MSF'2022

MATERIALS SCIENCE OF THE FUTURE: RESEARCH, DEVELOPMENT, SCIENTIFIC TRAINING

5-7 APRIL, 2022, NIZHNY NOVGOROD, RUSSIA

ABSTRACTS

2022

International conference “Materials science of the future: research, development, scientific training (MSF’2022)” (5-7 April, 2022, Nizhny Novgorod, Lobachevsky University): Abstracts. – Nizhny Novgorod: Nizhny Novgorod University Press, 2022. – 153 pp.

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The subjects for discussion of the conference participants are the current state of affairs and development prospects in all areas of materials science; the training of highly qualified personnel; creation of closer consolidation of science, business and higher education for solving fundamental and applied problems.

Electronic version of the book can be found at:
http://www.materials-science.unn.ru/

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non multa, sed multum

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- Ferro-Piezoelectrics, Semiconductors, Superconductors, Environmental Materials, Composite, Ceramics, Thin Films, Nanomaterials, Advanced Materials for Additive Manufacturing, Metal Engineering Materials, Functionally Graded Materials etc.
- Powder Processing, Processing Technologies, Piezoelectric Technologies, MEMS-Processing, etc.
- Material Design, Microstructure Properties, Physical Properties, Mechanical Properties, Strength Properties, Finite-Element Modeling, Mathematical Modeling, Physical Modeling, Physical Experiment, etc.
- MEMS, Hetero-structures, Piezotransducers, Energy Harvesting, Superconductive Devices, Light-Emitting Diodes, Multimedia Communication, Fiber Reinforced Composites, Construction Health Monitoring, Lubricant and Tribology, etc.

Section 2
Chemistry of Materials

- Medical Materials, Nanotechnology
- Formation, structure and properties of solid-phase substances and materials
- Thermodynamic aspects of materