text{HCOO})_2$. A comparative assessment of the effect of the synthesis method on the phase composition, morphology, and physic-chemical properties of the $\text{Zr}_{1-x}\text{Sc}_x\text{O}_2$ samples was carried out.

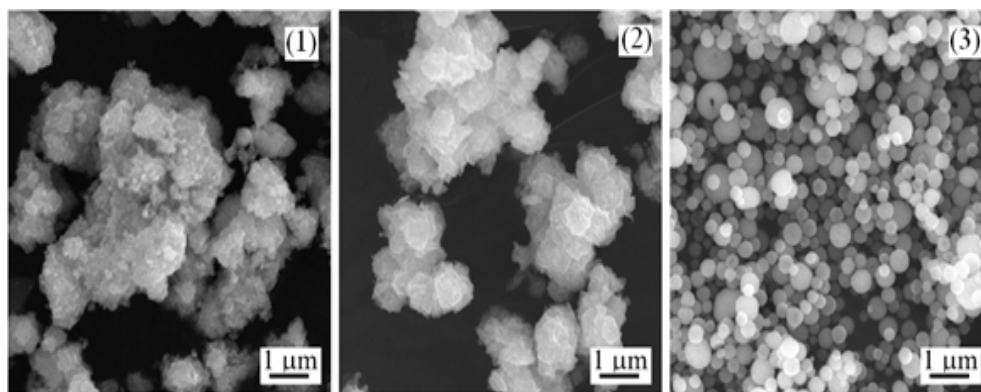


Figure 1. Samples of $\text{Zr}_{1-x}\text{Sc}_x\text{O}_2$ obtained by methods (1), (2) and (3) at 700 °C.

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PECULIARITIES OF NANOMATERIALS SYNTHESIS IN COMBUSTION REACTIONS

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One of the most promising methods for obtaining nanosized particles of metals, simple and complex oxides, including in the form of coatings on supports of various types, is synthesis in combustion reactions (a variant of the Solution Combustion Synthesis method). The advantage of this method is the ability to vary the functional properties of materials over a wide range by changing the synthesis conditions.

To synthesize materials using this method, a nitrate-organic composition containing nitrates of the corresponding metals and an organic component (polyvinyl alcohol, polyvinylpyrrolidone, etc.) is first prepared. The required amounts of components are calculated according to the combustion reaction with the formation of water, nitrogen dioxide and carbon dioxide as gaseous reaction products. It has been found that the thermal decomposition of the precursor is accompanied by processes of generation of high-density electric charges, which significantly affect the formation of nanoparticles, their size, shape, the value of the specific surface area of materials, oxygen non-stoichiometry (in the case of oxides and complex oxides) and, accordingly, the functional properties of materials (magnetic, catalytic, etc.). The synthesis can be carried out both in the absence of external field or under the influence of electromagnetic and magnetic fields (constant or alternating). Also it can be carried out using compositions with different organic components, with the different method of heating the reactor, with or without preliminary drying of the composition in the air to obtain a film, etc. All of these conditions affect the processes of charge generation, the formation of nanoscale particles of materials and the functional properties.

Trends and dependencies of functional properties on the method and conditions of synthesis in combustion reactions have been established for catalytic materials (based on lanthanum manganite, cerium dioxide, silver in an inorganic matrix of aluminium oxide, etc.), magnetic materials (based on hexaferrites, manganites), antibacterial agents (silver particles and coatings, silver-containing composites).

Within the framework of one of the priority areas of science in the Russian Federation the industry of nanosystems, the obtained results may be useful for the creation and improvement of thermocatalytic devices, SOFC, magnetic refrigerators and control systems, antibacterial drugs.

PRODUCTION OF ACTIVATED CARBONS USING NEW TYPES OF RAW MATERIALS

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The gradual depletion of the classical raw material base for the production of activated carbon (AC), as well as the need for industry for new types of carbon sorbents, is an urgent problem of our time. The solution of this problem is the search for alternative sources of new types of raw materials that will allow the creation of carbon sorbents with predefined specific properties.

The petroleum coke as a product of deep processing of oil residues may be one of such raw materials sources. As a result of the conducted research, the principal possibility of obtaining crushed carbon sorbents with the properties of molecular sieves having a specific surface area of up to 384 m²/g, a sorption pore volume of up to 0.20 cm³/g with a pore size of up to 0.66 nm is shown^{1,2}.

In the field of production of granular activated carbons, it is important to expand the range of binders. One of the promising and affordable types of binders that can be used while maintaining the classical technology for producing granular coals are coal tar obtained in the process of coking coal. Coal tar has a high dynamic viscosity and a high content of coke residue, which complicates the processes of mixing coal-resin composition and forming granules. In order to improve the rheological characteristics, it is possible to introduce various additives into the binder. In the course of the conducted research, the choice of a surfactant of a nonionic type was justified as a corrective additive. This made it possible to reduce the dynamic viscosity of the binder by 32%, while the specific surface area increased by 29%, and the strength by 5%³.

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THE STUDY OF STRUCTURE CHARACTERISTICS OF SOILS ON PERM TERRITORY

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The adsorption and filtering abilities of soils and subsoils depend on their morphology and are the determining characteristics in the case of studying the pollutant migration. Therefore, the study of the morphological characteristics of soils is an important stage in the research of the spread of pollutants, including petroleum products, which is an urgent problem for the Perm region because of the activities of oil producing and oil refining enterprises in the region. To carry out the research, soil samples were taken using the drilling method from two wells located at a distance of 100 m from each other, from depths from 0 to 10 m. Soil samples were taken on the territory of the city of Perm (left bank terrace of the Kama River). The studied samples were brought to an air-dry state over several days and then sieved to determine the particle size distribution. The mineralogical composition of the samples was determined by X-ray phase analysis. The results show a qualitative similarity in the mineralogical composition. The main minerals of the samples are quartz (22–45%), plagioclase (15–27%), feldspar (up to 13%) and clay minerals (up to 35%). The last ones are mostly represented by smectites, illite, and chlorite. Differences in the quantitative composition of fractions depend on the depth of sampling.

The method of low-temperature nitrogen adsorption (77K) showed that the morphological characteristics of soils are largely determined by the content of the clay fraction. The specific surface area of the studied samples ranges from 20 to 40 m²/g, the total pore volume is from 0.03 to 0.05 cm³/g, with about 70% of the total pore volume being meso- and macropores.

ELECTROCHEMICAL SYNTHESIS OF ALUMINA-ZIRCONIUM OXIDE SYSTEMS PRECURSORS DOPED WITH RARE EARTH ELEMENTS

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Alumina-zirconium oxide materials doped with rare earth elements (REE) are of interest due to excellent physical properties, such as low thermal conductivity¹, ionic conductivity², luminescence³, etc.

Precursors of complex oxide systems were obtained by the electrochemical method, with anodic dissolution of aluminum (electric generation of Al^{3+} , OH^- ions, etc.) in a coaxial electrolyzer without a membrane⁴ in aqueous solutions in the presence of ions: Zr^{4+} , La^{3+} , Y^{3+} , Ce^{3+} , Nd^{3+} , Dy^{3+} , Cl^- and NO_3^- . The process of precursors formation is due to the hydrolysis of the anode dissolution products, the formation of polyheteronuclear metal complexes, their polycondensation and the producing of primary solid phase particles.

According to the X-ray diffraction analysis data the samples to treatment at temperature 1200 °C are presented by t-ZrO_2 , c-ZrO_2 and $\theta\text{-Al}_2\text{O}_3$ phases. The XRD patterns, SEM study and local microanalysis data allow concluding that rare earth atoms are included in the crystal lattices of aluminum and zirconium oxides.

The proposed approach makes it possible to obtain complex oxide systems modified with rare earth elements based on the $\text{Al}_2\text{O}_3\text{-ZrO}_2$ binary system, characterized by the presence of a tetragonal zirconium dioxide phase.

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SYNTHESIS, FUNCTIONAL PROPERTIES AND ELECTRODE PERFORMANCE OF NEW $\text{Pr}_{1.6}\text{Ca}_{0.4}\text{Ni}_{1-y}\text{Cu}_y\text{O}_{4+\delta}$ MATERIALS FOR INTERMEDIATE TEMPERATURE ELECTROCHEMICAL APPLICATIONS

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Cobalt-free Ruddlesden-Popper phases of the $\text{Ln}_2\text{NiO}_{4+\delta}$ series ($\text{Ln}=\text{La}, \text{Nd}, \text{Pr}$ or mixture of REE) are considered as promising materials for the fabrication of air electrodes of intermediate temperature (IT, 600–750 °C) electrochemical devices based on solid electrolytes. Among them, $\text{Pr}_2\text{NiO}_{4+\delta}$ exhibits the highest oxygen diffusion properties and superior electrochemical performance in the series, as well as the possibility of proton transport in the layered structure. However, $\text{Pr}_2\text{NiO}_{4+\delta}$ is characterized by phase instability at temperatures below 950 °C when exposed to an oxidative atmosphere. This study aims to improve the phase stability of the oxide in the IT region through the doping strategy at both the Pr and Ni positions. The work represents a comprehensive study of the structure of $\text{Pr}_{1.6}\text{Ca}_{0.4}\text{Ni}_{1-y}\text{Cu}_y\text{O}_{4+\delta}$ ($y=0.0\text{--}0.4$) complex oxides, the electronic states of the elements, oxygen over-stoichiometry, and functional properties that are important for the electrochemical applications, such as thermal linear and volume expansion, and electrical conductivity. Efforts are being made to increase the stability while maintaining high electrochemical activity of the electrodes based on the developed new materials by the selecting of optimal conditions for the synthesis of the materials using different organic fuels, developing of the multilayer electrode design, and determining the most suitable conditions for sintering the electrode layers. The electrochemical properties of the $\text{Pr}_{1.6}\text{Ca}_{0.4}\text{Ni}_{1-y}\text{Cu}_y\text{O}_{4+\delta}$ electrodes are studied by impedance spectroscopy method on the symmetrical cells based on doped CeO_2 and $\text{BaCe}(\text{Zr})\text{O}_3$ solid electrolytes. It is shown that the electrode polarization resistance is in the range of 0.29–0.45 $\Omega\text{ cm}^2$ at 700°C depending on the Cu content, which is comparable to that of $\text{Pr}_2\text{NiO}_{4+\delta}$. The electrode response in a water-containing atmosphere (5–20 vol. % H_2O) was investigated for its usefulness in electrode applications in proton-conducting membrane fuel cells and electrolysis cells. The selected electrodes are subjected to an accelerated long-term study under severe conditions of high temperature and increased water content for 1000 hours.

HIGHLY-CONDUCTIVE CATHODE SUBLAYERS FOR $\text{CeO}_2\text{-Sm}_2\text{O}_3$ SOLID ELECTROLYTE AS AN EFFECTIVE WAY TO ENHANCE ITS ELECTROCHEMICAL PERFORMANCE

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Reduction of the operating temperatures of Solid Oxide Fuel Cells (SOFCs) is the important step toward their successful commercialization. Many efforts have been made to search for efficient electrolyte materials for operation in the intermediate-temperature (IT) range (600–750 °C). Doped CeO_2 solid electrolytes show promising conductivity level at these temperatures and possess high catalytic activity to hydrogen oxidation due to partial n-type electronic conductivity under anode conditions. However, the appearance of electronic conductivity affects the open circuit voltage (OCV) of the SOFC cell, which worsens its energy efficiency and fuel utilization ratio. Deteriorating of the rate of oxygen reduction reaction (ORR) at the cathode at decreased operating temperatures can significantly contribute to the degradation of cell performance. The rate of oxygen reduction may be increased by introducing cathode sublayers, which possess higher ionic conductivity compared to the parent electrolyte, for example, doped Bi_2O_3 electrolytes and those with mixed oxygen ion and p-type electron conductivity under cathode conditions. The study has shown, that mixed valence $\text{Pr}^{3+/4+}$ used as a co-dopant allows increasing ionic conductivity in $\text{CeO}_2\text{-Sm}_2\text{O}_3$ and induce partial electronic conductivity in air, increasing the grain boundary conductivity by about two orders compared to the base solid solution. Additionally, $\text{Pr}^{3+/4+}$ ions may serve as a trap for the n-type electronic carriers thus decreasing the level of leakage current in CeO_2 -based cells. In this work, the comparative study of the influence of thin-film cathode modifying layers based on $\text{Bi}_2\text{O}_3\text{-Er}_2\text{O}_3$ and $\text{CeO}_2\text{-Sm}_2\text{O}_3\text{-Pr}_6\text{O}_{11}$ solid electrolytes formed using electrophoretic deposition method on the $\text{CeO}_2\text{-Sm}_2\text{O}_3$ electrolyte membrane cell performance was carried. Additionally, the active composite cathodes based on $\text{LaNi}_{0.6}\text{Fe}_{0.4}\text{NiO}_{3-\delta}$ and $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_{3-\delta}$ compatible with cathode sublayers in sintering temperatures and temperature expansion coefficient (TEC) were developed.

STRENGTHENING OF TITANIUM COMPOSITE BY MEDIUM-ENTROPY CERAMICS (W, Ti, Ta)₂C OBTAINED BY SPARK PLASMA SINTERING METHOD

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The development of methods to improve and regulate the properties of functional materials is considered a key objective of materials science. Entropic materials are of interest due to their outstanding properties such as hardness, strength, corrosion resistance, etc. The concept of strengthening materials by adding entropic systems to them is a completely new approach. A completely new approach is the concept of strengthening materials by adding entropic systems to them, in particular entropic ceramics.

This work presents a method of obtaining a composite material based on titanium by a combination of mechanical activation (MA) and spark plasma sintering (SPS) methods with a hardening additive based on a fine powder of high-solid equimolar medium entropic ceramics (SEC) (W,Ti,Ta)₂C

Table 1. Physical characteristics of the obtained composites

Atomic content MEC, %	Density, g/cm ³	Microhardness, μ HV	Average grain size, μ m
0.2	4.5760	409	9
0.5	4.5734	450	9
1	4.5713	417	5

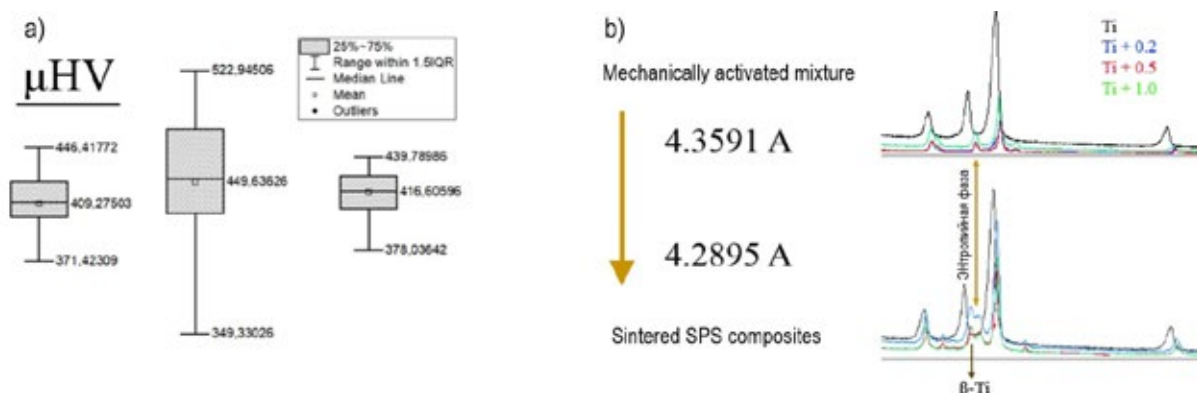


Figure 1. (a) Dispersion of hardness values. (b) Phase changes during the SPS process

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OPTIMIZATION OF THE ANNEALING PROTOCOL TO INCREASE THE HIGH-TEMPERATURE STABILITY OF Pt-Rh/Zr FILMS

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Platinum-based thin film microheaters are of great importance in modern science. The main issue in their use as heating elements in gas sensors is the long-term drift of their electrical characteristics due to recrystallization. Recrystallization can be suppressed and films can be stabilized at high temperatures by alloying them with refractory metals, such as rhodium, and by creating composites with refractory oxides (ZrO_2) located at grain boundaries, inhibiting their growth. An essential condition for ensuring long-term stability of thin film devices is annealing at temperatures higher than the operating temperature.

The aim of this work was to optimize the annealing protocol of Pt-Rh/Zr films on a porous substrate of anodic aluminum oxide to create microheaters for gas sensors with high long-term stability.

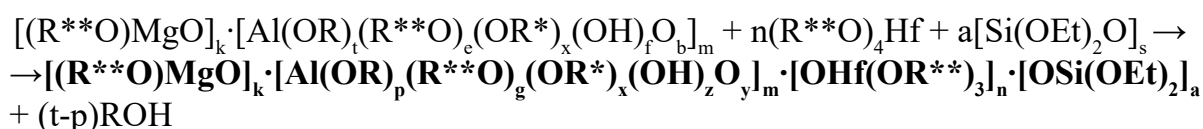
Pt-Rh/Zr films annealed using a one-step protocol (12 hours at 900 °C) consist of a fine-grained bottom layer enriched with zirconium, with large platinum-enriched hillocks on the surface. The average size of the hillocks in this case was 202 ± 69 nm. In order to increase the uniformity of the morphology, a two-step annealing protocol was proposed (4 hours at 450 °C, followed by 12 hours at 900 °C), where the low-temperature step is necessary for complete oxidation of Zr in the film bulk. This protocol allowed obtaining films with significantly uniform morphology, with an average grain size of 60 ± 27 nm. Thin Pt-Rh/Zr films after two-step annealing at 450 – 900 °C exhibited a resistivity of $17 \times 10^{-6} \Omega \times \text{m}$. Thus, the new annealing protocol allows one to obtain Pt-Rh/Zr films with uniform morphology and stable electrical characteristics, which are essential for the development of devices operating at high temperatures.

CERAMIC FORMING ORGANOMAGNESIUMOXANEALUMOXANES, MODIFIED WITH HAFNIUM AND SILICON: SYNTHESIS, PROPERTIES, PYROLYSIS

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Organomagnesiumoxanealumoxanes¹⁻³, simultaneously modified with hafnium and silicon, were synthesized by sequential co-condensation of organomagnesiumoxanealumoxane (Al/Mg \approx 2) with hafnium acetylacetonate and ethyl silicate-40 according to the scheme:



Where $k = 2-3$, $m = 4-5$, $n = 0.08-0.2$, $s = 0.25-0.5$; $k/m + t + e + x + 2b + f = 3$;

$k/m + n/m + a/m + p + g + x + 2y + z = 3$;

$R - C_2H_5$, $s - C_4H_9$, $i - C_4H_9$; $R^* - C(CH_3)=CHC(O)OC_2H_5$; $R^{**} - C(CH_3)=CHC(O)CH_3$.

Pyrolysis of the resulting oligomers at temperatures ≥ 1300 °C leads to the formation of nanostructured powders (particle size 14–40 nm) of spinel $MgAl_2O_4$ modified with Hf and Si oxides

It is known that ZrO_2 increases the crack toughness, flexural strength, heat resistance and chemical inertness of $MgAl_2O_4$ ⁴. Therefore, the introduction of HfO_2 should also result in an improvement in the mechanical properties, thermal stability and chemical inertness of $MgAl_2O_4$ ⁵.

It is shown that the introduction of silicon reduces the grain size by more than 10 times (the particle size of hafnium-containing $MgAl_2O_4$ is 130–900 nm).

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INFLUENCE OF THE TWO-COMPONENT DISPERSE PHASE ON THE PROPERTIES OF CERAMIC COATINGS FORMED BY PEO ON MAGNESIUM ALLOY ML10

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Plasma electrolytic oxidation (PEO) is a technology for the surface modification of Mg alloys (MA), which allows the formation of wear- and corrosion resistant oxide layers. Progress in recent years has been observed in the field of application of dispersed nano-sized particles (NPs) as electrolyte modifiers¹.

The purpose of the work is to study the nature and boundaries of synergistic effects that determine the properties of oxide layers formed on MA ML10 when two substances are jointly introduced into the NP electrolyte in the form of a dispersed phase – SiO₂ and BN in the ratio (x/y),%: 0/100; 20/80; 40/60; 60/40; 80/20 and 100/0 in a total concentration of 3 g/l

It has been established that NPs introduced into the electrolyte either as a single substance or as part of a mixture increase the productivity of the process by 15–50%. The additives had an ambiguous effect on the surface mechanical properties: BN increases the hardness of the formed coating compared to the base version without NPs (0/0), and SiO₂ decreases it. The adhesive strength of coatings obtained at approximately equal SiO₂/BN ratios increased by ~15%, and the best effect in terms of anti-corrosion properties was achieved at increased contents of SiO₂ NPs in the dispersed phase of the electrolyte (80–100%).

Table 1. Properties of the base oxide layer and hybrid ceramic coatings

xSiO ₂ +yBN, (x/y),%	T, μm	HV _{0.01} , MPa	F _c , N/μm	i _{corr} , nA/cm ²	Z _{f=0.01Γ_n} , MΩ·cm ²
0/0	40,5±4,7	580±105	0,83±0,17	10,7±0,6	5,1±3,2
0/100	56,2±5,1	600±120	0,57±0,06	6,5±3,8	6,9±3,8
20/80	59,9±8,3	525±150	0,67±0,10	7,3±5,2	3,1±1,5
40/60	46,4±6,3	480±50	0,91±0,14	4,3±3,1	2,5±0,1
60/40	50,7±6,3	490±100	0,94±0,18	5,7±2,2	2,6±0,1
80/20	50,3±6,5	500±35	0,77±0,13	2,9±1,8	7,3±2,0
100/0	49,9±8,7	425±120	0,62±0,11	4,9±2,9	9,7±4,4

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DIRECT EFFECT OF RADIATION ON ACETYLACETONE AND HEXAFLUORACETYLACETONE

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Acetylacetone (AA) and hexafluoroacetylacetone (HFAA) are considered as convenient complexing agents for the separation of radionuclides. Analysis of the products reveals significant differences between the radiolysis of AA and HFAA. The intramolecular hydrogen bond suppresses the transfer of a proton from the primary radical cation to the molecule and also promotes the cleavage of the C-OH bond in the enol form. As a result, the formation of keto alcohol (4-hydroxy-2-pentanone) is not observed at room temperature, but is effective under boiling conditions. Intramolecular hydrogen bonding contributes to structural stress in the radical cation, which under normal conditions increases the yield of C-OH bond cleavage and the inhomogeneous formation of acetate (4-oxopent-2-ene-2-yl acetate). The heaviest primary products in AA are dimers of the radical having an unpaired electron at the C(3) atom (yields - 0.015 and 0.05 $\mu\text{mol/J}$ at room temperature and under boiling conditions, respectively)¹.

In irradiated HFAA, the yield of such dimers is significantly lower. At the same time, a significant part of $\dot{\text{C}}(3)$ is involved in the formation of recombination products with other radicals, primarily with $\dot{\text{C}}(1)$. The observed initial yield of hexafluoroacetylacetone degradation is 0.29 ± 0.2 and 0.32 ± 0.2 $\mu\text{mol/J}$ at 293 and 343 K, respectively. Compared to AA radiolysis, the twice lower yield of HFAA degradation and the low yield of $\dot{\text{C}}(3)$ dimers indicates not only effective quenching of excitation, but also complicated diffusion due to the high viscosity and density of HFAA. It is likely that most radiolytic reactions in liquid HFAA occur predominantly in the “cage”, i.e. near the site of formation of primary intermediates, where the range of intermediates is very limited². In liquid HFAA, the products of cleavage of all single bonds are observed: C-CF₃, C-F, C-OH and C-H. As a result, monoketones, trifluoroacetic acid, keto alcohols and tautomeric tetraketones are formed.

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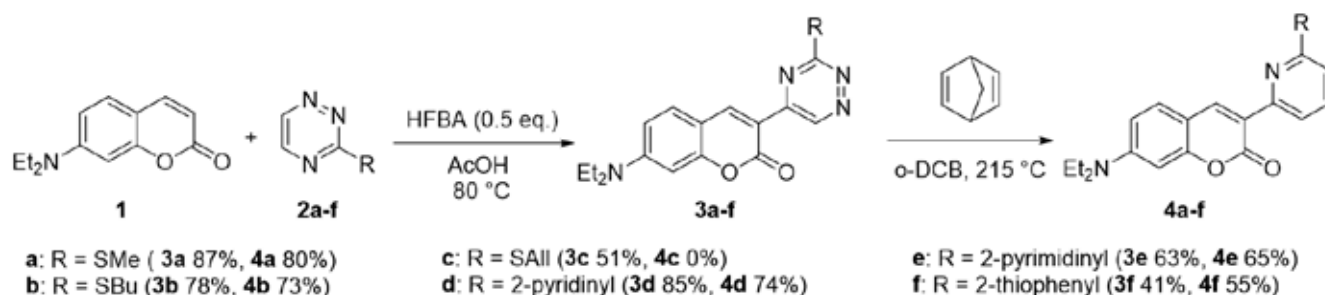
SYNTHESIS AND PROPERTIES
OF 3-AZINYLCOUMARINE DYES

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7-Aminocoumarin dyes represent a privileged class of organic compounds that have found their application in nonlinear optics, organic light-emitting diodes and solar cells. For example, 3-pyridinyl-7-aminocoumarins are used as a chemosensors and bio-imaging agents.¹

We found that the reaction of 7-(diethylamino)coumarin **1** and 3-substituted-1,2,4-triazines **2a-f** in the presence of a catalytic amount of heptafluorobutanoic acid (HFBA) in acetic acid at 80 °C leads to the formation of C-H/C-H cross-coupling products **3a-f** in one simple step, which enter the Boger reaction to form the respective 3-pyridinyl-7-aminocoumarins **4a-f**.



The study of photophysical properties has shown that compounds **3a-f** and **4a-f** have luminesce in the visible region of the spectrum with good quantum yields.

Table 1. Photophysical properties of **3a-f**, **4a-f**

	λ_{abs} , nm	λ_{em} , nm	Φ , %	τ , ns		λ_{abs} , nm	λ_{em} , nm	Φ , %	τ , ns
3a	473	545	29.9	2.40	4a	421	480	67.3	2.68
3b	472	545	35.8	2.32	4b	422	480	79.2	2.72
3c	472	543	29.3	2.45					
3d	468	539	25.9	1.94	4d	418	480	81.8	2.73
3e	475	549	34.3	2.07	4e	417	479	82.3	2.75
3f	470	542	33.2	2.51	4f	418	481	66.8	2.60

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CHANGES IN THE CRITICAL CURRENT VALUES OF SUPERCONDUCTING MATERIALS AFTER MECHANICAL LOADS

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Superconductors attract a great attention from researchers because of their unique ability to conduct electricity without any loss. High temperature superconductors (HTS), in particular, are characterized by a high current density and almost zero losses during electricity transmission.¹ These materials have a number of environmental benefits, such as energy savings, resource conservation, and non-flammability, as well as nontoxicity.² However, when creating elements that carry current, mechanical stresses occur, leading to areas with lower current levels. This work aims to study changes in the critical current values in HTS materials using the Hall magnetometer method after the application of mechanical loads.

Second generation HTS tapes, coated with a layer of copper as a protective layer, as well as tin-plated tapes were used for the study. The copper HTS tape thickness was 48 ± 1 microns, and the tinned tape thickness was approximately 70 microns. Mechanical testing was carried out at room temperature by compressing stacks of tape with a load up to 400 MPa with steps of 50 MPa using a Hall magnetometer to measure the trapped magnetic field. Based on the results, an assessment of the change in critical current values of the HTS tape depending on applied mechanical deformation was made. The data can be useful for manufacturing of superconducting devices.

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RHEOLOGICAL PROPERTIES OF POLYMER COMPOSITIONS BASED ON POLYACRYLONITRILE AND PETROLEUM ASPHALTENES

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Carbon fibers (CF) have unique properties, which makes them one of the most promising multi-purpose materials. They are characterized by high tensile strength, low specific gravity, low coefficient of thermal expansion and chemical inertness. In industrial production at present, polyacrylonitrile (PAN) fibers are the main precursors of CFs for structural purposes in the world. At the same time, one of the main problems with CFs based on the PAN precursor is associated with the high cost of production, taking into account the fact that about half of the cost (50%) falls on the production of the precursor - PAN fiber.

Thus, the problem of high production costs leads to the search for new and cheap sources of raw materials for the production of CFs. As an alternative source, a by-product of the process of solvent deasphalting of oil residues - asphalt, which is mainly used as a component or raw material for the production of petroleum bitumen or boiler fuels, can be considered.^{1,2}

This report will present the results of rheological studies of PAN-asphalt polymer compositions of various compositions. In the temperature range from 160°C to 185°C, the influence of asphalt content on the rheological characteristics of the polymer composition melt, as well as on the time during which the melt retains the rheological characteristics necessary for extrusion, was established. Prospects for the use of asphalt as a plasticizing additive in PAN copolymers are evaluated. The dependence of the influence of the amount of asphalt in various PAN-asphalt compositions on rheological properties was determined in order to assess the suitability of the polymer composition for extrusion and fiber spinning.

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PRODUCTION OF CAPACITOR TANTALUM POWDERS BY CALCIUM VAPOR REDUCTION OF Ta_2O_5

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A large specific surface area and a low impurity content characterize tantalum powders obtained by reduction of its pentoxide with alkali-earth metals. Due to this, they have found wide application as a material for anodes of tantalum capacitors.¹ At the same time, the main developments are devoted to the production of powders using magnesium as a reducing agent.^{1, 2} The purpose of this work was to obtain capacitor tantalum powders by reducing Ta_2O_5 with calcium vapor.

Reduction was carried out at a temperature of 800-850 °C with constant evacuation of the reactor. The particles of the resulting tantalum powder are conglomerates of smaller particles with a porous structure (Figure 1). The pores are in the nanometer range, and their surface makes up most of the total surface of the powder.

To give the porous structure of the powder the required parameters, it was heat treated in a vacuum in the temperature range of 900-1300 °C, and then in the presence of a reducing metal (calcium or magnesium) at 830-850 °C. Depending on the heat treatment conditions and anodizing voltage, powders with a specific charge from 40,000 to 120,000 $\mu\text{C g}^{-1}$ were obtained.

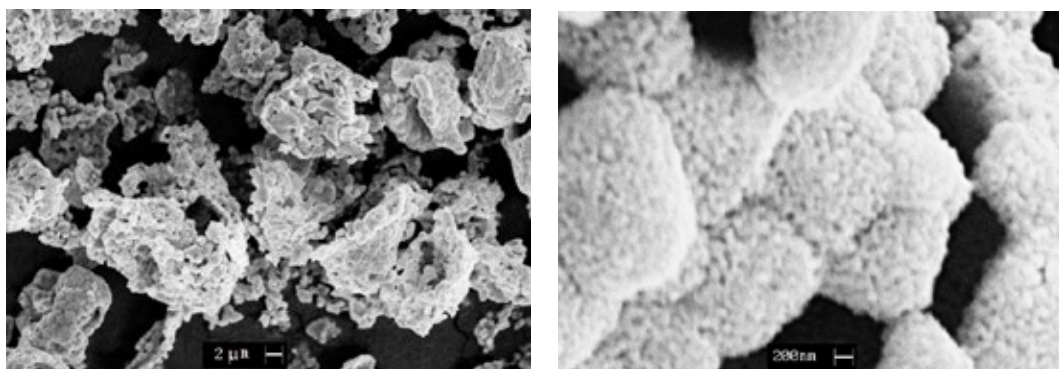


Figure 1. SEM images of calcium-thermic tantalum powder

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SYNTHESIS AND CHARACTERISTICS OF POLYALUMOCARBOSILANE

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SiC ceramics based on polycarbosilanes (PCS) are widely used in the production of ceramic fibers and composite materials with high strength, thermal and oxidative stability and corrosion resistance.¹ To increase the temperature and oxidative stability of ceramic materials obtained on the basis of PCS, various heteroatoms are introduced into its structure, acting as sintering agents and inhibitors of crystallite growth. Particularly, polyaluminocarbosilanes (AlPCS) are important precursors of SiC ceramics, which exhibit high thermal (up to 2200 °C) and oxidative resistance.² As a rule, AlPCS is usually prepared by the reaction of PCS or polydimethylsilane (PDMS) with organoaluminous compounds (such as aluminum acetylacetonate, aluminum butoxide, dimethylaluminium chloride) at high temperature³.

We have prepared samples of aluminum-modified polycarbosilane by the thermal rearrangement reaction of PDMS with the addition of $\text{Al}(\text{acac})_3$ at different pressures in order to determine the effect of the modifier on the speed of the process and the properties of the resulting polymer. The results of the elemental analysis showed the presence of aluminum in all samples synthesized with the addition of a modifier. By the method of gel-penetrating chromatography, it was shown that the process of obtaining PCS from PDMS was accelerated in the presence of aluminum acetylacetonate. In addition, it was found that a decrease in pressure, at which the thermochemical rearrangement process was carried out, resulted in the increase in the molecular weight distribution in the final product, which worsened the fiber-forming properties of the polymer.

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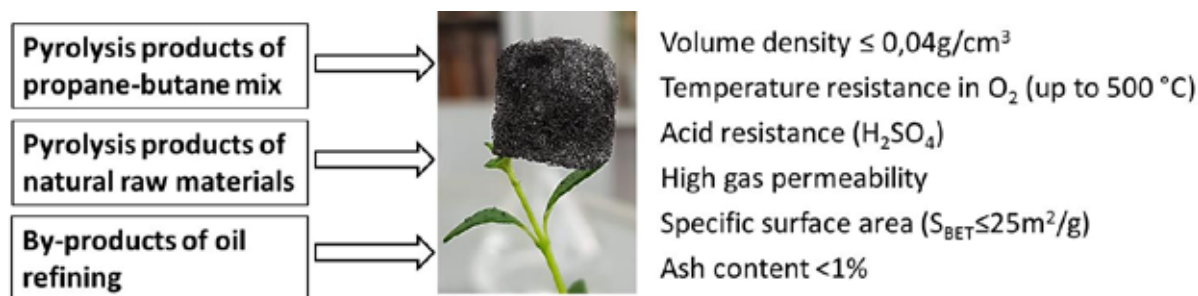
SYNTHESIS OF CARBON MATERIAL WITH FOAM STRUCTURE FROM AVAILABLE RAW MATERIALS FOR OBTAINING ADSORBENTS AND CATALYSTS

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In recent years, there has been increased interest in the synthesis of carbon materials with a foam structure and the development of approaches to control the morphology of the material. Information on the composition and formation of a liquid hydrocarbon precursor, obtained using gas chromatography–mass spectrometry and elemental analysis, makes it possible to expand the raw material base for the synthesis of carbon foam.

The work shows a method for producing carbon foam with a cellular structure using as raw materials both available hydrocarbon gases (propane-butane mixture) and heavy petroleum products (coal tar, coke raw materials, heavy pyrolysis tar, catalytic gas oil), as well as natural raw materials (nut waste, solid fossil fuels of a low stage of metamorphism).



The obtained carbon foam samples were studied as oil sorbents and catalyst supports. It was established that the sorption capacity of the resulting carbon foam when removing oil and oil products from the surface of the water ranged from 13 to 24 g/g, depending on the density of the oil product. The palladium catalyst based on cellular carbon foam showed high (more than 85%) selectivity for 1,4-butenediol in the hydrogenation reaction of 1,4-butyndiol with substrate conversion above 90% while maintaining the indicated catalytic characteristics in a multi-cycle experiment.

The work was supported by the Ministry of Science and Higher Education of the Russian Federation within the governmental order for Boreskov Institute of Catalysis (project FWUR-2024-0039). The studies were carried out using facilities of the shared research center “National Center of Investigation of Catalysts” at Boreskov Institute of Catalysis, Omsk Regional Center of Collective Usage SB RAS.

PREPARATION AND APPLICATION OF PHENOLS CONTAINING CYCLOACETAL AND GEM-DICHLOROCYCLOPROPANE FRAGMENT

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We involved condensation process of salicylic aldehyde with glycols and *O*-alkylation of pyrocatechol with halomethyloxacycloalkanes^{1,2} for the synthesis of phenols containing a cycloacetal or a *gem*-dichlorocyclopropane fragment.

The antioxidant activity assessment of the obtained compounds was carried out. It has been shown that the corresponding derivatives of *tert*-butylpyrocatechol inhibit the liquid-phase oxidation of hydrocarbons and 1.5-5 times more active than ionol³. These compounds exhibit the ability to prevent oligomerization and resin formation of styrene during its rectification. The best results were obtained when using salicylic aldehyde preparations with etriol and pentaerythritol.

The alkylation of phenol and pyrocatechol with vinyl-*gem*-dichlorocyclopropanes, available products of dichlorocarbonation of industrial dienes, was studied. The conditions (reaction duration, temperature, molar ratio of reagents, type and nature of catalyst) for the selective formation of target alkylation products were determined. The effectiveness of their use as antioxidant additives for motor oils and fuels has been proven.

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CERAMIC MATRIX FROM BORIC ACID PRODUCTION WASTE FOR CO-60 IMMOBILIZATION

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Modern society actively uses advanced developments of the scientific community, including in the field of nuclear energy. The Co^{60} isotope is formed in nuclear reactors and is known for its radioactivity; its presence in liquid radioactive waste complicates their long-term safe disposal. Therefore, the search for new methods of immobilization of this radionuclide in particular is relevant.

Ceramic matrices have high technical and physicochemical properties, which is why they are one of the best materials for the immobilization of dangerous radionuclides. This work is devoted to the study of ceramic matrices created by spark plasma sintering of calcium silicate, which is obtained from borogypsum, a waste product from the production of boric acid.

Spark plasma sintering at 1000 °C showed the best results. Since at this temperature the best hydrolytic stability (Fig.1a) and homogeneity of surface morphology (Fig.1b) are achieved.

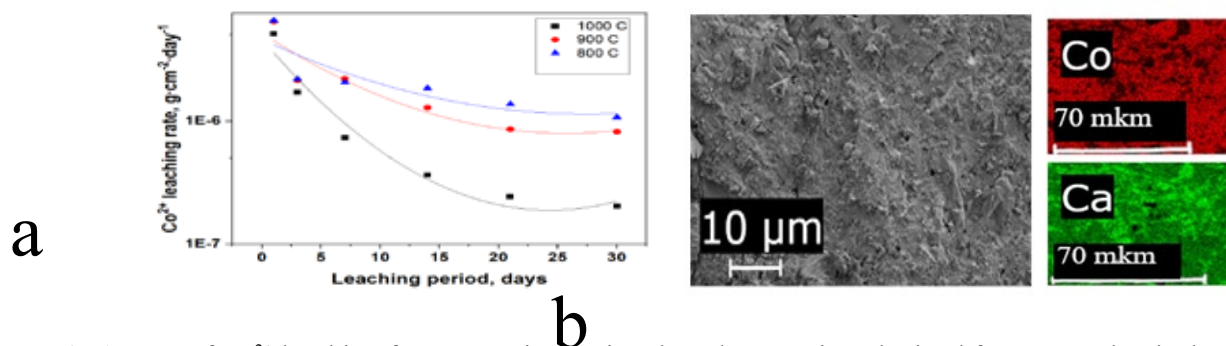


Fig.1. Rate of Co^{2+} leaching from ceramic matrices based on CaSiO_3 obtained from waste by the hydrothermal method (a), and SEM-EDS image of Co-saturated and consolidated $\text{CaCoSi}_2\text{O}_6$ at 1000°C (b)

The work was carried out within the framework of the State Task No. FZNS-2024-0013, topic: “X-ray absorption spectroscopy on synchrotron radiation sources for the directed chemical synthesis of functional materials in demand in the nuclear industry».

EMPLOYING NANOSCALE ADDITIVES TO CONTROL THE ICE STRENGTH

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Development of cold climate regions requires large quantities of ecologically safe construction materials from local sources. Ice is a promising material, but pure ice has low strength, is brittle and tends to creep. Various ice reinforcement technologies based upon macroscopic additives have been tested with limited success.

The papers [1-4] present different approach to ice strengthening by means of adding organic or inorganic nanoparticles (NP) to the water to be frozen, Cellulose, silica, alumina and titanium dioxide NPs with 20-80 nm diameter have been tested. Addition of 1 wt. % of NPs to the ice results in reduction of grain size, manifold increase in its strength and an order of magnitude increase in specific energy of destruction. Analysis of experimental data shows that the ice strength is reversely proportional to the square root of average grain size for all studied NP materials. It evidences for the strength of the ice composite is limited by intercrystallite cracks which initial lengths is proportional to average grain size.

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THE STUDY OF ELECTROCHEMICAL BEHAVIOR OF SYNTHETIC VALLERIITES

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The properties of two-dimensional materials differ significantly from the properties of three-dimensional analogues, which causes great interest in them. Using hydrothermal synthesis in an autoclave, we obtained 2D materials, analogs of the natural layered mineral valleriite¹. The electronic properties of such materials make them promising for use in various fields, for example, (electro)photocatalysis, optics, manufacturing of solar cell elements, etc.

It have been obtained cyclic current-voltage dependences in aqueous solutions of synthetic samples, previously characterized by X-ray diffraction. For the synthesized samples, the composition was varied and doped with ions of various metals. Doping metals can be part of both sulfide and hydroxide layers of valleriite.

The introduction of manganese, tin, or cobalt ions into the structure of vallerite leads to the appearance of peaks corresponding to the reactions of compounds of these metals. In the case of doping metals such as Li, Pt, Pd and Ni, redox processes corresponding to the electrode material are not observed. In this case, there is a change in the magnitude of currents corresponding to the cathodic or anodic decomposition of water. An analogue of valleriite, tochilinite, demonstrates more active electrochemical behavior; the most interesting results were obtained when it was doped with nickel and has prospects for use as an electrocatalyst for the decomposition of water. In general, the electrochemical behavior of materials is determined by the position of the Fermi level on their surface.

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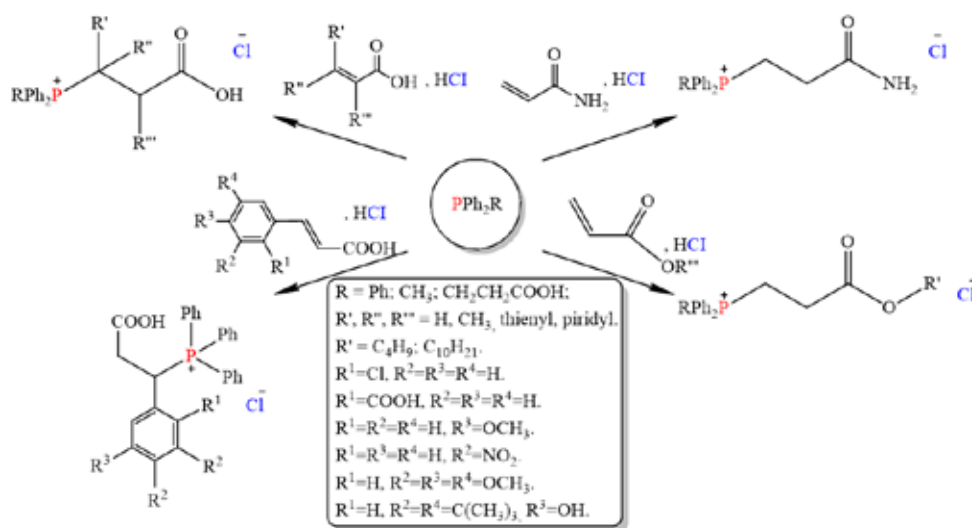
NEW APPROACHES TO THE SYNTHESIS OF QUATERNARY PHOSPHONIUM SALTS BASED ON ONE-POT REACTIONS

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Quaternary phosphonium salts are of interest to researchers due to their wide biological activity. Arylphosphonium compounds have also recently been actively used as drug delivery systems¹. In this regard, the development of new methods for the synthesis of such compounds is an urgent task¹.

The convenient and effective approach to the synthesis of quaternary phosphonium salts based on tertiary phosphines and unsaturated electrophilic compounds: substituted acrylic, cinnamic acids, as well as on the basis of amides and esters of acrylic acid has been developed (Scheme 1).



Scheme 1.

This method makes it possible to obtain wide ranges of phosphonium salts with antimicrobial activity under identical conditions.

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NEW MATERIALS BASED ON MICROBUBBLES FOR ULTRASONIC IMAGING AND THERANOSTICS

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Ultrasound imaging is a non-invasive and cost-effective diagnostic tool in routine clinical practice, which is often limited by its low contrast resolution profile. The introduction of ultrasound contrast agents can solve this problem by providing significant echogenicity to the surrounding tissue. Gas-filled microbubbles measuring 1–8 μm are traditionally used as ultrasound contrast agents, where the gas core provides the necessary echogenicity and the shell prevents fusion or rapid dissolution of the core and determines the stability of the microbubble.

Albumin-coated microbubbles are common contrast agents for ultrasound imaging, their poor acoustic stability limits their use, but this can be improved by the inclusion of hybridization molecules - copolymers, small molecules, etc. For example, the introduction of a copolymer of N-vinyl-2-pyrrolidone and acrylic acid (P(VP-AA)) can improve the performance of microbubbles coated with bovine serum albumin. It is important to understand the influence of copolymer structure on the properties of microbubbles. In this work, we evaluate the synthesis and acoustic response of BSA@P(VP-AA) microbubbles obtained using a series of P(VP-AA) copolymers with end groups –C8H17 and –C18H37 and molecular weight thresholds from 3.5 to 15 kDa. Both simulation experiments and experimental data show significant interactions between the protein and copolymers in the complexes that were used to synthesize a 60-composition microbubble library. C8H17-terminated copolymers provided microbubbles with 200-fold concentration, 4-fold increased acoustic response, and 2.5-fold increased ultrasonic signal lifetime compared to plain BSA microbubbles. The improved acoustic performance was maintained during in vivo cardiac ultrasound imaging with no change in liver accumulation after copolymer administration.

The work was carried out with the financial support of the Russian Science Foundation, project 21-73-10254.

MODELING CHEMICAL STABILITY AND SEARCHING FOR NEW MATRIXES FOR IMMOBILIZATION

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Stable matrices have a wide range of applications in various fields of chemistry. One of the most actively researched areas recently is the search for materials for strong and stable matrices for the immobilization of radioactive waste. This work proposes a technique for modeling stability and searching for materials during the immobilization of strontium-90.

The simulation was carried out by replacing Sr atoms with Zr atoms, corresponding to radioactive decay. The effect of yttrium intermediate formation on the strength of the matrices was also investigated. In addition, the case of the introduction of Zr atoms into positions that do not correspond to Sr positions was considered.

The following criteria for stability were chosen: change in the volume of the unit cell, the value of the forces acting on the atoms and the tension in the structure. The simulation was carried out by creating a supercell and sequentially replacing a certain number of randomly selected strontium atoms, which made it possible to simulate the process of radioactive decay and compare the degree of replacement with the time elapsed from the moment of burial. Optimization of the structure geometry was carried out using the pretrained neural network potential chgnet.¹

More than 20,000 structures were modeled and optimized, for each of which the volume, forces acting on the atoms and stress were calculated. The possibility of random selection of substitution atoms at each stage was confirmed by whisker plots of changes in volume, forces and stresses. The results identified a number of structures that remain stable over long periods of time when used as templates. One of the most durable classes of compounds turned out to be perovskites.

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The work was carried out with the financial support of the Russian Science Foundation, project 23-73-30006.

STUDY OF THERMODYNAMIC PROPERTIES COMPLEX EUROPIUM OXIDES WITH PYROCHLORE STRUCTURE

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Complex oxides of rare earth elements with a pyrochlore structure are used as thermal barrier materials for gas turbine engines and power plants^{1,2}.

The goal of this research was to study the thermodynamic properties of compounds $\text{Eu}_2\text{M}_2\text{O}_7$ ($\text{M} = \text{Sn}, \text{Ti}$) with the pyrochlore structure over a wide temperature range.

The method of solid-state interaction of initial oxides with the use of tableting of samples and preliminary mechanical activation is most often used for synthesis. This method was used for the synthesis of $\text{Eu}_2\text{Sn}_2\text{O}_7$, and for the synthesis of $\text{Eu}_2\text{Ti}_2\text{O}_7$, the method of preliminary precipitation of hydroxides was used, followed by high-temperature annealing. It was shown that single-phase products can be obtained only after annealing at a temperature of 1773 K.

The heat capacity of europium stannate was measured in the range of 7-1572 K, and the heat capacity of europium titanate - 7-1800 K. A flat anomaly in the temperature range of 10-60 K on the temperature dependence of the heat capacity $\text{Eu}_2\text{Ti}_2\text{O}_7$ was confirmed, which may indicate a change in magnetic properties. No anomalies were found on the temperature dependence of the heat capacity of europium stannate. Temperature dependencies of standard thermodynamic functions - entropy $S^\circ(T)$, enthalpy increments $H^\circ(T)-H^\circ(0)$ and reduced Gibbs energy $F^\circ(T)$ - were calculated based on smoothed heat capacity values. The values of the Gibbs free energy of formation from simple substances for $\text{Eu}_2\text{Sn}_2\text{O}_7$ and $\text{Eu}_2\text{Ti}_2\text{O}_7$ of were estimated.

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DEVELOPMENT AND ANALYSIS OF NEW METHOD FOR FABRICATING ELECTROCALLY CONDUCTIVE STRUCTURES ON PLASTIC SUBSTRATE USING LASER MODIFICATION TECHNIQUE

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In this work, a new technological method for the fabricating electrically conductive, copper-based structure on plastic substrates for flexible electronics systems¹⁻³ is developed and analyzed. This method is based on laser-assisted modification of a plastic surface and chemical copper plating techniques, which do not require the use of special composite materials, expensive chemical components or precious metal compounds. In this developed process, a solution of a surface activator based on phosphomolybdic acid is applied to the plastic surface. During laser modification process performed by a specially developed laser setup, the catalytic centers based on molybdenum monocarbide are formed and become the initiating centers for copper deposition during electrochemical plating process. To determine the optimal fabrication conditions at the microlevel, the obtained electrically conductive structures were characterized using scanning electron microscopy. In addition, by measuring electrical resistance it was shown that the resulting copper structures can be used to create electronic devices with high packing density.

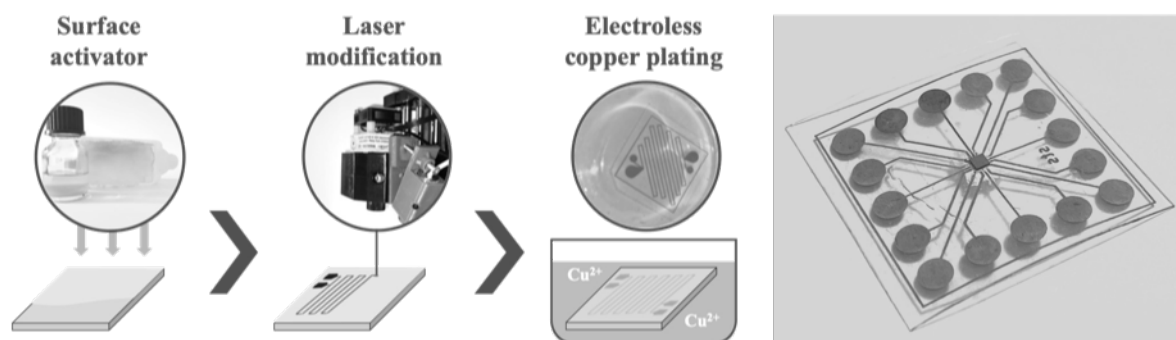


Figure 1. Stages of fabricating process for electrically conductive structures on plastic and the obtained sample.

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MODERN FIBROUS HEAT AND SOUND INSULATION MATERIAL FOR CIVIL AVIATION

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One of the promising areas in aviation materials science is the development of new heat and sound insulating materials (HSIM) with improved performance characteristics, such as density, sorption humidity and water absorption.

At the National Research Center “Kurchatov Institute” - VIAM, fiberglass-based samples HSIM were obtained using the aeration deposition method and a new binder of the VS-74 brand. The samples’ characteristics of new HSIM being developed in comparison with the serial materials ATM-1 and Microlite AA blankets (USA) are presented in table 1.

Table 1. Main characteristics of thermal and sound insulation materials

Characteristics	The new developed HSIM	ATM-1	Microlite AA blankets
Density, kg/m ³	9,5	10,0	9,6
Sorption humidity (at $\phi = 98\%$ for 30 days), %	50,0	30,0	72,6
Water absorption (complete immersion in water), %	256,5	-	296,5
Weight loss after exposure at 70 °C for 168 hours, %	0,24	-	0,25
Burnout length according to AP-25 Annex F Part VI, mm	17	less than 51	less than 51
Duration of residual burning according to AP-25 Annex F Part VI, s	0	less than 3	less than 3
Index of specific optical density of smoke D4 (burning) according to AP-25 Annex F Part V	9	less than 200	less than 200
Index of specific optical density of smoke D4 (pyrolysis) according to AP-25 Annex F Part VI	2	less than 200	less than 200

As a result of the work, the new HSIM samples were obtained, that are not inferior in their technical characteristics to ATM-1 materials and Microlite AA blankets made in the USA. Moreover, the obtained samples are superior to imported and domestic analogues in terms of sorption humidity. Thus, the new HSIM is promising for use in modern aircraft and helicopter manufacturing.

MANUFACTURING OF CARBON FIBERS FROM POLYOXADIAZOLE PRECURSORS

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Despite outstanding recent progress in carbon fiber (CF) manufacturing processes and properties improvement due to precise control of their formation from polymers and subsequent heat treatment, source materials for their production is limited to pitches, rayon and polyacrylonitrile (PAN), all of which require thermal stabilization and/or oxidation. Therefore, active search for polymers that provide high-strength CF at reduced production cycle is underway. With this respect, aromatic polyamides and their derivatives draw special attention¹.

Several studies assessed one-stage carbonization of polyoxadiazole-based fibers (POD-CF) that result in up to 60 wt.% carbon yield². In the present study, we report thermal decomposition and polycondensation of POD-CF at 900-2800 °C heat treatment temperature. It is shown that they demonstrate no transformations up to 500-600 °C followed by rapid carbonization in 600-900 °C range. Results of structure study via X-ray diffraction and Raman spectroscopy are provided. With respect to density and Young's modulus POD-CF are between rayon- and PAN-based CFs, whereas their tensile strength is lower. Crystal structure and its evolution during heat treatment are close to PAN-based CFs indicating similarity of solid-state structural transformations.

Results of the study suggest that POD-CFs can be seen as possible alternative to mass-produced CFs providing reduction in production cycle time due to the fact that formation of ladder polymer, intramolecular cyclization and pre-carbonization stages, as well as catalytic carbonization, can be avoided.

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CORROSION RESISTANCE OF HIGH-ENTROPY ALLOYS BASED ON IRON SUB-GROUP METALS, DOPED WITH REFRACTORY METALS

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Currently, high-entropy alloys (HEAs) – alloys consisting of five or more components in an equiatomic ratio – are attracting increasing attention to the possibility of an optimal combination of various properties, such as strength, ductility, wear resistance and corrosion resistance. Doping $\text{Al}_x\text{CoCrFeNi}$ type HEAs with a small amount of other elements (in particular, refractory metals – Ta, Mo, W) can improve the characteristics of such alloys and control their properties.

In this work, corrosion resistance tests were carried out both in a 1M NaCl solution (the environment simulates sea water) and in a 0.5M H_2SO_4 solution (the environment is typical for the extraction of natural resources (including oil and gas)). Polarization curves were obtained and electrochemical impedance measurements were performed. It was determined that Ta negatively affects the behavior of HEAs in the solutions under study, while doping alloys with Mo or W can improve corrosion resistance of investigated HEAs. The results of studying (using a scanning electron microscope) the morphological features of the samples after testing indicate the galvanic nature of corrosion for all investigated HEAs.

Table 1. Potentials and current densities of corrosion and passivation in a 0.5M H_2SO_4 solution

Properties	Alloy	
	$\text{AlCoCrFeNiTa}_{0.1}$	$\text{AlCoCrFeNiW}_{0.1}$
E_{corr} , V	-0.235 ± 0.002	-0.132 ± 0.003
I_{corr} , $\mu\text{A}/\text{cm}^2$	35.03 ± 0.09	6.09 ± 0.05
ΔE , V	0.590	1.018
I_{pas} , $\mu\text{A}/\text{cm}^2$	3162	316

The study was supported by the Russian Science Foundation, project no. 23-23-00107, <https://rscf.ru/en/project/23-23-00107/>.

SYNTHESIS AND PHOTOPHYSICAL PROPERTIES
OF PENTAFLUOROPHENYL-4H-IMIDAZOLES

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Organic fluorophores find applications in various fields, including the development of semiconductors for solar cells, optoelectronics, bioimaging, and chemosensors. Recently, scientists have shown increased interest in designing photoactive systems based on five-membered non-aromatic systems, particularly imidazoles.

In this work, a two-step method was developed for the synthesis of novel fluorophores based on 4*H*-imidazole containing a pentafluorophenyl fragment. On the first stage, the starting 4-bromo-4*H*-imidazole-3-oxide reacts with pentafluorophenyllithium in the presence of acetyl chloride to form intermediate compound **2** in 70% yield. The Suzuki-Miyaura reaction was chosen as the final step to obtain the target fluorophores, resulting in a series of fluorophores **3a-d** with yields ranging from 60% to 95%.

The obtained compounds exhibit absorption in the range of 350 to 420 nm and emission in the region of 470-650 nm. Fluorescence quantum yields reach up to 90% depending on the solvent.

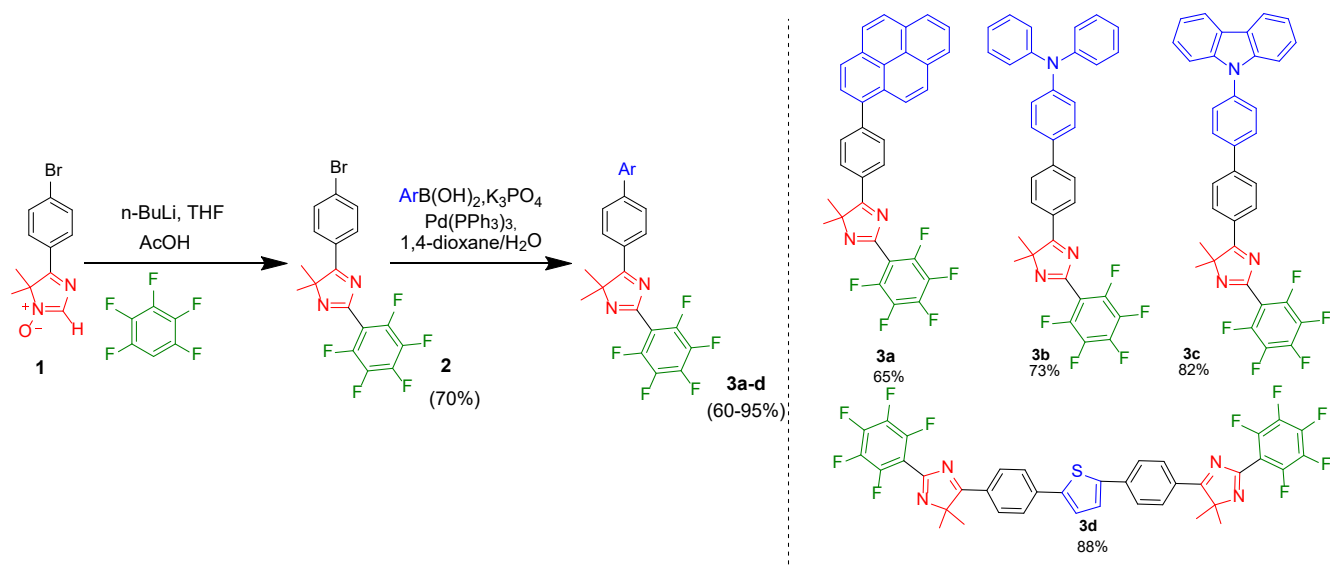


Figure 1. Synthesized pentafluorophenyl-4*H*-imidazoles.

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BIOACTIVE LIGANDS BASED ON 1,2,3-TRIAZOLES WITH LANTHANIDE COMPLEXES FOR BIOIMAGING

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Luminescent bioprobes based on Ln(III) lanthanide complexes are used as highly sensitive analytical sensors for visualizing various lesions in cells and tissues. However, the main problem with their widespread use in biosystems is their toxicity and low solubility. To solve these problems, it is proposed to use bioactive ligands and incorporate hydrophobic complexes into the structure of lyotropic liquid crystal matrices. The thermodynamic stability and dual polar-nonpolar nature of LC matrices provide encapsulation of compounds, as well as their controlled release and transport through biological membranes. The 1,2,3-triazoles and their derivatives play an important role in heterocyclic chemistry. The increased interest in these compounds is due, on the one hand, to their use as ligands for the synthesis of new compounds, on the other hand, due to their versatile biological and therapeutic activity. Lanthanide complexes, due to their unique optical properties, are actively used in immunoassays, tissue-specific imaging, and single-molecule detection in living cells. The combination of the biological activity of substituted 1,2,3-triazoles and Ln^{III} complexes will make it possible to create new multifunctional compounds for biomedicine.

In this work new complexes of lanthanides Tb^{III}, Eu^{III}, Dy^{III} with substituted 1,2,3-triazoles (TR), which have emission in the visible region of the spectrum, have been synthesized. The structure of the complexes was confirmed by IR spectroscopy data. A study of optical properties showed that the [Tb(AcAc)₂(TR)] complex has improved luminescent characteristics. The luminescence efficiency of the complex is 13% higher than that of the monoligand complex Tb(AcAc)₃.

The resulting complexes were incorporated into the structure of C₁₂EO₁₀/H₂O (60/40% wt.) and C₁₂EO₄/H₂O (70/30% wt.%) lyomesophases, which have a hexagonal and lamellar structure, respectively. A study of the immobilization of these hybrid systems on the unicellular organism *Paramecium Caudatum* using fluorescence microscopy showed that these systems are effectively adsorbed on the surface of the microorganism. They are not subject to destruction in the cellular environment and exhibit high luminescence. Thus, the proposed systems have high potential for tissue imaging, drug delivery monitoring, and non-invasive technologies.

The work was carried out with the financial support of the Russian Science Foundation, project 24-23-00187.

MECHANOCHEMICAL SYNTHESIS AND CATALYTIC ACTIVITY OF A NEW MgNiCo/AlFeY HIGH-ENTROPY LAYERED DOUBLE HYDROXIDE

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High-entropy materials are considered as promising materials with specific properties. A separate category of high-entropy materials consists of high-entropy compounds, characterized by the fact that the manifestation of high entropy is observed not for a mixture, alloy or solution, but as part of a single-crystal structure corresponding to one phase. High-entropy compounds are considered to be compounds that include 5 or more different “equivalent” elements, usually metal cations, isomorphically replacing each other in the structure of the substance.

High-entropy layered double hydroxides (HE-LDHs) represent a new group of potentially high-entropy materials, but their properties are currently insufficiently studied.¹ Most known LDHs contain 2-4 different metal cations. It is known that many LDHs have catalytic activity.² It was of interest to obtain a new HE-LDH and evaluate its catalytic activity.

Using the method of mechanochemical synthesis by grinding the initial reagents in an agate mortar followed by hydrothermal treatment, a new HE-LDH with the composition MgNiCo/AlFeY was obtained. The structure and elemental composition of the sample were confirmed by X-ray diffraction analysis, infrared spectroscopy and elemental mapping. The photocatalytic properties of the resulting layered hydroxide during the photodegradation of the cationic dye malachite green were studied. The peroxidase-like activity of the HE-LDH sample was assessed in the standard oxidation reaction of the chromogenic substrate 3,3',5,5'-tetramethylbenzidine. The resulting sample demonstrated both photocatalytic and peroxidase-like activity.

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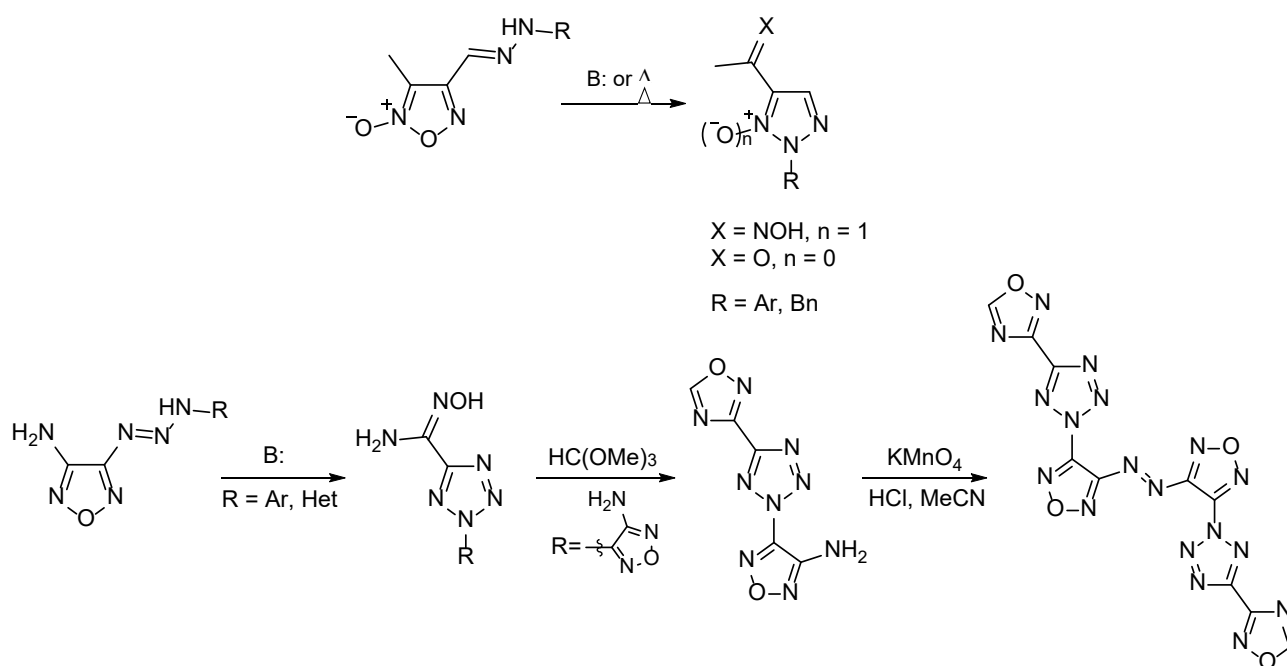
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ONE-STEP SYNTHETIC INTERCONVERSIONS OF 1,2,5-OXADIAZOLES INTO OTHER AZOLES

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Azole-to-azole interconversion, also referred to as Boulton-Katritzky rearrangement, has a significant meaning in heterocyclic chemistry, as it can yield one-step synthetic routes between different types of azoles. In present work, we investigate interconversion of 1,2,5-oxadiazoles to 2H-1,2,3-triazoles¹ and 2H-tetrazoles. In this study a new energetic compound was obtained by means of azole-to-azole rearrangement.



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ZnFe_2O_4 : COMPARATIVE ANALYSIS OF SYNTHESIS METHODS FOR ELECTRODE MATERIALS

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The developing field of hydrogen energy requires economically affordable efficient electrode materials, optimal use of zinc ferrite-based ceramics due to excellent functional properties. The paper analyzes the data of the ZnFe_2O_4 material obtained by the most common synthesis methods: sol-gel autocombustion, dehydration of layered double hydroxide (LDH) and mechanochemical. The density of ceramics is shown (Table 1), each sample is characterized by a decrease in grain size with an increase in sintering temperature.

Table 1. Ceramic density indicators $\text{Fe}_2\text{O}_3/\text{ZnFe}_2\text{O}_4$

Synthesis method	Sintering temperature, °C	Density, g/cm ³
Sol-gel autocombustion	1000	4,0943
	1100	4,7232
Mechanochemical	1000	4,4203
	1100	5,0962
LDH dehydration	1000	4,3709
	1100	4,8048

The highest value of specific capacity is observed for ceramics with a lower density (sol-gel 1000). The correlation of the above data suggests the possibility of using sol-gel ceramics as cathode materials.

The work was performed within the framework of the state assignment of Sakhalin State University No. FEFF-2024-0001

SYNTACTIC FOAM BUOYANCY ELEMENTS FOR UNDERWATER EQUIPMENT

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This paper presents the main results of previously conducted studies on the creation of syntactic foams and composite lightweight fillers with high specific strength based on them to ensure the buoyancy of deep-sea equipment.

Spheroplastic (abroad – syntactic foam) is a composite, in the polymer matrix of which hollow glass microspheres with a volumetric filling close to the limit are distributed. The role of the polymer matrix is usually performed by thermosetting binders, most often epoxy, as well as polyester and vinyl ester.

Depending on the depth of operation, this material today has an average density of $0.38 - 0.70 \text{ g/cm}^3$, is characterized by high hydrostatic strength, water resistance and relatively low volumetric compression, which allows it to be used as a lightweight filler for devices with a maximum immersion depth of up to 11,000 m.

Based on the achieved work at the National Research Center “Kurchatov Institute” - Central Research Institute of Structural Materials “Prometey”, a wide range of spheroplastics used in underwater shipbuilding was developed, the effect of the bulk modulus on the strength of spheroplastics was studied, the characteristics of hollow glass microspheres were analyzed, the modes of preparation of spheroplastics were calculated based on kinetic data and worked out, a calculation method for predicting the strength properties of spheroplastics based on the parameters of the original components was developed, a technique for determining the hydrostatic strength and water absorption of spheroplastics was developed, and a method for measuring the elastic properties of polymer binders and composites based on epoxy matrices and dispersed fillers was introduced.

THE EFFECT OF ANNEALING TEMPERATURE ON THE MICROHARDNESS OF TITANIUM ALLOYS

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One of the new contenders for leading positions in the creation of implants are the titanium alloys under development due to their very good mechanical and corrosion resistance and biocompatibility, which contain only non-toxic elements and meet the needs of the implant in terms of mechanical, anticorrosive and biocompatible properties, exhibit high mechanical strength and fatigue resistance, low modulus of elasticity, good wear resistance, etc.

In order to determine the optimal homogenizing annealing of samples Ti-(36-40) Zr-9Nb and for further plastic deformation, microhardness was studied in five states: after smelting, after smelting and homogenizing annealing at temperatures of 900-1200 °C, carried out in order to destroy the dendritic structure after smelting. The results of the study are shown in Figure 1

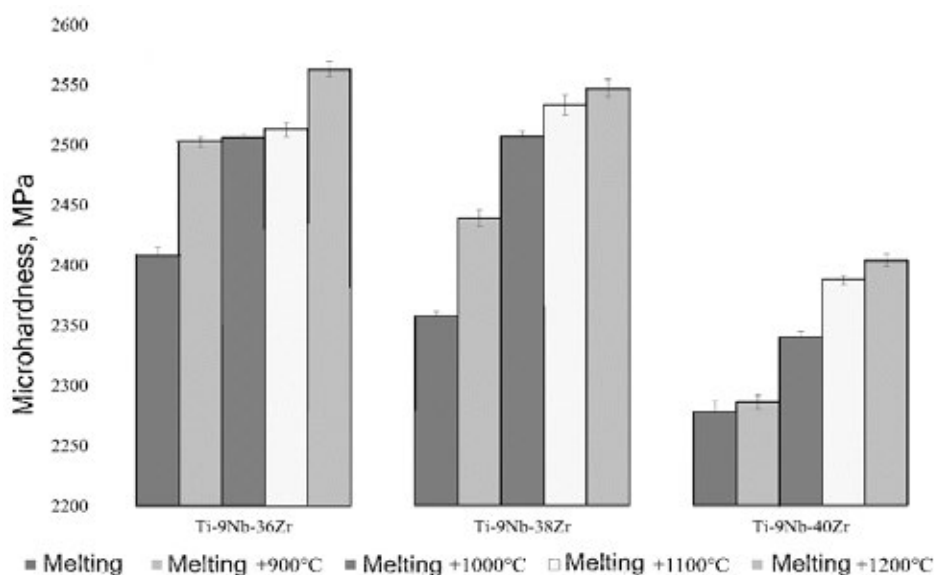


Figure 1. Microhardness of Ti-9Nb-(36-40)Zr

Annealing, according to the results of the analysis, increases the microhardness of ingots, as the β -phase decomposes with the release of a harder α -phase during slow cooling. As a result, the resulting structure contains $\alpha+\beta$ phases. However, this is not observed in Ti-9Nb-36Zr and Ti-9Nb-40Zr due to the low release of the α phase.

The work was carried out with the financial support from the Russian Foundation for Basic Research (RGNF), project 24-13-00186.

Na⁺-Ag⁺ ION EXCHANGE TECHNOLOGY FOR GLASS-CERAMIC PHOTACATALYSTS WITH HYBRID Ag-AgBr NANOSTRUCTURES

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Solar energy-activated photocatalysis is a sustainable approach to provide solutions for environmental issues. However, the search for highly efficient, sunlight-driven, chemically stable, and reusable photocatalysts is still in progress. Recently, glass-ceramics doped with semiconductors have been proposed for photocatalytic applications.^{1,2} We propose a new approach for fabrication of photocatalytic glass-ceramics with hybrid nanostructures via Na⁺-Ag⁺ ion exchange.

Glasses based on the Na₂O-Al₂O₃-ZnO-SiO₂-F system and doped with Sb₂O₃ and Br were synthesized and studied. Depending on Sb₂O₃ and Br doping Ag, AgBr or Ag-AgBr nanostructures were formed via low-temperature Na⁺-Ag⁺ ion exchange and subsequent heat treatment. The glasses were characterized with UV-VIS spectroscopy, XRD, and SEM. Photocatalytic performance of the samples was evaluated by degradation kinetics of methyl orange (MO) aqueous solutions under irradiation of a mercury lamp.

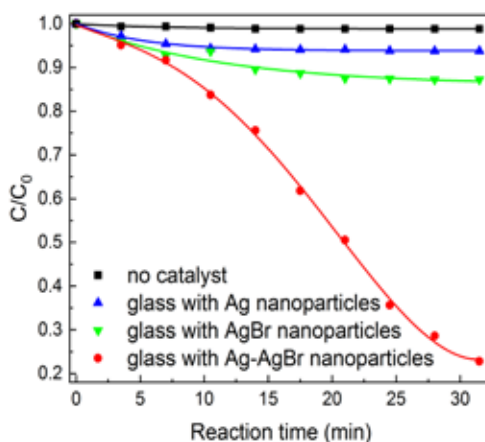


Figure 1. Photocatalytic degradation of MO aqueous solution without a photocatalyst and in the presence of the glass-ceramic samples in a cuvette.

Glass-ceramics doped with Ag and AgBr nanoparticles resulted in low photocatalytic degradation of MO to 94% and 87% of the initial concentration, respectively. However, the sample with Ag-AgBr nanostructures showed excellent photocatalytic activity in degrading MO solution to 23% already after 30 minutes of irradiation. The proposed approach for photocatalytic ion-exchanged glass-ceramics is a simple and low-cost technique that allows the formation of metal-semiconductor nanoparticles and can be further extended to other Me-MeHal (Ag-AgI, Cu-CuBr, etc.) nanostructures.

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CRYSTALLINE STRUCTURE FEATURES AND HIGH-TEMPERATURE PROPERTIES OF SOLID SOLUTIONS $\text{Sr}_{4-x}\text{Y}_x\text{Co}_4\text{O}_{12-\delta}$ ($x = 0.0-0.5$)

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A characteristic feature of perovskite-like cobaltites is the rather small energy separating states with different charge and spin values of cobalt ions. This leads to anomalies in magnetic and electrotransport properties at low temperatures. At elevated temperatures, cobaltites exhibit significant oxygen nonstoichiometry, high parameters of mixed, oxygen-ion and electron conductivity, and electrocatalytic activity. In this regard, some results from a recent study¹ on solid solutions $\text{Sr}_{4-x}\text{Y}_x\text{Co}_4\text{O}_{12-\delta}$ at $T < 300$ K attract attention. However, the interrelation of properties with oxygen non-stoichiometry remains unexplored.

In this work, we consider the thermodynamic and transport characteristics of $\text{Sr}_{4-x}\text{Y}_x\text{Co}_4\text{O}_{12-\delta}$ cobaltites, where $x = 0.0, 0.1, 0.2, 0.3$, and 0.5 . The materials were synthesized via the glycerol-nitrate route with annealing in air at 1473 K. The powder X-ray diffraction data reveal the hexagonal structure (space group R32) at $x = 0.1$. With an increase in yttrium content, a transition to a cubic structure (space group Pm3m) is observed. The absolute values of oxygen non-stoichiometry were determined by a complete reduction of samples in a 5% H₂–95% Ar gas mixture flow. The changes in oxygen content with temperature were studied in the air using thermogravimetric analysis (Setsys Evolution thermal analyzer). The temperature dependence of relative linear expansion was measured using a Linseis L75 dilatometer in the temperature range of 298 – 1273 K in the air. A four-probe method was used for measuring electrical conductivity and the Seebeck coefficient at variations of oxygen partial pressure and temperature. Oxygen content dependencies on pressure and temperature were obtained by the coulometric titration method. The obtained data are discussed within the frameworks of polaron charge transport theory and statistical-thermodynamic analysis of quasi-chemical reactions of structural defects.

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The work was supported by the Russian Science Foundation (project №22-12-00129).

THE DEFECT FORMATION AND STABILITY OF $\text{LnBaMn}_2\text{O}_{6-\delta}$ ($\text{Ln} = \text{Pr}, \text{Nd}, \text{Sm}$) PEROVSKITES UNDER CHEMOCYCLING CONDITIONS

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Chemical looping with oxygen decoupling is a promising technology for decarbonizing the environment. So-called oxygen storage materials are used as functional materials, which must have thermodynamic and phase stability under redox reaction conditions, as well as a wide range of oxygen non-stoichiometry.

Double-ordered manganites have distinctive functional properties that determine their high potential for developing oxygen-storing materials. In this work, by combining thermogravimetric methods with the monitoring of the structural properties of the materials by powder X-ray diffraction, phase stability boundaries have been studied. The ordering of the A-sublattice in an air atmosphere was shown to be maintained at temperatures up to 800 °C. However, at higher temperatures, a sharp decrease in cation disordering and a peak amount of the disordered phase $\text{Ln}_{0.5}\text{Ba}_{0.5}\text{MnO}_{3-\delta}$ is reached in the temperature range of 1200-1300 °C.

By combining the method of coulometric titration and thermogravimetry, the equilibrium values of oxygen content in the crystal have been determined as a function of oxygen partial pressure and temperature. Double manganites $\text{LnBaMn}_2\text{O}_{6-\delta}$ were found to be capable of reversible oxygen exchange with the gas atmosphere in a range of oxygen content from $\delta = 0$ to 1 while maintaining a tetragonal structure. Defect formation models have been developed for two stable regions with different oxygen non-stoichiometry and different structural features. The thermodynamic parameters of defect formation have been calculated. The enthalpy of reduction of a cation in the B-sublattice was found to vary with the radius of the lanthanide. Manganites with larger cations in the A-sublattice require more energy to release the oxygen ion from the lattice.

This work is partly supported by the Russian Science Foundation under grant of № 22-19-00129.

COMPOSITE MATERIALS WITH A CORE-SHELL STRUCTURE FOR EFFECTIVE INHIBITION OF COMBUSTION PROCESSES

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An urgent problem is the imperfection of existing fire extinguishing powder compositions both in terms of flame suppression and operational characteristics^{1,2}. In this regard, this research is focused on developing an approach to creating a new generation of heterogeneous fire inhibitors capable of self-organization during the synthesis process with the formation of a “core-shell” structure, as well as assessing the activity of the composite materials in the process of interrupting combustion reactions.

The proposed synthesis is based on the spray drying method, which makes it possible to obtain spherical particles of the “core-shell” type. Monoammonium phosphate is used as the core, the shell is formed from magnesium hydroxide nanoparticles. This approach allows us to enhance the effect of inhibiting combustion reactions: with the help of the decomposition products of monoammonium phosphate - polyphosphoric acid - the combustion chain reactions are broken and the diffusion of oxygen from the external environment to the combustion zone is delayed, while with the aid of the endothermic decomposition reaction (~1400 J/g) magnesium hydroxide, the combustion zone is cooled as a result of the released water vapor (~80 ml/g). In addition, the formed shell of surface-modified magnesium hydroxide nanoparticles allows, on the one hand, to effectively protect the core of the composite from the action of air moisture minimizing the likelihood of particle agglomeration, on the other hand, to significantly reduce the forces of interparticle interaction of the powder system, which will eliminate the use of additional inert additives used to reduce rheological parameters in order to increase the flowability of powders.

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IMPROVEMENT OF DOFETILIDE SOLUBILITY USING CYCLODEXTRINS: SOLUTIONS AND SOLID DISPERSIONS

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Dofetilide (DFT) is a modern antiarrhythmic drug used for the treatment of cardiovascular pathologies. Due to low solubility of this drug compound, high doses of DFT are required to achieve therapeutic effects, which causes serious side effects. A promising approach to increase the effectiveness of drugs while reducing undesirable effects is the use of cyclodextrins (CDs) as solubilizers and delivery systems. Cyclodextrins are cyclic oligosaccharides, which, due to the presence of a macrocyclic cavity, are able to encapsulate molecules of bioactive compounds and, thus, increase their solubility and bioavailability.

The purpose of this study was to evaluate the ability of dofetilide to complexation with native and modified cyclodextrins in solution and solid state. Phase solubility diagrams of DFT in the presence of cyclodextrins were plotted in buffer solutions with physiological pH values (2.0 and 7.4). It was found that the solubilizing effect of cyclodextrins is more effective in a neutral environment: aqueous solubility of DFT in the presence of β -cyclodextrin (β -CD), 2-hydroxypropyl- β -cyclodextrin (HP- β -CD) and sulfobutyl- β -cyclodextrin (SBE- β -CD) increased by 3.6, 11.8 and 18.1 times, respectively. The stability constants of the DFT/HP- β -CD and DFT/SBE- β -CD complexes have optimal values for improving the bioavailability and stability of hydrophobic drugs: 344 M^{-1} and 429 M^{-1} . The formation of amorphous solid dispersions of DFT/ β -CD, DFT/HP- β -CD and DFT/SBE- β -CD, obtained by grinding, was confirmed by a complex of physicochemical methods (IR spectroscopy, XRD, DSC, TG and SEM). It has been established that the solubility and dissolution rate of DFT in solid dispersions increases. It was concluded that the most promising approach to increasing of DFT bioavailability would be the creation of parenteral dosage forms using modified cyclodextrins.

The work was carried out with financial support of Russian Science Foundation, project 23-23-00193.

VISUALIZATION OF Ln^{3+} ADSORPTION BY HETERODOPED CARBON NANOMATERIALS USING PHOTON-COUNTING COMPUTED TOMOGRAPHY

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Computed tomography (CT) is the most commonly used noninvasive method of 3D visualization of living and inanimate objects. Semiconductor photon-counting detectors significantly expand the capabilities of the method and allow analyzing its structure considering also the chemical composition of each voxel¹. The present study demonstrates the potential use of the photon-counting CT (PCCT) as a noninvasive method for analysis of adsorption in filtering systems, using visualization of the adsorption of Ln^{3+} ($\text{Ln} = \text{La}, \text{Gd}$) on the surfaces of raw carbon nanoflakes (CNFs), CNFs heterodoped with nitrogen or phosphorus atoms, their oxidized analogues and amorphous SiO_2 as example.

The samples of CNFs, N-, and P-doped CNFs served as adsorbents were obtained by pyrolytic decomposition of hexane, acetonitrile, or PPh_3 solution in toluene at 900 °C in the presence of the MgO template. The oxidation was carried out with a solution or vapors of boiling nitric acid. Amorphous SiO_2 was obtained from rice husk ash or by catalytic hydrolysis of TEOS.

PCCT studies were performed using phantoms of the filtering systems. $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ solution was added to the adsorbent, the suspensions were stirred during the day, filtered and dried. PCCT scans were performed with identification of the zones with high contents of water and Ln^{3+} . The studies demonstrated adsorption of water and Ln^{3+} on the surface of P-CNFs and to a lesser extent of SiO_2 .

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This research was supported by Russian Science Foundation (project number 22-15-00072).

HYBRID MATERIALS BASED ON LAYERED YTTRIUM HYDROXIDE AND PORPHYRINYL PHOSPHONATES AS ADSORBENTS FOR METHYLENE BLUE FROM WATER

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Layered rare earth hydroxide (LRH) — a new class of layered inorganic anion-exchange materials, significant interest in which is associated with the possibility of combining luminescent, magnetic, and catalytic properties of lanthanides and intercalated anions to create multifunctional materials based on their compounds. Water-soluble porphyrins are a promising class for intercalation to LRH. Hybrid organic-inorganic materials obtained by combining porphyrins with different inorganic matrices, including layered ones, have high potential applications in various fields of science, such as solar energy, photodynamic therapy, biovisualization, and others.

Previously, water-soluble anionic porphyrins containing $-\text{SO}_3^-$ functional terminal group were intercalated in LRH, which led to an increase in thermal stability and changes of their photoactive and enzyme-like properties. There is a problem of porphyrin leaching from hybrid materials, one way to solve this problem is to use porphyrins containing anchoring groups (e.g., porphyrinylphosphonates). The aim of this work was to obtain new hybrid materials based on tetrasubstituted [(hydroxoethoxyphosphoryl)phenyl]-porphyrins and their metal complexes with layered yttrium hydroxide.

The interaction of porphyrinyl(monoester)phosphonates with layered yttrium hydroxide has been investigated for the first time. It is demonstrated that the obtained hybrid materials are able to sorb cationic dye methylene blue from aqueous solutions. The obtained result opens the prospect of application of new composites as sorbents for removal of organic pollutants from water.

STRUCTURAL DIVERSITY AND PROPERTIES OF BISMUTH IODIDE COMPLEXES OF DIFFERENT CLASSES

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Halide complexes of p-elements are interesting because of their structural diversity and physical and chemical properties, which can be used as components of solar cells. The key point is the study of compounds based on lead iodide. The creation of lead-free solar cells is an important direction, since lead and its compounds can be toxic and unstable in relation to environmental factors. These problems require further research and development of new approaches to the synthesis and study of halide complexes of p-elements (for example, bismuth complexes). Of particular interest are heterometallic compounds of bismuth(III) with a monovalent metal, where it is possible to obtain both three-dimensional and two-dimensional anions.

Within this work, experiments are aimed at obtaining heterometallic iodide complexes of bismuth with copper and silver. As a result, depending on the modification of the organic cations based on pyridine and 1,n-bis(pyridyl) alkanes, different classes of bismuth compounds are formed. The report discusses the structural features and optical properties of the obtained compounds.

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LOW-TEMPERATURE POLYETHYLENIMINE-BASED COMPOSITE MATERIALS FOR CO₂ ABSORPTION TASKS

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In recent years, much attention has been paid to reducing greenhouse gas emissions, in particular CO₂. This interest is caused by the increase in the concentration of CO₂ in the atmosphere, which has a negative impact on the environment and human health. CO₂ can be removed from gas mixtures using sorption technologies. One of the most promising CO₂ chemisorbents is branched polyethylenimine (PEI). A large number of amino groups in the composition of PEI leads to the high sorption capacity of the material ($\sim 365 \text{ mg}(\text{CO}_2)/\text{g}(\text{PEI})$), but this polymer is a viscous liquid, therefore the rate of CO₂ absorption is very low, which makes it difficult to use it in its pure form. To improve the dynamics of chemisorption, PEI is dispersed in the pores of supports with a developed porous structure.

In our work, porous Al₂O₃, SiO₂, Zr-Si aerogels, and polymer matrices (PMMA, SDVB) were used as porous supports for PEI. The aim of the work was to study the dependence of the CO₂ absorption characteristics of the obtained composite materials on the choice of the support. Composite sorbents were synthesized by impregnating the support with alcohol solutions of PEI, followed by the evaporation of the solvent. The sorption characteristics of the obtained materials were investigated by the methods of thermogravimetric analysis and differential scanning calorimetry. The experiments were carried out at 30°C using the 85% He/15% CO₂ gas mixture. Based on the results of the work, it was determined that PMMA and SDVB are the most effective supports for PEI. Specifically, the efficiency of using the active component in SDVB pores reaches a value of 339 mg (CO₂/g(PEI)). Testing of materials in adsorption cycles “sorption (30°C)/desorption (100°C)” showed their stability (99% of the initial CO₂ sorption capacity is preserved after 10 cycles). Heat consumption for the sorbent regeneration was calculated to be $\sim 2.9\text{--}3.5 \text{ kJ/g}(\text{CO}_2)$. It can be concluded that the obtained materials are promising for use in CO₂ capture technologies due to their high sorption capacity, stability, and low energy costs for regeneration.

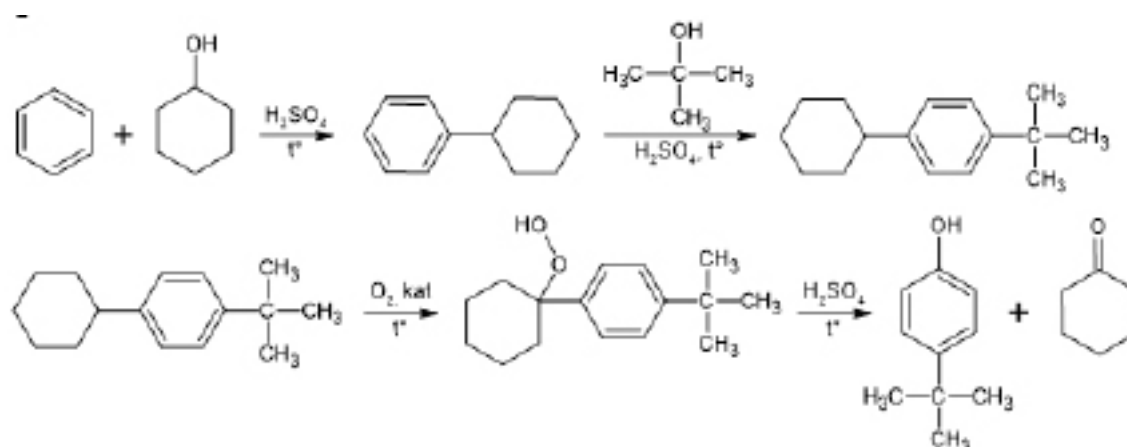
The work was supported by the Russian Science Foundation (grant № 23-23-10080, <https://rscf.ru/project/23-23-10080/>) and the Novosibirsk Region (agreement № r-47 dated April 3, 2023).

HYDROPEROXIDE METHOD FOR THE SYNTHESIS OF *para*-*tert*-BUTYLPHENOL AND CYCLOHEXANONE

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Industrially implemented methods for the production of cyclohexanone (CH-one) and *para*-*tert*-butylphenol (PTBP) have a number of technological limitations. Thus, the oxidation of cyclohexane to a mixture of cyclohexanone and cyclohexanol proceeds under severe conditions with low conversion of 3-5 % and selectivity of product formation of 70-75 %¹. Alkylation of phenol with isobutylene in industry is carried out in the presence of ion-exchange resins. Despite the high yield, this technology has significant disadvantages: the need for regeneration of catalyst, formation of PTBP isomers with close and high boiling points, which complicates the separation of the target compound². To solve these problems, we are developing an alternative method for the obtaining of PTBP and CH-one, which consists in the synthesis of *para*-*tert*-butylcyclohexylbenzene (PTBCHB), oxidation of PTBCHB to hydroperoxide, acid decomposition of which proceeds with the formation of PTBP and CH-one.



Scheme 1. Hydroperoxide method for the joint obtaining of cyclohexanone and *para*-*tert*-butylphenol.

The main stages of the proposed method were investigated, and the intermediate and target compounds were identified by gas-liquid chromatography, IR- and ^1H NMR-spectroscopy.

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PHENOLICS CONJUGATE WITH γ -ALOOH AS EFFECTIVE BIOCOMPATIBLE NANOANTIOXIDANTS

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Molecular forms of natural phenolic antioxidants have limited pharmacological efficacy due to low bioavailability, biocompatibility and stability. One of the promising directions of their practical application is associated with immobilization on pseudobemite nanoparticles (γ -AlOOH), which have the necessary chemical and colloidal stability and nontoxicity.

In the present study, gallic acid, caffeic acid, ferulic acid and curcumin were used to modify γ -AlOOH nanoparticles. The possible binding mechanism of phenolic compounds with γ -AlOOH is covalent and electrostatic interactions.

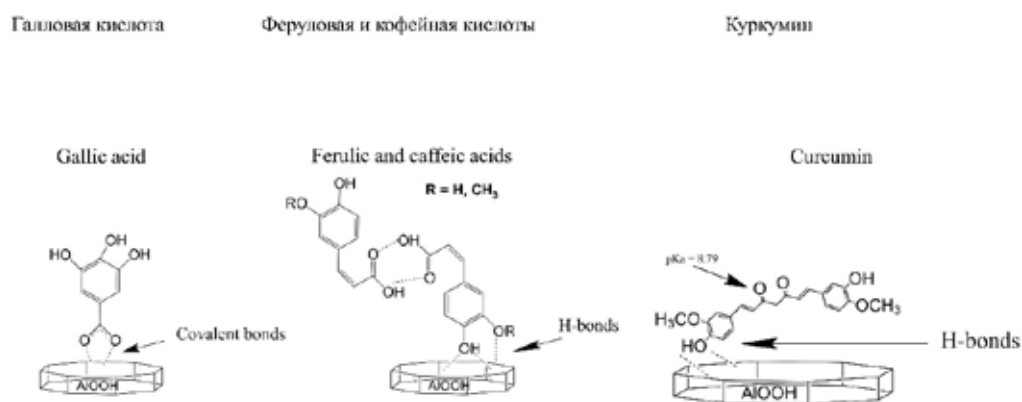


Fig. 1. Schematic representation of phenols' binding mechanism on boehmite surface

The synthesized pseudobemite-phenols conjugates are characterized by good solubility and biocompatibility, and exhibit high antioxidant activity in different test systems, including cellular (mammalian erythrocytes). The obtained nanoantioxidants are promising for further in-depth study and biomedical applications. The material presented in this report is described in detail in papers¹⁻³.

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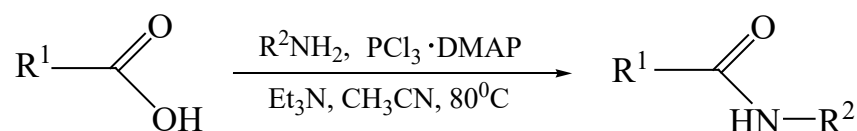
APPLICATION OF PHOSPHORUS TRICHLORIDE COMPLEX WITH DMPA FOR ONE-POT SYNTHESIS OF AMIDES AND AMIDIINES WITH PSYCHOTROPIC ACTIVITY

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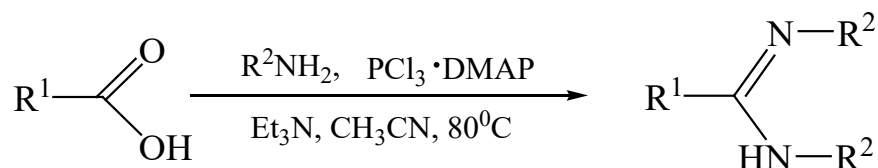
Existing methods for the preparation of amides and amidines have a significant drawback associated with the multi-stage process; they include the synthesis of acid chlorides of carboxylic and imidic acids¹ and, as a consequence, the yield of target compounds in terms of the original carboxylic acid is low. In the present study, transformations of benzoic and 1-adamantanecarboxylic acids to produce amides and amidines were developed in one step without isolation and purification of intermediates.

Amides were synthesized in the presence of a complex of phosphorus trichloride with DMAP, received in situ in acetonitrile at the molar ratio of reagents $R^1COOH:PCl_3:DMAP:R^2NH_2:Et_3N=1:1:1:1$ in one stage at a temperature of 80 °C for 2 h:



$R^1 = \text{Ph, Ad}$; $R^2 = \text{Ph, } p\text{-BuC}_6\text{H}_4, m\text{-NO}_2\text{C}_6\text{H}_4, p\text{-NO}_2\text{C}_6\text{H}_4, p\text{-BrC}_6\text{H}_4, p\text{-ClC}_6\text{H}_4, o\text{-MeC}_6\text{H}_4, m\text{-MeC}_6\text{H}_4, p\text{-MeC}_6\text{H}_4, p\text{-MeOC}_6\text{H}_4, \text{Ph-CH}_2$

Amidines were prepared under the conditions described above, at the molar ratio $R^1COOH:PCl_3:DMAP:R^2NH_2:Et_3N=1:1,5:1,5:3:1$ for 8 hours:



$R^1 = \text{Ph, Ad}$; $R^2 = \text{Ph, } o\text{-MeC}_6\text{H}_4, m\text{-MeC}_6\text{H}_4, p\text{-MeC}_6\text{H}_4, p\text{-OMeC}_6\text{H}_4, o\text{-PrC}_6\text{H}_4, p\text{-ClC}_6\text{H}_4$

Thus, it has been established that the complex of phosphorus trichloride with DMAP makes it possible to receive secondary amides and amidines from carboxylic acids and arylamines in one stage with yields of 62-94% and 78-95%, respectively. It has been established that the synthesized compounds in the adamantane type have psychotropic (anxiolytic) activity.

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NEW PRECURSORS FOR THE SYNTHESIS OF SELENIDE AND TELLURIDE COLLOIDAL QUANTUM DOTS

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Bulk lead and mercury selenides and tellurides possess band gap of 0 eV for HgTe and 0.32 eV for PbTe at r.t. and normal pressure. These properties give thin films based on these chalcogenide colloidal quantum dots (CQDs) a potential for applications in photosensors for near and middle IR-range for HgSe/PbSe and far-IR for HgTe¹. This unmatched combination of physical properties makes them perspective materials for creation of photosensors and electroluminescent devices².

Broad practical application of these selenide and telluride colloidal quantum dots hampered by the absence of reliable and economically feasible methods of CQDs preparation for different spectral ranges with high colloidal stability and narrow mean size distribution.³

Solution of tricyclohexylphosphine telluride was applied for the preparation of HgTe CQDs as a tellurium precursor for the first time. This reagent is easy-to-handle, as well as provides the high reproducibility of procedures in contrast to the solution of tellurium with trioctylphosphine.⁴ Samples of HgTe CQDs with first absorption peak at the range from 1.38 mm to 2.8 mm.

New reagent based on selenium and decene-1 was suggested and successfully applied in the synthesis of PbSe and HgSe CQDs.⁵ Important advantage of this reagent is oxidative stability to the air oxygen.

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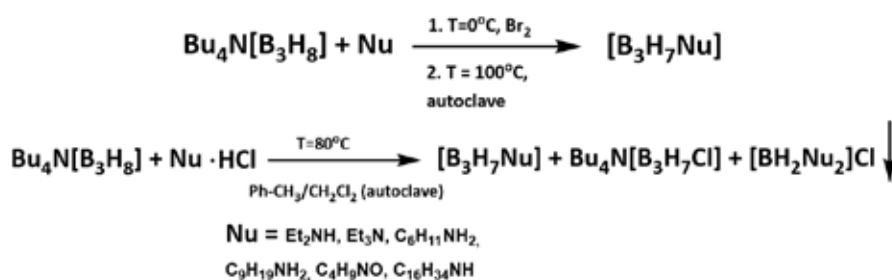
Supported by RSCF, project 23-23-00300.

SYNTHESIS AND PROPERTIES OF NEW SUBSTITUTED DERIVATIVES OF THE OCTAHYDROTRIBORATE ANION

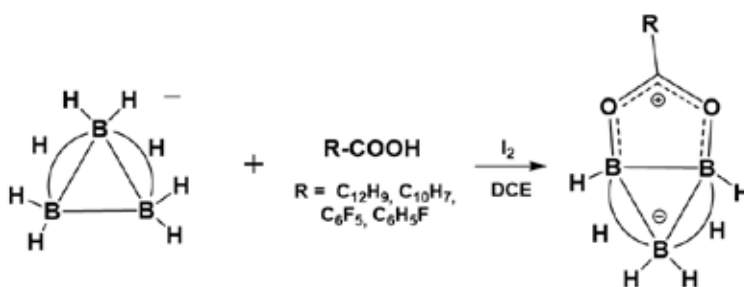
Shulyak A.T., Lukoshkova A.A., Selivanov N.A., Bykov A.Yu., Zhizhin K.Yu., Kuznetsov N.T.

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The $[\text{B}_3\text{H}_8]^-$ anion, having an aromatic structure, is capable of entering into nucleophilic hydride substitution reactions with the formation of substituted derivatives $[\text{B}_3\text{H}_7\text{Nu}]$. Although these reactions are a complex multifactorial process a number of substituted derivatives with various amines (diethylamine, morpholine, isononylamine, dioctylamine, cyclohexylamine) have been obtained using hydrochlorides of these amines, as well as in the presence of bromine.



It is known that octahydrotriborate is capable of reacting with carboxylic acids to form neutral disubstituted derivatives I. Such connections form a strong conjugated system, which makes these connections quite stable. In the course of the work, a number of disubstituted derivatives with aromatic carboxylic acids, as well as with acids containing several nucleophilic centers, were obtained; directed methods for the synthesis of disubstituted and monosubstituted derivatives were developed, which expands the possibilities of their further application.



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DEGRADATION FEATURES OF HfB_2 -SiC CERAMIC MATERIALS IN THE SHORT-TERM EXPOSURE OF CO_2 -PLASMA

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Ultrahigh-temperature ceramic materials based on $\text{ZrB}_2(\text{HfB}_2)$ -SiC are of great interest as candidates for application in promising aerospace engineering. Estimation of the possibility of their use, for example, in the atmospheres of such planets as Mars and Venus, requires modelling experiments in high-speed flows of high-enthalpy CO_2 using high-frequency induction plasmotrons. In order to reveal the peculiarities of the initial stages of the degradation mechanism of HfB_2 -30vol.%SiC material, we have studied its behavior under relatively short-term exposure to a supersonic flow of dissociated CO_2 . It is established that as a result of relatively short exposure (within 5 min) on ultrahigh-temperature ceramics of HfB_2 -30vol.%SiC composition by supersonic flow of dissociated CO_2 on the surface the temperature 1615-1655°C is established, there is a tendency to its insignificant growth at a rate of ~8°/min. It was found that under the selected conditions under the surface oxide layer HfO_2 - SiO_2 the formation of a porous region depleted of SiC has not yet occurred, as it was noted at longer exposures (14 min)^{1,2}.

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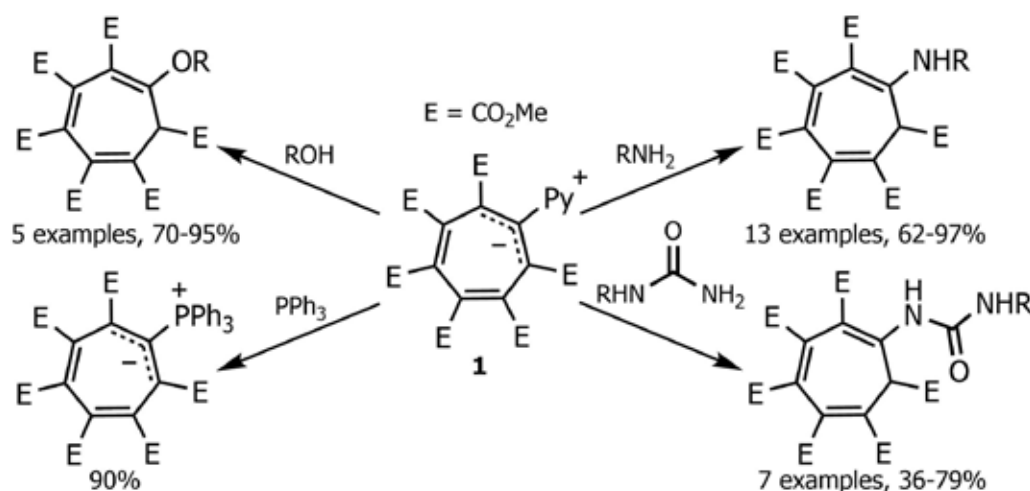
THE ANTIAROMATIC NUCLEOPHILIC SUBSTITUTION IN HEXA(METHOXYCARBONYL)PYRIDINIUM-1- YLCYCLOHEPTATRIENIDE

Sokolova A.D., Belyy A.Yu.

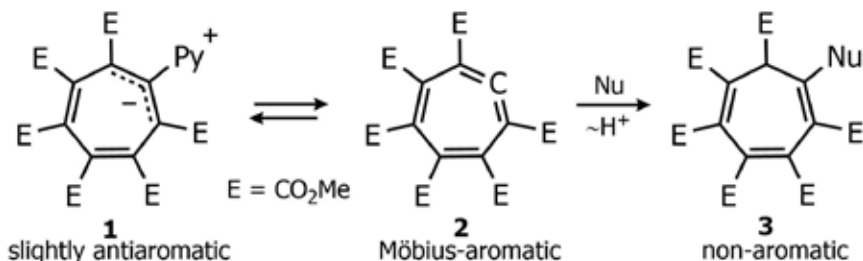
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Recently, hexa(methoxycarbonyl)pyridinium-1-yl-cycloheptatrienide **1** with a zwitterion structure¹ was obtained in our laboratory.

This zwitterion undergoes a nucleophilic antiaromatic substitution with a wide range of substrates, leading to a number of new cycloheptatrienes and zwitterions.



The reaction mechanism includes the elimination of pyridine to form cycloheptatetraene **2**, which is then undergoes the addition by a nucleophile, and the subsequent proton migration gives the product. Our quantum chemical calculations confirmed the Möbius aromaticity of the intermediate **2**. Thus, the reaction of the antiaromatic substrate proceeds via the aromatic intermediate and leads to the non-aromatic product.



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The work was financially supported by the Russian science foundation, project 23-73-10181.

DEVELOPMENT AND EXPANSION OF TECHNOLOGY FOR PRODUCING THERMOSTABLE ALUMINUM OXIDE

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It is important to ensure high thermal stability of the material, as well as a developed surface when developing aluminum oxide synthesis technology. When expensing the technology for the synthesis of thermostable aluminum oxide, it is important to preserve the properties of the material, namely, thermal stability, high surface values and developed porosity^{1,2}.

A laboratory sample in the amount of 150 g and an enlarged sample in the amount of 1 kg were synthesized by controlled two-jet precipitation of aluminum hydroxide from a solution of sodium aluminate with a solution of nitric acid. The resulting precipitates were filtered and washed on a filter with an estimated amount of water, followed by drying at 120 ° C and firing at 900 ° C to obtain aluminum oxide.

The results of the study have a direct technological purpose and can be used in the implementation of the developed technology in the industrial field of manufacturing automotive three-way catalysts, and therefore are significant for the country in the matter of technological sovereignty.

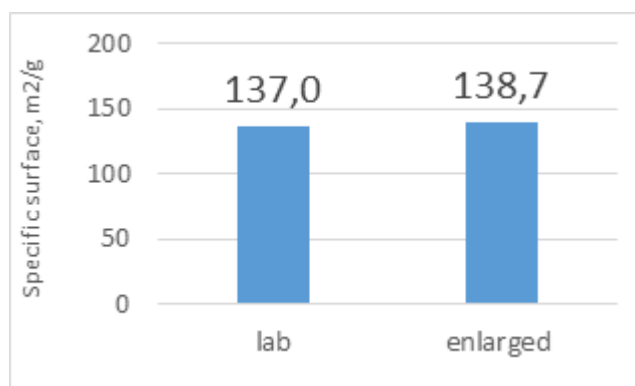


Figure 1. Results of specific surface area for laboratory and enlarged samples

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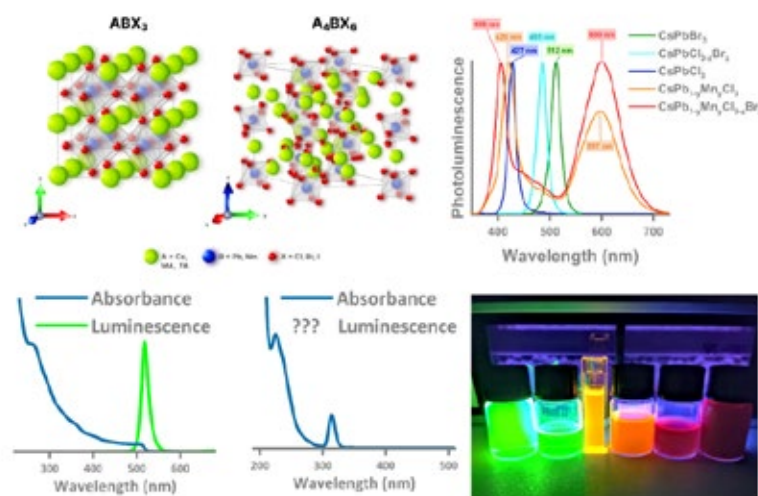
PEROVSKITE NANOPARTICLES: SYNTHESIS, OPTICAL PROPERTIES AND POTENTIAL APPLICATION

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Perovskites represent a class of semiconductor materials with the general formula ABX_3 , where A is an organic or inorganic cation, B is a lead or manganese cation, and X is a halogen. These materials exhibit distinctive optical and electronic properties. The interest in perovskites is driven by the potential for their use as a material for developing components of highly efficient solar batteries, light-emitting diodes (LEDs), active media for generating laser radiation, as well as a material for creating sources of non-classical radiation [1]. The study focused on synthesizing and examining the optical properties of nanoparticles with the structure of perovskite compounds $CsBX_3$ and Cs_4BX_6 , where B = Pb, Mn, and X = Cl, Br, I [2].



The potential use of perovskite nanoparticles compositions as a light-emitting layer in diodes was demonstrated.

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This study was supported by grant of the Russian Science Foundation (№ 23-19-00884) and was performed using the equipment of the JRC PMR IGIC RAS.

VULCANIZATION AT THE INTERFACE OF SUPRAMOLECULAR FORMATIONS AND CO-VULCANIZATION OF RUBBERS

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The research topic is aimed at a new approach to vulcanization of elastomeric compositions, both based on individual rubbers and their combinations. The possibility of vulcanization at the interface of supramolecular formations and co-vulcanization of rubber phases comes from the existence of a supramolecular structure in polymers, proved by Soviet scientists V.A. Kargin, A.I. Kitaygorodsky and G.L. Slonimsky, due to various types of ordering of macromolecules in their mutual arrangement. At the present time, the authors propose a solution to the problem of vulcanization at the interface of phases by synthesized sulfiding complexes. The prerogative in the creation of sulfiding complexes belongs to lactam-containing melts. It is the original properties of ϵ -caprolactam that allows melts to preserve the structuring ability of sulfur, which is in an allotropic modification other than in the α -form. The effectiveness of the use of sulfiding complexes is manifested, first of all, in increasing the strength properties of elastomeric compositions. This fact contributes to the practical implementation of experimental data determining an increase in the wear resistance of the tread of tires. As for the co-vulcanization of rubbers, the positive research results indicate the possibility of an alternative replacement of hydrogenated butadiene-nitrile rubber with a composition of domestic butadiene-nitrile (BNC) with fluoro rubber. The choice of these rubbers meets the requirements of the operating conditions of rubbers with the requirements of oil and gas resistance and gas tightness, while conventional sulfur vulcanization does not meet the requirements of operation.

The conducted studies using a sulfiding complex emphasize both the fact of the existence of supramolecular formations and the need to use the most acceptable vulcanizing systems that provide the elastomeric composition as a whole with a more significant level of physico-mechanical properties.

THERMAL EXPANSION OF SCANDIUM-DOPED BARIUM STANNATE

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Thermomechanical compatibility is one of the most important parameters when selecting functional materials for protonic ceramic fuel cells. In general, the change in linear parameters of electrolyte material layer with proton conductivity during thermal cycling is caused by a combination of factors. Along with thermal expansion during heating as well as contraction during cooling, such factors may include: phase decomposition involving the formation of impurities, phase transitions, hydration/dehydration.

In the present work, the thermomechanical properties of acceptor-doped barium stannate $\text{BaSn}_{1-x}\text{Sc}_x\text{O}_{3-\delta}$ ($0 \leq x \leq 0.40$) were investigated by dilatometry and high-temperature X-ray diffraction analysis (HT-XRD) in ambient air atmosphere upon heating from 25 to 1000 °C. All the investigated compounds crystallize into a cubic perovskite structure at room temperature; no phase decomposition or phase transition were observed. The contribution associated with hydration and dehydration to the overall lattice parameter change was determined. The average ($\sim 14 \cdot 10^{-6} \text{ K}^{-1}$) and differential TECs from dilatometry data were calculated.

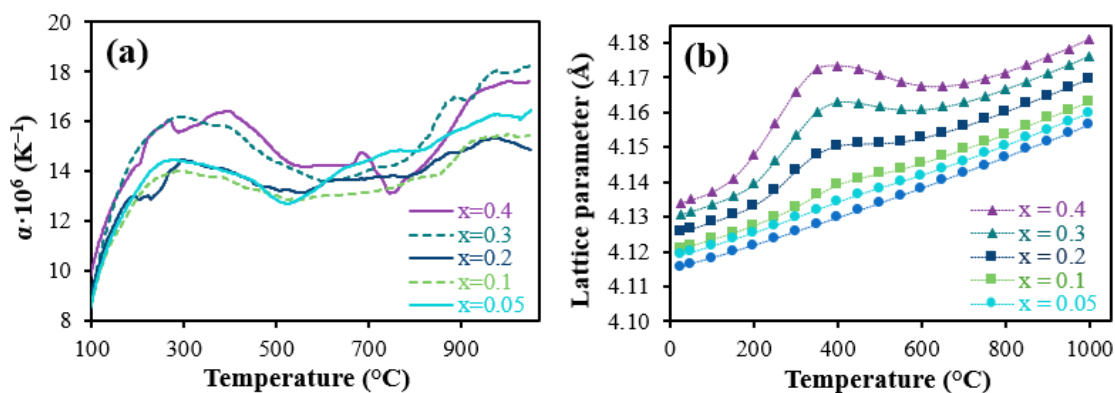


Figure 1. Thermal expansion of $\text{BaSn}_{1-x}\text{Sc}_x\text{O}_{3-\delta}$ upon heating: differential TECs calculated from dilatometry data (a), temperature dependences of the lattice parameter refined by the Rietveld analysis using HT-XRD data (b)

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SYNTHESIS OF THE FIRST REPRESENTATIVES OF TRISPYROPOLYHETEROCYCLIC PYRROLIDINE DERIVATIVES

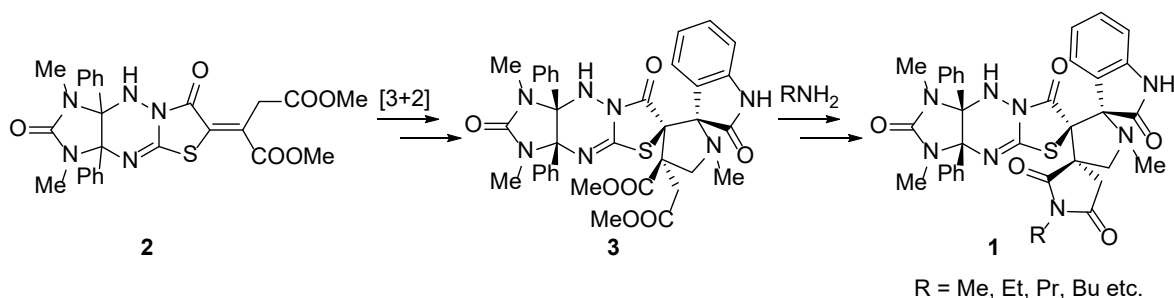
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Promising objects of study in organic and medicinal chemistry are pyrrolidine derivatives linked with other heterocyclic fragments. These structures are part of a number of natural alkaloids exhibiting various types of biological activity^{1,2}.

A common method for the synthesis of spiropyrrolidines is based on the [3+2]-cycloaddition reaction of azomethine ylides with electron-deficient alkenes, but it allows one to obtain only mono- and dispyro-linked pyrrolidine derivatives³.

We have developed for the first time a method for the synthesis of trispiro-linked pyrrolidine derivatives **1**, based on sequential reactions of [3+2]-cycloaddition of azomethine ylides to tetrasubstituted alkene **2**, with the further formation of a new pyrrolidinedione ring in dispirocyclic adducts **3** with the participation of amines.



High diastereoselectivity makes it possible to obtain the target structure **3**, containing five chiral centers, in the form of single diastereomers.

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PASSIVATION OF SILVER IN SOLUTION, CONTAINING HEXAFLUOROCYRCONIC ACID

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Silver coating significantly changes its properties under the influence of an atmosphere, containing hydrogen sulfide and other sulfur compounds. This causes the metal to tarnish. In industry, the most popular are optical and electrical contact properties of silver¹.

Various surface treatments have been developed to protect silver items. Traditionally used for passivation are the solutions based on chromium (VI) compounds, the main disadvantage of which is high toxicity and carcinogenicity.

This work is devoted to the development of processes for chromate-free passivation of silver surfaces.

As a result of the work performed, a solution containing hexafluorozirconium H_2ZrF_6 and gallic acids, ammonium paratungstate $(NH_4)_{10}W_{12}O_{41}$ and nickel nitrate was developed, in addition, the optimal process parameters were determined. Studies have shown that the permissible pH values of solutions are in the range of 4.5-5.5 units, and the working temperature range is 18-25°C.

It has been established that when processing silver and alloy SRM 92,5 in the developed solution, a passivation layer is formed on the metal surface, providing protection against darkening.

It has been shown that the developed passivating zirconium-containing coatings are comparable in corrosion resistance and protective ability to chromate layers.

Using the ellipsometric method, the thickness of the coatings was determined depending on the duration of their deposition. The thickness of the coatings increases in the first 1 minute and stabilizes at values of ~240 nm.

Wear resistance tests have shown that the developed coatings are much more resistant to harsh environmental influences than chromate films.

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BIOFLAVONOIDS-BASED GLASS-LIKE MATERIAL

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The development of new functional materials based on bioflavonoids is promising for medicine and pharmacy research. These natural compounds are well-known for their high safety profile, pharmacological activity, and profitability in production.

Previously, a composition containing flavanone dihydroquercetin and the amino acid L-lysine was derived. When water is removed, a film structure is formed. To determine the nature of the films, thermogravimetric analysis (TG) and differential scanning calorimetry (DSC) were performed, using NETZSCH TG 209 F1 Libra and NETZSCH DSC 204 F1 Phoenix, respectively.

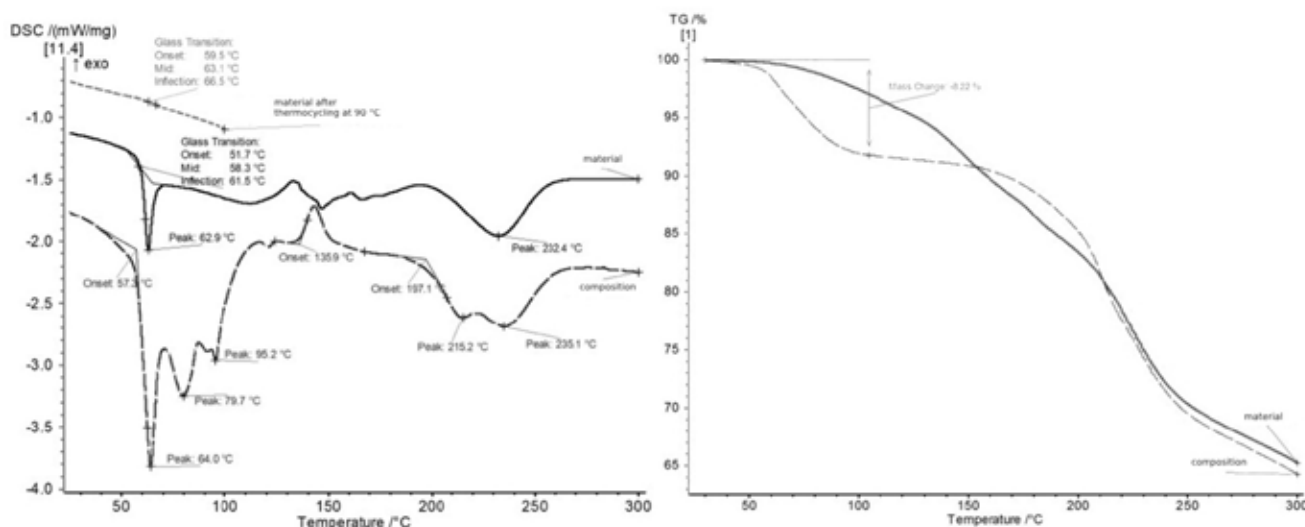


Figure 1. DSC and TG curves of obtained samples

The DSC curve of the functional material possesses a distinct bend around 60 °C, which can be attributed to the glass transition process. This isn't observed for the initial composition. Some pseudopolymorphic phase transitions are present, which may also be associated with the removal of crystal water. Notably, the DSC curve of the film lacks the most of the endo-effects observed for a physical mixture (composition).

THE PRODUCTION OF A NANOSTRUCTURED NICKEL-PALLADIUM CATALYST USING THE REPLICA METHOD

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Research on nanostructured materials and nanoparticles of various types, their properties, and synthesis methods has been rapidly advancing over the past few decades due to the potential for their wide range of applications as chemical sensors, catalysts¹, and other materials. In this study, nanostructured nickel was modified with palladium nanoparticles using a replica method.²



Figure 1. Schematic diagram of the production of a nickel-palladium catalyst

The resulting material exhibits catalytic activity in the methanol electrooxidation reaction. However, the possibilities for using a Ni/Pd catalyst are not limited to this reaction, and the material also has potential for use in hydrogenation, dehydrogenation, dehydrocyclization, and other heterogeneous catalytic processes.

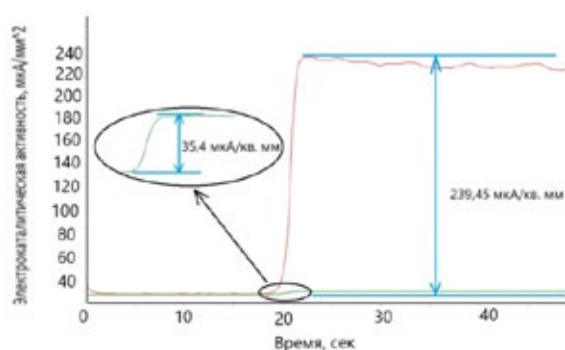


Figure 2. Shows the values of the change in current strength when 0.1 mM of methanol was added to flat nickel (1) and nanostructured nickel with palladium particles (2).

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THE EFFECT OF A BONDING ADDITIVES ON THE ABILITY TO FORM A CALCIUM PHOSPHATE LAYER IN VITRO ON THE SURFACE OF MATERIALS BASED ON TOKEM-250 FOR THE $\text{TiO}_2\text{-SiO}_2\text{-P}_2\text{O}_5/\text{ZnO}$ SYSTEM

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One of the actual problems in the creation of materials for the treatment of bone defects is the development of two- and three-dimensional matrices or frameworks with a high ability to form natural tissue on its surface.

$\text{TiO}_2\text{-SiO}_2\text{-P}_2\text{O}_5/\text{ZnO}$ materials are spherical layered granules based on Tokem-250 with an average particle size of 1 mm obtained by a combination of template and sol-gel synthesis methods¹. Polyvinyl alcohol ($\text{TiO}_2\text{-SiO}_2\text{-P}_2\text{O}_5/\text{Zn_PVA}$) and liquid glass ($\text{TiO}_2\text{-SiO}_2\text{-P}_2\text{O}_5/\text{Zn_LG}$) were selected as bonding additives. The ability to form a calcium phosphate layer *in vitro* was studied in SBF solution using the method proposed by Kokubo².

It was found that the formation of calcium-phosphate layer takes place in 3 stages (Table 1.). The introduction of a bonding additive is slightly slows down the process of calcium phosphate layer formation on the surface of the samples at stages 1 and 2, which is explained by steric difficulties caused by bonding additives. Ca^{2+} and Mg^{2+} ions are more intensively deposited on the surface of the $\text{TiO}_2\text{-SiO}_2\text{-P}_2\text{O}_5/\text{Zn_LG}$ sample due to the large number of active silicon centers forming strong bonds with calcium and magnesium ions. The results obtained are of interest for the further study.

Table 1. Coefficient of Ca^{2+} and Mg^{2+} ions accumulation on the material surface

Sample	k (0 - 3 day)	k (4 - 8 day)	k (9 - 14 day)
$\text{TiO}_2\text{-SiO}_2\text{-P}_2\text{O}_5/\text{Zn_LG}$	1.48	1.52	1.33
$\text{TiO}_2\text{-SiO}_2\text{-P}_2\text{O}_5/\text{Zn_PVA}$	1.26	0.86	1.23
$\text{TiO}_2\text{-SiO}_2\text{-P}_2\text{O}_5/\text{Zn}$	1.78	1.73	1.22

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SPECIAL CEMENTS BASED ON FERRITIC CALCIUM SULFOALUMINATE CLINKER

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The increased volume of capital construction and various ways of its realization cause the necessity of development of special effective cements, increasing the technical level of the construction industry.

A number of compositions and methods to obtain special cements are known, the properties of which are largely determined by the kinetics and amount of calcium hydrosulfoaluminate and calcium hydrosulfoferrites formed in the process of structure formation and hardening of cement paste. Depending on the composition of special clinker and its ratio with Portland cement clinker, superfast hardening cements, high-strength, shrinkage-free, expanding, and stressing cements are obtained¹. Sulfated clinkers are mainly used as special clinkers for these cements. Promising is the use of calcium sulfoaluminate clinkers, which are close to sulfoaluminate clinker in terms of their properties in the initial curing period, and to sulfoferrite clinker in terms of resistance².

The physical-mechanical and deformation properties of cements based on calcium sulfoaluminate clinker containing 45....50% of calcium sulfoaluminate indicate that they can be used as independent binders. The strength of such cement in grades age is 40 MPa, and self-stressing at the same time reaches 1.8 MPa.

The increased content of calcium silicates in ferritic calcium sulfoaluminate clinkers, as well as the presence of high-basic calcium silicates in combination with calcium sulfoalumoferrites, causes the expansion of the hardening system without loss of strength. The increase in strength is determined by high-calcium hydrosilicates.

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A POTENTIOMETRIC STUDY OF GALLIUM CONTAINING MELTS BASED ON ALKALI METAL CHLORIDES IN THE PRESENCE OF MOLYBDENUM METAL IN THE SYSTEM

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Selection of components present in spent nuclear fuels (SNF) in a “molten salt – liquid metal (alloy)” system is a prospective pyroelectrochemical method of SNF reprocessing, allowing handling SNF after a short cooling time and extract apart from fissile materials other valuable components. One of preferable liquid metal electrodes is metallic gallium or gallium based alloys¹. Developing an optimized process requires comprehensive information concerning electrochemical behavior of all elements taking part in the process, including components of metallic alloys together with gallium.

The present work was aimed at a potentiometric study of gallium containing chloride melts held in contact with metallic gallium and molybdenum (a widely used construction material in work with molten salts). 3LiCl–2KCl and 6NaCl–9KCl–5CsCl eutectic mixtures were selected as molten chloride electrolytes because these mixtures are of particular interest for practical implementation of pyrochemical technologies of SNF reprocessing².

Chromopotentiometric measurements were performed in 400–700 and 550–750 °C temperature intervals for 3LiCl–2KCl and 6NaCl–9KCl–5CsCl based melts, respectively. All measurements were conducted under an inert atmosphere (argon). As a result, temperature dependencies of formal standard electrode and redox potentials of gallium for Ga⁺/Ga, Ga³⁺/Ga and Ga³⁺/Ga⁺ redox couples were determined.

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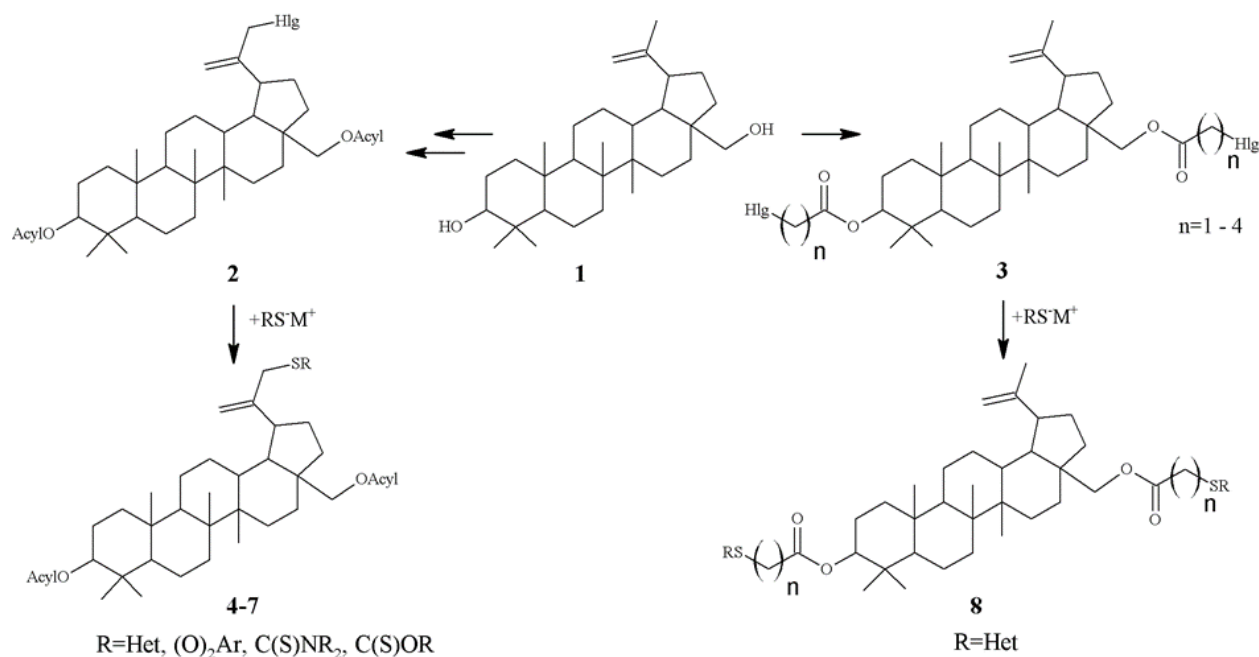
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THE INTRODUCTION OF SULFUR-CONTAINING PHARMACOPHORE GROUPS INTO THE BETULIN MOLECULE AS A PATHWAY TO NEW BIOLOGICALLY ACTIVE COMPOUNDS

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Betulin **1**, a pentacyclic triterpenoid of the lupan type, and its derivatives have a wide range of bioactive (including pharmacological) properties ¹. Due to the significant content (up to 35%) in birch bark, it is an affordable raw material for obtaining potential BAC. In this work, sulfur-containing groups were introduced into the betulin **1** molecule to the C-3, C-28 and C-30 atoms, which are present in many medicinal substances and plant protection chemicals ²⁻⁴, by reactions 30-halogen- **2** and 3,28-bis(halogenacyloxy) **3** betulin derivatives with heterocyclic thions(thiols), aryl sulfonates, dithiocarbamates and dithiocarbonates.



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NEW HIGH ENTROPY OXIDES WITH THE PYROCHLORE STRUCTURE

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The purpose of our work is to study the physicochemical characteristics of the formation and stabilization of high-entropy oxide phases, to search for new phases of this kind and to study the properties of samples of the studied phases with the aim of using them as structural and functional materials. This research is aimed at obtaining and studying the structure and properties of samples of new high-entropy oxide phases with the pyrochlore structure (primarily with the $A_2B_2O_7$ structure variant) based on multicomponent systems, which are characterized by isovalent and heterovalent isomorphism.

During the study, the following tasks are solved:

- obtaining samples of a new class of high-entropy oxide phases with the pyrochlore structure for systems that had not previously been the object of research from the standpoint of creating high-entropy oxide phases;
- investigating the composition and structure, as well as the properties of the obtained samples (including properties of interest from the point of view of using the obtained samples to create a thermal barrier coatings);
- analysis of the experimental data obtained in order to formulate general patterns for the formation of high-entropy oxide phases with the pyrochlore structure, which will also include a criterion for the stability of phases of this kind.

The synthesis of experimental samples is carried out by solid-phase sintering. Scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD) are used to confirm the composition and structure. The thermal expansion coefficients of the resulting materials are being studied, as well as their thermal conductivity, and phase stability over a wide temperature range. In addition, as part of the study, a thermodynamic description of high-entropy crystalline oxide phases with the pyrochlore structure are being carried out.

The research was supported by the Russian Science Foundation and with the support of the government of the Chelyabinsk region, grant No. 24-13-20009, <https://rscf.ru/project/24-13-20009/>.

SYNTHESIS, STUDY OF THE STRUCTURE AND PROPERTIES OF “HIGH-ENTROPY ALLOYS / ENDOGENOUS CARBIDES” METAL MATRIX COMPOSITES

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The purpose of our research is to develop a new surfacing material based on Al-Co-Ni-Fe-Cr-W-C, Mn-Co-Ni-Fe-Cr-W-C, and Co-Ni-Fe-Cr-W-C systems. It is planned to create a composite material that combine a high-entropy matrix with endogenous reinforcing carbide particles. As part of our work, experimental samples of “high-entropy alloys / carbides” composites are being obtained and their studies were carried out. In addition, thermodynamic modeling of phase equilibria in the systems under study is being carried out.

The samples were obtained by smelting mixtures of simple substances (purity of at least 99.99%) in corundum crucibles in a vacuum laboratory furnace with graphite heaters. The temperature in the furnace was set to 1650 °C at a heating rate of 600 °C/hour, then held for at least 30 minutes to average the composition of the samples, after which the furnace was cooled down at a rate of 600 °C/hour and the crucibles were removed from the working space. Then, the ingots were removed from the crucibles and cut. The resulting metal (most of them) was subjected to heat treatment/homogenization in the same furnace at temperatures of 400, 600, 800, 1000 °C for 5 hours.

Then the composition and structure of the obtained samples were studied using Scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD), and the stability of the phase composition was studied using differential scanning calorimetry (DSC) on a NETZSCH STA 449 F3 Jupiter and heat resistance using a Q-1500 D derivatograph.

The investigation on the stability of the obtained samples made it possible to establish that the studied systems are quite resistant to oxidation in the considered temperature range (20-1100 °C).

The results of an experimental study of heat resistance demonstrate the high resistance of the studied systems to oxidation at temperatures below 900-1000 °C. This indicates the promise of using the developed materials in high-temperature applications.

The work was supported financially by the Russian Federation represented by the Ministry of Science and Higher Education of the Russian Federation, project number (agreement number) No. 075-15-2022-1243.

INVESTIGATION OF CATHODE MATERIAL – PROTON-CONDUCTING ELECTROLYTE INTERPHASE: CATION INTER-DIFFUSION AND ELECTROCHEMICAL PROPERTIES

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In the last decade of active search of materials for solid oxide fuel cells (SOFCs) attention of researchers were shifted to investigation of proton-conducting oxides. Activation energy of proton transport is lower than that of oxide-ion conductivity, which provides relatively low working temperature of SOFCs with proton-conducting electrolytes (400–700 °C). Nevertheless, technology of SOFCs fabrication includes high temperature processing and, therefore, investigation of chemical compatibility of SOFCs materials stays actual. The aim of the present work is to study the processes of cation inter-diffusion at the $\text{RBaCo}_2\text{O}_{6-d}$ ($\text{R} = \text{Gd}, \text{Pr}$) | $\text{BaCe}_{0.7}\text{Zr}_{0.1}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-d} + 1 \text{ wt. \% NiO}$ interphases as well as electrochemical properties of the cathode materials.

Chemical compatibility of the $\text{RBaCo}_2\text{O}_{6-d}$ ($\text{R} = \text{Gd}, \text{Pr}$) cathode materials and the $\text{BaCe}_{0.7}\text{Zr}_{0.1}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-d} + 1 \text{ wt. \% NiO}$ proton-conducting electrolyte was investigated by calcining physical mixtures of powders (50:50 wt. %) at temperature range 1100–1250 °C with following phase identification by X-Ray diffraction analysis.

Cation inter-diffusion was studied by diffusion couple method. The oxides were prepared in the form of ceramic pellets and fixed as diffusion pairs cathode | electrolyte in special device. For each pair was performed two independent experiments: at 1100 °C during 20 h and 1200 °C during 48 h. The microstructure and element distribution at cross section of the diffusion couples after annealing were identified by scanning electron microscopy with VEGA 3 microscope (Tescan, Czech Republic) equipped with detector for energy dispersive X-ray spectroscopy.

The area specific resistance (ASR) of the $\text{RBaCo}_2\text{O}_{6-d}$ ($\text{R} = \text{Gd}, \text{Pr}$) cathodes was measured by means of impedance spectroscopy method with Z500-PX (Elins, Russian Federation) impedance analyzer. The experiment was carried out at 10 Hz–0.5 MHz and 550–700 °C frequency and temperature ranges, respectively. The impedance spectra were analyzed with ZView 2.0 software.

As a result of work, methods for reducing of negative influence of cation inter-diffusion at the $\text{RBaCo}_2\text{O}_{6-d}$ ($\text{R} = \text{Gd}, \text{Pr}$) | $\text{BaCe}_{0.7}\text{Zr}_{0.1}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-d} + 1 \text{ wt. \% NiO}$ interphases were proposed.

This work was supported by State Assignment № 123031300049-8.

STUDY OF SOLID SOLUTIONS $K_{2-x}Cs_xZn_3(P_2O_7)_2$

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Diphosphates are often characterised by a rather high "flexibility" of structure due to changes in the orientation of P_2O_7 dimers, which leads to frequent polymorphism and wide isomorphic substitutions in the crystal lattice. This makes them interesting objects to investigate the relationship between crystal structure and functional properties.

In the system $K_2Zn_3(P_2O_7)_2 - Cs_2Zn_3(P_2O_7)_2$, solid solutions $K_{2-x}Cs_xZn_3(P_2O_7)_2$ were obtained by solid-phase reactions. It has been shown by X-ray phase analysis methods that solid solutions with $0.4 \leq x \leq 0.6$ are formed on the basis of a crystal structure that is isostructural to $Rb_2Zn_3(P_2O_7)_2$ (phase I), and in the range $1.4 \leq x \leq 2.0$ on the basis of the structure of $Cs_2Zn_3(P_2O_7)_2$ (phase II).

The obtained solid solutions are not isostructural, however, they have very similar structural bases and their space groups are also related by crystallographic group-subgroup relations: $P2_1$ for phase I and $Rb_2Zn_3(P_2O_7)_2$, and $P2_1/c$ for phase II and $Cs_2Zn_3(P_2O_7)_2$. Both of the above solid solutions contain a $[Zn_3(P_2O_7)_2]_\infty$ framework consisting of P_2O_7 groups connected by angles to six ZnO_4 tetrahedra in the cavities of which two crystallographically independent alkali metal cations (hereinafter referred to as M) are located. In phase I, both alkali cations are 9-coordinated with O atoms, and their polyhedra, joining along the edges, form $[MO_9]_\infty$ chains. Phase II is characterised by the presence of MO_9 and MO_{12} polyhedra, which join together to form a three-dimensional framework.

For the discovered crystalline materials one of the most interesting directions of use, as well as for related compounds^{1,2}, is the creation of luminophores and other optical materials transparent in the UV range on their basis.

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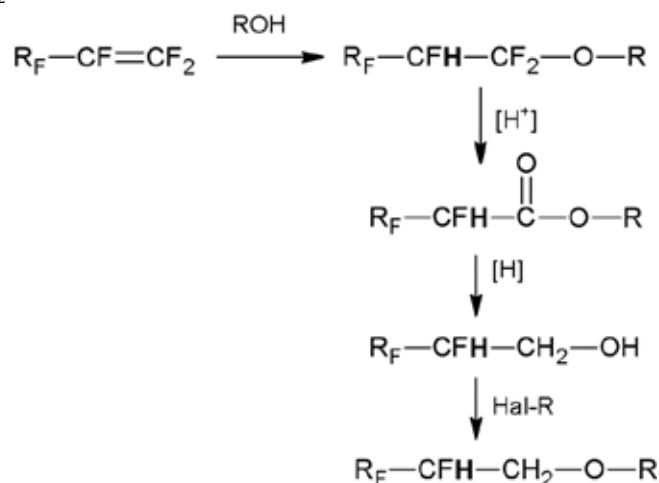
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THE USE OF PERFLUORALKENES IN THE SYNTHESIS OF FLUORINATED ETHERS

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Fluorine-containing compounds are widely used to obtain products with valuable properties. Partially fluorinated ethers take a special place among such substances. Promising areas of application of fluorinated ethers include the field of fluorous chemistry, covering fluorous biphasic catalysis and fluorous biphasic separation¹. The use of calculation methods makes it possible to show the relationship between the structure and properties of studied compounds. Reliability of projection of properties is ensured by a sufficient amount of experimental data². The study of polyfluoroalkylethyl ethers allowed us to establish a linear relationship of phase characteristics (fluorous partition coefficients (*P*) and fluorophilicity (*f*) in a series of CF₃- and HCF₂-terminal homologs³.



This work shows the possibilities of using perfluoroalkenes in the synthesis of ethers with different fluorine contents with the aim of further studying their phase parameters using chromatographic analysis methods.

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PRODUCTION OF ULTRA-THIN HYBRID MATERIALS BASED ON PLANAR INORGANIC PARTICLES AND POLYDIACETYLENE DERIVATIVES FOR ORGANIC ELECTRONICS

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Nowadays, more and more attention of researchers in the field of organic electronics is paid to projects aimed at reducing the cost of devices, increasing their lifetime and resistance to external negative influences, as well as minimizing the negative impact on the environment while maintaining high efficiency. Some of the most promising materials for solving the problems of modern organic electronics are considered to be hybrid materials, which combine in a single structure mechanical and semiconducting properties of inorganic particles and high conductive properties of organic polymers. However, there is still a need to create new approaches to obtain ultrathin flexible coatings, opening up the possibility of creating flexible thin-film devices of new generation.

In this work, three types of inorganic matrices have been used: 2D particles of Graphene Oxide (GO), molybdenum sulfide MoS_2 , and a mixture of these particles. These components were chosen due to their excellent semiconducting, mechanical and surface properties, as well as the simplicity of their preparation. 10,12-pentacosadiynoic acid (PDA) was chosen as the organic constituent of the system. In order to obtain ultrathin coatings of GO/PDA and MoS_2 /PDA, it is necessary to have methods available to obtain ultrathin films with a molecularly controlled structure. In this work, a simple method for the preparation of ultrathin hybrid materials based on monolayer GO and MoS_2 and PDA particles was proposed. For this purpose, GO/PDA and MoS_2 /PDA adsorption layers were vertically transferred onto an indium tin oxide (ITO) glass substrate using an automatic dipper. According to atomic force microscopy data, the thickness of such coatings is 5-10 nm. The obtained hybrid coatings were integrated into electronic cells with the architecture of glass+ITO/hybrid coating/ C_{60} /BCP/Al, with subsequent study of their electrophysical properties.

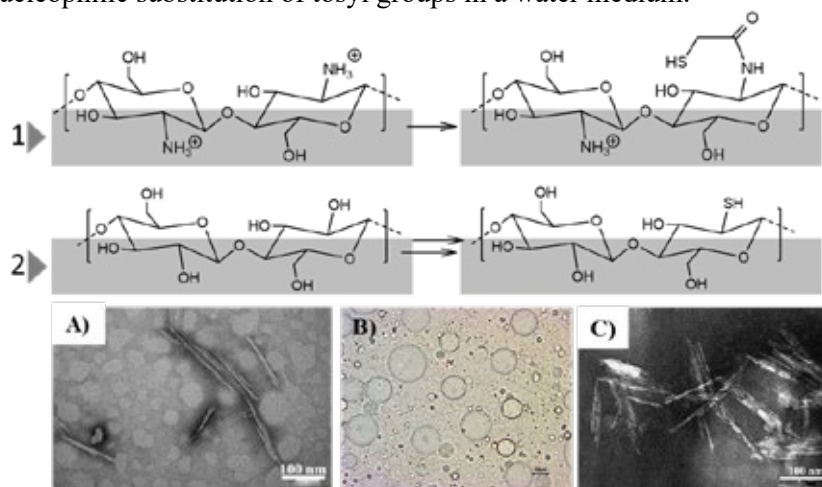
In the future, it is planned to study the possibility of obtaining multicomponent systems using other planar inorganic particles such as carbon nitride (C_3N_4), boron nitride (BN) and others.

CHITIN AND CELLULOSE NANOCRYSTALS MODIFIED BY THIOL GROUPS

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Polysaccharide nanocrystals are actively used in the field of creating new materials and designing systems assembled from nanoscale elements. Nanocrystals with a surface modified by thiol groups, like "thiomers," are promising for the development of mucoadhesive, sorbents, and drug delivery. The surface of chitin nanocrystals (ChNC) and cellulose nanocrystals (CNC) with an average size of 6 nm × 150 nm (micrographs A, B) is modified with thiol groups. Carbodiimide-activated fragments of thioglycolic acid or N-acetylcysteine have been used to modify ChNC in water media (1). Modification of CNC (2) was carried out sequentially by synthesis of tosylates in an emulsion medium (emulsion micrograph, C) and then nucleophilic substitution of tosyl groups in a water medium.



As a result of transformations, nanocrystals retain their morphology, size and supramolecular structure. It has been shown that SH-groups on the surface of nanocrystals are partially oxidized and are included in a dense network of hydrogen bonds. The rheological properties of SH-nanocrystal hydrosols are close to the properties of parent particles hydrosols; the addition of H₂O₂ at neutral pH values leads to a change in the viscosity of the system. SH-nanocrystals have a high ability to sorption of Cr (VI) in acidic media and are sensitive to UV irradiation.

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PREPARATION OF CARBOXYLATED POLYSTYRENE MICROSPHERES UNDER MICROFLOW CONDITIONS

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Polystyrene microspheres (PM) are widely used to detect the protein composition of biological samples by multiplex assay. PM suitable for this method must be monodisperse and contain functional groups on the surface to bond covalently antibodies and fluorescent labels. To prepare carboxylated PM a copolymer of styrene with unsaturated acrylic or methacrylic acids is used. Traditional polymerization methods of PM preparation often lead to high polydispersity of PM, which requires long-term optimization of synthesis parameters. In contrast, PM preparation under microflow conditions makes it possible to solve these problems through precision control of synthesis parameters as well as to reduce the consumption of reagents.

The aim of this study is to develop a method of preparation narrowly dispersed carboxylated PM with an average size of 5-6.5 μm under microflow conditions. The influence of the flow rate ratio of continuous and dispersed phases (CP / DP), the content and structure of acids (acrylic and methacrylic) in DP on the main characteristics of PM, including size, polydispersity (CV) and the content of -COOH groups were studied while the method of producing PM were developed. A T-shaped chip with a channel width of 100 μm was used as a flow reactor.

As a result of the study, it was established that a decrease in size of PM was caused by an increase in the CP / DP ratio from 75 to 200. Under these conditions, carboxylated PM were obtained in the size range from 19.5 to 3.7 μm and CV from 7.7 to 2.2 %. An increase in the CP / DP ratio above 200 was critical for the formation of PM. The decrease of the content of -COOH groups on the PM surface from 0.1444 to 0.1225 $\mu\text{mol/mg}$ was observed when the PM size decreased from 19.5 to 3.7 μm . observed. The use of more hydrophobic methacrylic acid as a co-monomer made it possible to increase the content of -COOH groups on the surface to 0.1560 $\mu\text{mol/mg}$. Thus, microspheres obtained from a copolymer of styrene with methacrylic acid within the CP / DP ratio of 166 with an average size of 6.2 μm , CV of 3.1%, and a content of -COOH groups of 0.1560 $\mu\text{mol/mg}$ can be used in multiplex assay.

HIGH ENTROPY PEROVSKITE-LIKE OXIDES WITH COMBINATION OF DIFFERENT VALENCY CATIONS

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High-entropy ceramic materials are characterized by being solid solutions with a unified crystal lattice, having a mixing entropy surpassing $1.5R$. Beyond the threshold of $1.5R$, the entropy component outweighs the enthalpy contribution in solid solution formation, resulting in the entropic stabilization of the material. The mixing entropy (S_{mix}) is computable as¹:

$$S_{mix} = \sum_{i=1}^n x_i \cdot \ln x_i \quad (1)$$

Where x_i – atomic fraction of i-th cation.

High-entropy compounds, including ceramics, boast a range of advantages such as low thermal conductivity, enhanced mechanical properties, inhibition of grain growth at elevated temperatures, enhanced thermal and corrosion resistance, and more².

Initially, the key requirement for creating high-entropy compounds was the utilization of cations with closely matched ionic radii and valences. However, recent studies have demonstrated that employing metals with varying oxidation states can serve as an additional stabilizing factor in the synthesis of these compounds³. Nevertheless, the impact of combining different valence cations on the structure and attributes of high-entropy compounds remains a subject of inquiry.

Taking the example of complex perovskite-like oxides such as $\text{SrM}_{0.2}\text{W}_{0.2}\text{Nb}_{0.2}\text{Ti}_{0.2}\text{Ni}_{0.2}\text{O}_3$, where M could stand for Fe or Mn, exhibiting a tetragonal crystal lattice of the $I4/m$ type akin to $\text{Sr}_2\text{CrTaO}_6$, the distribution of cations in the B-sublattice positions was refined. The analysis uncovered a distinct pattern of ordering within these perovskite-like oxides resembling the rock salt structure: titanium and tungsten occupy a specific position, while iron (or manganese) and nickel occupy another, with niobium evenly spread across the positions. This observation indicates the potential for structural ordering in highly entropic compounds.

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LIPID NANOCARRIERS FOR THERAPY OF ACUTE ORGANOPHOSPHATE POISONING

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Highly toxic organophosphorus compounds (OPs), such as chemical warfare agents and pesticides, are considered as one of the major threats to human health. The acute toxicity of these compounds is caused by the disruption of the catalytic activity of the crucial enzyme acetylcholinesterase (AChE). Limited penetration of AChE reactivators, such as pralidoxime chloride, through the blood-brain barrier significantly reduces the effectiveness of treatment for OP poisoning. To solve this problem a novel strategy has been proposed that involves the development of nanoscale carriers for intranasal administration of pralidoxime chloride into the brain. Liposomes have great potential due to their low toxicity, biodegradability, biocompatibility, etc. To adapt liposomes for delivery from the nose to the brain, we propose a supramolecular approach that involves non-covalently modifying liposomes with polymers and cationic surfactants.

Various physicochemical analyses were conducted on the nanocontainers obtained, including assessment of morphology, size, charge, stability and release rate. Biological studies were also conducted *in vitro* (cytotoxicity, hemolysis and hemagglutination), as well as *in vivo*. The results showed that lipid formulations had high stability high encapsulation efficacy and a prolonged release of the substrate. Intranasal administration of nanocontainers led to their effective penetration into the rat brain, as demonstrated by photographs of rat brain sections. *In vivo* tests will be performed on the leading systems in order to evaluate the efficacy of oxime therapy using a model of paraoxon-induced rat poisoning.

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HIGH-PURITY METALORGANIC COMPOUNDS FOR MICROELECTRONICS: SYNTHESIS AND QUALITY CONTROL

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Manufacturing of a number of key components of modern microelectronics (microprocessors based on transistors with reduced topological norms, new types of non-volatile memory elements) require a material base of high-purity substances (5-6N), including volatile metalorganic compounds (MOCs). As a rule, the range of such MOC currently produced in the Russian Federation is limited and/or does not guarantee the required purity.

This work is aimed at creating laboratory methods for the synthesis and analytical control of high-purity MOCs for the deposition of dielectric layers (hafnium, zirconium, titanium oxides) and metallization (copper, ruthenium, cobalt). The most popular MOCs were selected as the “basic” objects of study: cyclopentadienyl and/or amide derivatives ($\text{CpZr}(\text{MMe}_2)_3$, $\text{Ti}(\text{NMe}_2)_4$, $\text{Zr}(\text{NMe}_2)_4$, $\text{Hf}(\text{NMeEt})_4$, $\text{Ru}(\text{EtCp})_2$, $\text{Co}(\text{Cp})_2$) and copper acetylacetonate ($\text{Cu}(\text{acac})_2$). Based on the analysis of thermal properties, alternative promising and available MOCs have been proposed, for example, copper methyliminoacetylacetonate ($\text{Cu}(\text{Mei-acac})_2$) and M(IV) carboxyamides.

Informative and rapid methods of atomic emission and mass spectral analysis with inductively coupled plasma have been developed, which make it possible to determine impurities of 54 elements in M(IV) and Cu MOC at the purity level of 5N and 6N. The purity of the obtained laboratory batches of the considered MOC (20 g) was $\geq 5\text{N}$, that exceeds that for domestic commercial samples (2-4 N). The model thermal cycling of the most chemically active MOC, $\text{Ti}(\text{NMe}_2)_4$, has shown that after 0.5 years of storage in standard borosilicate glass, the qualification of the sample reduce from 5N8 to 5N. Analysis of the literature and our own data on the thermal properties of MOC made it possible to identify the temperature limits for deposition and vaporization during further preparation of thin-films for microelectronics through vapor-phase deposition methods.

The work was carried out with the financial support of the Ministry of Science and Higher Education of the Russian Federation, state assignment 122111500007-6.

CRYSTAL STRUCTURE AND PROPERTIES OF OXIDES IN THE $\text{PRCOO}_{3-\delta}$ - $\text{PRFeO}_{3-\delta}$ - $\text{BACOO}_{3-\delta}$ - $\text{BAFeO}_{3-\delta}$ SYSTEM

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Perovskite-type oxides $\text{ABO}_{3-\delta}$ (where A is rare earth or alkaline earth element, and B is transition metal) have attracted significant attention due to potential applications in solid oxide fuel cells (SOFCs), as ceramic membranes for high temperature oxygen separation and as oxygen evolution reaction [11]. In the case of the $\text{SrMO}_{3-\delta}$ ($M = \text{Fe}, \text{Co}$) oxides, a number of phases with various crystal structures were reported depending on the annealing conditions or hence on the oxygen content. In this work, we report on the influence of A- and B-site substitutions in $\text{SrFeO}_{3-\delta}$ by Pr and Co, respectively, ($\text{Sr}_{1-x}\text{Pr}_x\text{Fe}_{1-y}\text{Co}_y\text{O}_{3-\delta}$) on crystal structure and oxygen content and properties for samples all prepared in air at 1100 °C.

A series of $\text{Sr}_{1-x}\text{Pr}_x\text{Fe}_{1-y}\text{Co}_y\text{O}_{3-\delta}$ were synthesized by the glycerin nitrate technique. Final annealing was performed at 1100 °C in air for 120 h, employing several steps (the duration of about 20 h each) with intermediate grinding, followed by a slow cooling down to room temperature at the rate of about 100°/h. Phase identification was performed by X-ray diffraction (XRD) at room temperature in air. According to X-ray diffraction data, it was established that the homogeneity range of $\text{Sr}_{1-x}\text{Pr}_x\text{Fe}_{1-y}\text{Co}_y\text{O}_{3-\delta}$ solid solutions significantly depends on the metal content in the A and B sublattices.

The changes of oxygen content in the $\text{Sr}_{1-x}\text{Pr}_x\text{Fe}_{1-y}\text{Co}_y\text{O}_{3-\delta}$ solid solutions were measured by thermogravimetric analysis as a function of temperature and oxygen partial pressure. The absolute value of oxygen content in the samples was determined using a direct reduction of the samples in the TG cell by hydrogen and red-ox titration. An introduction of lanthanide into the strontium ferrite increases the oxygen content.

Total conductivity and Seebeck coefficient of solid solutions were measured simultaneously using a 4-probe technique versus temperature in air. The temperature dependencies of total conductivity of all samples possess a maxima at approximately 350°C. At higher temperature the total conductivity of material decreases with temperature rise. Seebeck coefficient for all compounds reveals positive values within the entire temperature and oxygen partial pressure ranges that indicate predominant *p*-type conductivity.

This work was prepared within the framework of the budgetary plans of the Hydrogen Energy Laboratory (Ural Federal University).

POLYMORPHISM AND MAGNETIC PROPERTIES OF HALOGENIDES OF 4d- AND 5d-METALS

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In modern physics of condensed state, the study of the properties of van der Waals magnetics is of great interest. According to the Mermin-Wagner theorem, 2D and 1D Heisenberg systems cannot be ordered at finite temperature. Discussions on the formation of the magnetically ordered state in recent works on van der Waals magnetics are related to the establishment of the role of anisotropy, which shifts the focus of interest from 3d-metals to representatives of 4d- and 5d-metals. However, many such van der Waals systems, such as MoS_2 and WSe_2 , have been found to be non-magnetic. The rare cases of magnetic response in compounds with 4d- and 5d-metals are mainly related to an odd number of electrons on the 4d/5d-metals or clusters.^{1,2} For example, authors of paper³ show that chlorides with the dimeric structure of α - and ϵ - MoCl_5 exhibit ferromagnetic ordering at low temperatures, while antiferromagnetic ordering is observed for WCl_5 .

The present work presents the synthesis and investigation of thermodynamic properties of a number of representatives of van der Waals magnetics with dimeric, chain and ladder structures: tungsten(V) bromide WBr_5 ,⁴ rhenium(V) chloride ReCl_5 ,⁵ osmium(IV) chloride OsCl_4 and molybdenum(V) oxobromide MoOBr_3 and others, exchange interactions in which exchange interactions are due to both intramolecular interactions and intermolecular interactions via halogen bonds. For halides WBr_5 and ReCl_5 structural phase transitions have been investigated.

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THE EFFECT OF THE CONDITIONS OF THE REACTION OF REDUCTION OF POTASSIUM ZIRCONIUM FLUORIDE WITH METALLIC SODIUM.

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Sodium-reduced zirconium powders have high chemical stability, strength and heat resistance, which makes them ideal for use in pyrotechnics. They can be used as the main component in powder charges for small arms, flares, pyrotechnic fireworks and other products.

The main problem in obtaining zirconium powders is the low reproducibility of the main characteristics of the product. Previous researchs^{1,2} have established the effect of the size of the initial components on the quality of the resulting powder. In current studies, the relationship between the reaction temperature, the duration of exposure of the product at reaction end temperatures and the granulometric composition, as well as the active zirconium in the mixture, has been established. In addition, the morphology of the surface of the obtained powders was studied.

Experiments on the production of zirconium powder were carried out both in air and in an inert argon atmosphere and in vacuum. The ratio of components, the presence of sulfur and phosphorus additives also varied widely, and the effect of the phase state on the resulting product was studied. Such a large-scale study allowed us to assume the reaction mechanism, take into account the dependence of the characteristics of the resulting product on the conditions and temperature of the reaction, and at the same time determine the necessary parameters for obtaining sodium-reduced zirconium powders.

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PHASE EQUILIBRIA IN THE Ag–In–Pd–Sn SYSTEM

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Intermetallic compounds of palladium with indium, tin, and silver, on the one hand, exhibit high efficiency as catalysts¹. On the other hand, their formation in lead-free solder applications can seriously compromise the mechanical and electrical properties of the chip solder joints². In both instances, information on the conditions for formation, stability, and crystal structure of these intermetallic compounds is crucial.

Phase equilibria in the Ag–In–Pd–Sn quaternary were studied at 500 and 800 °C. The samples were synthesized from high-purity metals and annealed in evacuated quartz ampoules for 1000 to 2000 hours, depending on the composition and temperature. The annealed samples were examined using scanning electron microscopy (SEM), energy dispersive X-ray (EDX) analysis and X-ray diffraction (XRD).

As a result of our research, we have established the concentration limits for a solid solution based on face-centered cubic (FCC) components at both temperatures. Isostructural ternary compounds of the Ag–In–Pd, Ag–Pd–Sn, and In–Pd–Sn boundary systems having structural type Al_3Ti form a single-phase region in the quaternary. Silver practically does not dissolve in a solid solution of isostructural compounds $InPd_2$ and Pd_2Sn (structural type Co_2Si). The homogeneity region of the phase based on the $InPd$ compound (structural type $CsCl$) in the quaternary decreases sharply with increasing tin content.

In the course of the study of phase equilibria in the Ag–In–Pd–Sn quaternary a new ternary compound $Pd_3In_{1+x}Sn_{1-x}$ was found in the In–Pd–Sn boundary system at both temperatures. This phase occurs at 60 at. % Pd and a tin content of 12 to 20 at. %. It crystallizes in hexagonal syngony.

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HIGH-TEMPERATURE MODIFICATIONS AND OXYGEN NONSTOICHIOMETRY OF TERBIUM-BARIUM COBALTITE

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Double perovskites with general formula $\text{RBaCo}_2\text{O}_{6-\delta}$, where R is rare-earth metal, are objects of numerous studies. Mentioned oxides are perspective materials for creation of cathodes of solid oxides fuel cells. Present work is dedicated to study of crystal structure and oxygen nonstoichiometry of terbium-barium cobaltite $\text{TbBaCo}_2\text{O}_{6-\delta}$.

Complex oxide was synthesized using a standard ceramic technique. Tb_4O_7 , BaCO_3 and Co_3O_4 were used as starting materials. Attestation of synthesis product and its high-temperature modifications nature were studied by using an X-ray diffraction. Temperatures of terbium-barium cobaltite phase transitions were determined by using a differential scanning calorimetry method. Oxygen nonstoichiometry of complex oxide was studied by using a thermogravimetric analysis method.

It was shown that synthesized terbium-barium cobaltite has an orthorhombic elementary cell with space group $Pmmm$. Stability studying of terbium-barium cobaltite allowed to conclude that complex oxide is kinetically stable at temperatures lower than 600 °C and thermodynamically unstable at 800 °C. First-order phase transition at 70 °C in air atmosphere for terbium-barium cobaltite was described. It's accompanied by change of sample's volume and electrical conductivity. Space group of complex oxide does not change. At 390 °C in air atmosphere orthorhombic $Pmmm$ modification of terbium-barium cobaltite transforms in tetragonal $P4/mmm$ modification. The last one phase transition is accompanied by change of sample's volume and oxygen content in oxide. Temperature of described phase transition decreases with partial oxygen pressure in atmosphere decreasing.

Equilibrium $\delta - p\text{O}_2 - T$ diagram for terbium-barium cobaltite was obtained. Defect structure of complex oxide was suggested for describing experimental data. Model is based on oxygen exchange between oxide and atmosphere reaction and Co^{3+} disproportionation reaction. Thermodynamic functions of mentioned reactions were determined as a result of model equation verification. Suggested model describes experimental data pretty good ($R^2 = 0.990$).

SYNTHESIS OF TARGETED LIPID BASED ON FOLIC ACID

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The use of non-selective methods of cancer treatment leads to a negative effect on healthy human cells. Therefore, there is a need to develop selective methods, such as gene therapy, which is based on the introduction of therapeutic nucleic acids (TNA). For their delivery, various delivery systems are used, including cationic liposomes (CL).

CL have the following advantages: similarity to the chemical composition of cell membranes, low cytotoxicity, the ability to vary sizes, low immunogenicity, and biodegradability. However, they have low transfection activity. To increase it, a targeted lipid is added to the composition of CL, which makes them targeted to certain types of cells.

It is known that aggressive or undifferentiated tumors at advanced stages have an increased density of folate receptors, which makes it possible to selectively deliver TNA to tumor cells¹. To do this, it is necessary to modify the CL surface with a lipophilic derivative of folic acid. In this work, we have obtained a targeted lipid based on folic acid.

The synthesis was carried out in several stages. First, dimyristylglycerol was prepared from commercially available allylglycerol. Next, polyethylene glycol-containing lipid was prepared according to a previously described method². A folic acid molecule was then introduced at the terminal amino group in the presence of activating agents, resulting in the target compound.

Overall, a targeted lipid was obtained, which will be used to form CL with subsequent study of the physicochemical characteristics and efficiency of TNA delivery.

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The work was carried out with the support of the Innovation Promotion Fund under the UMNII program under contract 17456FY/2022 dated 26.04.2022

PREPARATION OF NEW SURFACE MODIFIED PARTICLES BASED ON POLYANTIMONIC ACID

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One of the promising trend in researching composite membranes is to improve properties of nanoparticles included in them by modifying their surface. The effect of doping of heterovalent ions on the proton conductivity of inorganic particles is reported in literature. At the same time, issues related to the surface of particles and interphase boundaries do not completely meet appropriate attention. In this regard, it is of interest to modify the surface of particles by co-crystallization of various phases and to study the proton conductivity of the resulting systems.

To carry out these studies, we chose polyantimonic acid (PAA), which has proton conductivity and is capable to accomplish co-crystallization with hydrated oxides (HO). The samples were prepared by turn co-crystallization of PAA and HO precursor salts. They have the form of a white dispersed powder with an average particle size of 100 nm.

The structure investigations of the samples obtained, their thermal stability, morphology and proton conductivity revealed that the symmetry of the crystal lattice does not change with the surface modification of particles and corresponds to a pyrochlore-type structure $sp.gr.symm.Fd3m$. Whereas, a change in the unit-cell parameter is observed, as well as in temperatures corresponding to the removal of gaseous products during PAA thermolysis. The electron microscope images show the areas of the formation of shells around PAA particles that differ in composition from the core itself. Issues related to the influence of particle modification on the proton conductivity of PAA have been discussed in this report.

The work was carried out with the financial support of the Russian Science Foundation No. 23-23-00140

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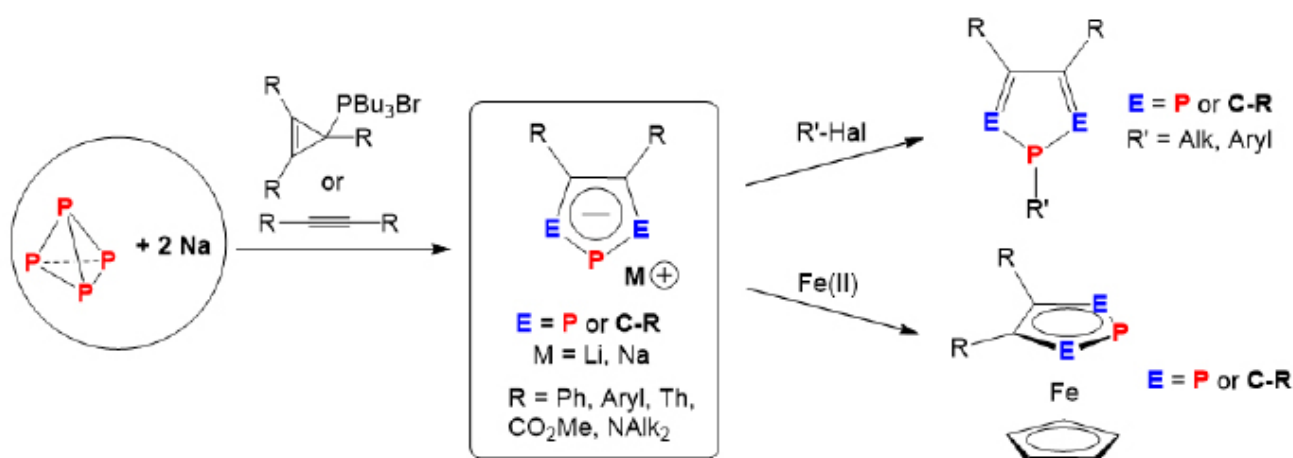
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PHOSPHACYCLOPENTADIENIDE ANIONS – BUILDING BLOCKS FOR ORGANOPHOSPHORUS CHEMISTRY

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Phosphacyclopentadienide (phospholide) anions and their derivatives are very attractive as building blocks for the construction of versatile organophosphorus molecular materials with useful and interesting catalytic, optical, luminescent, and magnetic properties.¹ Therefore, development of convenient methods for the straightforward synthesis of these phosphorus heterocycles and their derivatives through functionalization of elemental phosphorus P_4 has a significant interest.² This lecture features recent advances on the synthesis of various phosphacyclopentadienide anions and their chemical behavior toward organic substrates and transition metal complexes.



A rational and highly efficient method to access 1-mono-,³ 1,2-di-⁴ and 1,2,3-triphospholide⁵ anions in individual forms directly from white phosphorus P_4 , alkali metals and small molecules (alkynes and cyclopropenyl cations) have been developed. Interaction with various chiral and non-chiral alkyl halides has resulted in the formation of novel *P*-heterocycles, namely 1-mono-, 1,2-di- and 1,2,3-triphospholes. Reaction with iron(II) complexes was used as a convenient way for an efficient synthesis of a number of new phosphapherrocenes.⁶ First results on the application in materials science and homogeneous catalysis of phospholide derivatives (phospholes and their [4+2] cycloadducts) were also reported.⁷

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MUTUAL INFLUENCE OF SURFACTANTS AND NANOPARTICLES OF DIFFERENT NATURE IN AQUEOUS DISPERSIONS

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Surfactant-modified nanoparticles are a highly promising area of research for developing effective reagents for enhanced oil recovery. Nanoparticles, in the presence of surfactants, form stable dispersions and adsorb onto the oil reservoir, altering its wettability and significantly enhancing oil recovery.

In the study we analyzed surfactants of various types, including anionic (sodium dodecyl sulfate or SDS), cationic (cetyltrimethylammonium bromide or CTAB), nonionic (Tween 80), and amphoteric (cocamidopropyl betaine), in conjunction with three types of nanoparticles: Al-O (a mixture of Al, γ - Al_2O_3 , and spinel), Ti-O (a mixture of rutile and Magnelli phases) produced through plasma dynamic synthesis, and carbon nanoparticles (C-NPts) obtained through plasma treatment of technical asphalt. Also, we determined the impact of surfactant on nanoparticle dispersion stability through dynamic and electrophoretic light scattering methods by measuring the particle size and zeta potential, respectively. Conductometry and tensiometry were used to examine critical micelle concentration and interfacial tension at the n-hexane interface, respectively.

It was shown that micellar solutions of SDS and CTAB are promising for stabilization of Al-O nanoparticles and C-NPts in aqueous dispersions, as they promote the formation of particles with a zeta potential of $\sim |80|$ mV. Ti-O nanoparticles form stable aggregates of 270-300 nm in 10-50 mM CTAB.

Hydrophobic interactions between the surfactant tails and the surface of nanoparticles are assumed to determine the stabilization of C-NPts in surfactant solutions. Conversely, the stabilization of Al-O and Ti-O oxide nanoparticles is determined by the intrinsic charge of their surface. Electrostatic interactions cause adsorption when the surface of nanoparticles and ionogenic surfactant have opposite charges.

The work was financially supported by RSF, project 22-13-20016.

POLYCARBOSILANES AND COMPOSITE MATERIALS COMPONENTS BASED ON THEM

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The creation of new composite materials based on silicon carbide, serviceable for a long time in an oxidizing environment at temperatures up to 1500 °C. , is a challenge for promising products development for aircraft, nuclear technology and the automotive industry¹.

Polycarbosilanes (PCS) are pre-ceramic organosilicon poly(oligo)mers that are used to prepare components (fibers, matrices, binders, coatings) for the production of $\text{SiC}_f/\text{SiC}_m$, C_f/SiC_m composite materials (CM)².

The researches of GNIChTEOS have developed methods for the synthesis of PCS² and MPCS modified with compounds of refractory metals (Zr, Hf, Ta)¹ or compounds of aluminum and yttrium³. It has been found that the resulting PCS and MPCS are suitable not only for the production of SiC ceramics, but also have fiber-forming properties and are suitable for melt spinning and production of SiC fibers⁴.

PCS and MPCS were processed into polymer fibers by melt spinning and cured in an air atmosphere at temperatures up to 220 °C. Coreless ceramic SiC fibers were prepared by subsequent pyrolysis in vacuum or argon at temperatures up to 1100–1900 °C⁴.

SiC fibers were studied by SEM and X-ray phase analysis. The strength of the fibers reached 3200 MPa, the diameter of the fibers was in the range of 8-18 μm ⁵.

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MAGNETOMETRIC DETERMINATION OF DISTRIBUTION COEFFICIENT OF MAGNETITE NANOPARTICLES IN NON-MIXING LIQUIDS SYSTEM

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Magnetite nanoparticles (MNP) are being considered as a platform for drug delivery due to their biocompatibility, developed methods of synthesis and superparamagnetic properties which make possible determination of MNP in different media via magnetic signal and manipulation of them in organism by magnetic field. MNP are being modified in order to conjugate with biomolecules so their surface properties change, and so change their ability to penetrate tissues and cell membranes. Distribution coefficient of drugs in water-*n*-octanol system is important for understanding hydrophilicity/lipophilicity of both small and macromolecules and is used for simulation of their transfer through cell membrane but is infrequently applied for nanoparticles due to difficulties with their determination.

With the use of MPQ method (Magnetic Particle Quantification) developed at Biophotonics laboratory GPI RAS¹ we propose new technique of determination of MNP distribution coefficient in biphasic systems via magnetic signal. In this work we studied MNP distribution in water-non-polar liquid (1,2-dichloroethane, toluene, hexane, *n*-octanol) system.

With use of MPQ we have determined MNP distribution coefficient in non-mixing liquids systems that allows estimation of MNP penetration ratio through cell membrane or brain-blood barrier. Distribution coefficient of MNP depends on ζ -potential of their aqueous suspension, their surface functionalization and dielectric constant of organic phase.

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SYNTHESIS AND PROPERTIES OF NEW UPCONVERSION LUMINOPHORS $\text{Sr}_2\text{Y}_{8-X}\text{Yb}_Y\text{Ho}_X\text{Si}_6\text{O}_{26}$

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The report deals with new upconversion phosphors of the composition $\text{Sr}_2\text{Y}_{8-X}\text{Yb}_Y\text{Ho}_X\text{Si}_6\text{O}_{26}$ in the form of micro- and nanopowders, which we obtained for the first time by sol-gel method and by electron beam evaporation of targets from sintered microsamples. The nanopowders have an amorphous structure and an average size of ~26 nm. Stokes photoluminescence spectra showed that the transition from micro- to nanostate of the $\text{Sr}_2\text{Y}_{7.795}\text{Yb}_{0.2}\text{Ho}_{0.005}\text{Si}_6\text{O}_{26}$ sample results in an increase in intensity in the green region and a decrease in the red and IR regions. Presumably, this phenomenon is due to an increase in the population of ions at radiative levels with high energies. The anti-Stokes luminescence of micro- and nanopowders at different pumping powers with a 980 nm laser has been studied. It is found that this process is two-photon and when the sample transitions from micro- to nanoscale state, the efficiency of the anti-Stokes luminescence process increases. The colour of the luminescence becomes green.

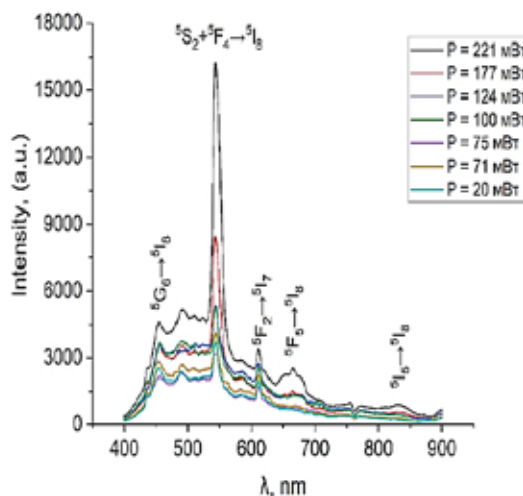


Figure 1. Antistokes photoluminescence spectrum of the nanoamorphic phosphor $\text{Sr}_2\text{Y}_{8-X}\text{Yb}_Y\text{Ho}_X\text{Si}_6\text{O}_{26}$ at different pump powers.

This work was carried out in accordance with the state assignment of IHTT Ural Branch of RAS No. 124020600004-7 and partially supported by RNF, project 22-19-00239.

ADSORPTION PERFORMANCE OF MAGNETIC CARBONACEOUS MATERIALS BASED ON BAU-A AND AG-3

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The approach of the magnetic carbonaceous materials preparation was suggested. It concerns the stages of iron (II) oxalate precipitation on the porous carbonaceous matrix and the salt decomposition in the products' atmosphere leading to magnetite formation. The magnetite obtaining was detected with X-ray diffraction method. The approach was tested using commercial activated carbons BAU-A and AG-3 as the porous matrixes.

The porous structure parameters (S_{BET} is specific surface area, V_{Σ} is total specific pore volume, V_{micro} and V_{meso} are specific volumes of micropores and mesopores respectively, D_{pores} is average diameter of the pores) determined with low-temperature nitrogen adsorption method as well as specific adsorptions of the benzene saturated vapors (A_{BSV}) and methylene blue from aqueous medium according to GOST 4453-74 (A_{MB}) for initial (BAU-A and AG-3) and prepared (BAU-A-M and AG-3-M) materials are shown in the table 1.

Table 1. Properties of the prepared magnetic carbonaceous materials

N	Sample	A_{BSV} , mg/g	A_{MB} , mg/g	S_{BET} , m ² /g	V_{Σ} , cm ³ /g	V_{micro} , cm ³ /g	V_{meso} , cm ³ /g	D_{pores} , Å
1	BAU-A	250	100	576	0.280	0.185	0.074	19
2	AG-3	185	152	621	0.317	0.129	0.067	20
2	BAU-A-M	230	68	426	0.282	0.132	0.134	26
3	AG-3-M	136	143	370	0.279	0.068	0.141	30

The adsorption isotherms of phenol and nitrobenzene were measured for both initial activated carbons and prepared magnetic ones. We arrived at the conclusion that adsorption performance of the activated carbons does not deteriorate significantly due to magnetite precipitation. Particularly, the methylene blue adsorption on AG-3 remains almost unchanged, the limit of phenol adsorption on the magnetic activated carbon BAU-A-M is 26% lower than on the initial BAU-A, the respective decreasing in the nitrobenzene adsorption limit is 34%.

INVESTIGATION OF THE PHOTOCATALYTIC PROPERTIES OF NANOSTRUCTURED Mn DOPED TiO₂

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Increasing the photocatalytic activity of titanium dioxide-based catalysts is important task of modern photocatalysis. One of the ways to increase the photoactivity of a material is modification of the structure with various cations, such as manganese.

The technique for obtaining nanostructured organic coatings was described in our earlier work¹. The following conditions were chosen to obtain doped coatings: voltage 30 V, anodizing time from 40 to 120 minutes, concentrations of Mn(NO₃)₂ in the electrolyte ranged from 0 to 1M. The heat treatment was carried out at a temperature of 400 °C for 1 hour with a heating-cooling rate of 1 °C/min in an air atmosphere.

The obtained samples were examined using scanning electron microscopy, X-ray spectrometry, and the incident photon-to-electron conversion efficiency (IPCE) was measured. Figure 1 shows the results of the IPCE - spectrometry, the properties of the coatings are confirmed by studies².

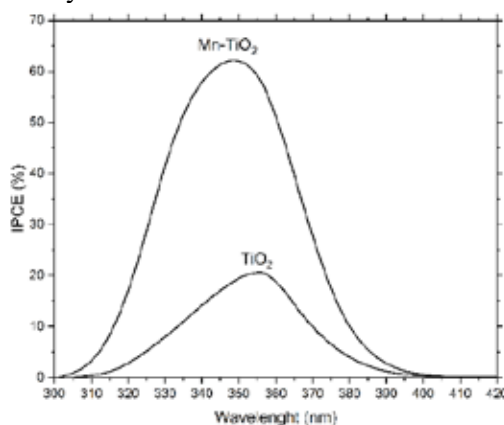


Figure 1 – Results of IPCE – spectrometry doped and undoped TiO₂

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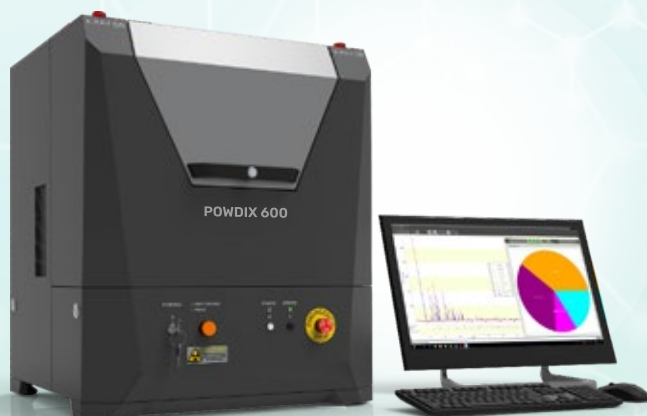
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Экологические проблемы планеты становятся все более значимыми и тревожащими, поэтому инновации, которые помогали бы эти проблемы решить, не просто привлекают интерес, а приобретают поистине глобальную актуальность. Сохранение окружающей среды и природных ресурсов для будущих поколений – суть новой этики прогресса.

ПРОГРЕСС, БЕЗОПАСНЫЙ ДЛЯ ПРИРОДЫ

Компания «ФосАгро» – лидер российской химической промышленности выступила с инициативой создания фонда для финансовой и научной поддержки перспективных ученых-химиков, в сферу интересов которых попадают охрана окружающей среды, здравоохранение, продовольствие, повышение энергоэффективности и рациональное использование природных ресурсов.

В 2013 году между ЮНЕСКО, Международным союзом теоретической и прикладной химии (IUPAC) и компанией «ФосАгро» было подписано соглашение о партнерстве в создании программы грантов для ученых, занимающихся так называемой «зеленой химией». Предметом этого направления в науке является создание производственных технологий и материалов, безопасных для природы и человека.

Так родился проект «Зеленая химия для жизни», помогающий талантливой молодежи не только материальными средствами для

продолжения исследовательской работы и реализации проектов, но и плодотворным общением со старшими коллегами – видными современными химиками, и организацией информационного обмена в научной среде. Это первый проект в истории ЮНЕСКО и ООН, реализуемый за счет средств российского бизнеса. ФосАгро выделила более \$2,5 млн на развитие и реализацию проекта.

ТРИНАДЦАТЬ МУДРЕЦОВ

Отбор заявок на участие в проекте – обязанность компетентного жюри, в которое входят 13 ученых из 11 стран. Проект-победитель должен соответствовать нескольким критериям. Оцениваются его научная новизна, глобальная и локальная значимость, соответствие принципам «зеленой химии», компетентность молодого ученого и его команды, оснащенность института и лабораторий, в которых предполагается вести проект. Качество работ очень высокое, и членам жюри приходится порой вступать в длительные диспуты по той или иной кандидатуре.

НАУЧНЫЙ ПОИСК БЕЗ ГРАНИЦ

В 2016 году был учрежден специальный грант за исследования в области применения фосфогипса. В 2019 году в штаб-квартире ЮНЕСКО в Париже в рамках открытия Года Периодической таблицы химических элементов было принято решение продлить грантовую программу «Зеленая химия для жизни».

Проблемы экологического характера, к сожалению, есть во всем мире, и во всем мире есть ученые, которые предлагают решения для многих из этих проблем методами и технологиями «зеленой химии». Это наглядно демонстрирует география проекта «Зеленая химия для жизни». За время реализации программы на рассмотрение жюри поступило более 1000 заявок, 55 грантов было присуждено молодым ученым из 33 стран. Самый главный результат грантовой программы – практическое применение разработок молодых исследователей.



ЖИЗНЬ ПОСЛЕ ГРАНТА

Дважды за первые 10 лет существования проекта победителями конкурса становились ученые из России. Одна из них – Галина Калашникова, заведующая лабораторией синтеза и исследования минералоподобных функциональных материалов Центра наноматериаловедения ФИЦ КНЦ РАН. В 2019 году грант «Зеленая химия для жизни» был присужден проекту «Разработка универсального и экологичного метода гранулирования синтетических титаносиликатных материалов (сорбентов, катализаторов, регенерируемых матриц), полученных на основе отходов региональных горно-обогатительных и металлургических производств».

Галина Калашникова:

– В рамках проекта удалось опробовать 5 разных методов грануляции для новых материалов с широким функционалом свойств (сорбенты, катализаторы для органического синтеза, керамические матрицы), которые мы синтезируем именно в нашей лаборатории. Мы смогли выбрать наиболее подходящий метод получения гранул для каждого из них, а также приоритетные нетоксичные связующие. Полученные гранулы были опробованы в качестве сорбентов для очистки жидких радиоактивных отходов от радиоизотопов 137-цезия и 90-стронция совместно с лабораторией хроматографии радиоактивных элементов и станцией переработки радиоактивных отходов Института физической химии и электрохимии им. А. Н. Фрумкина РАН.

Работа по проекту продолжается, несмотря на окончание действия гранта. Все полученные средства были потрачены только на выполнение основной задачи, благодаря чему мы приобрели необходимое оборудование, получили хороший опыт в работе с зарубежными коллегами и выстроили приоритетные направления дальнейшей совместной работы со многими научно-исследовательскими организациями.

Хочется пожелать организаторам конкурса еще больше новых проектов, которые были бы направлены на самые острые вопросы взаимосвязи экологии и современной промышленности.





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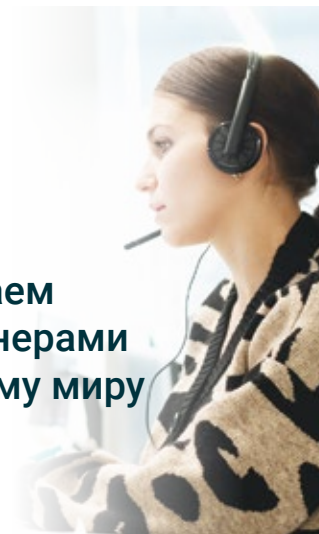
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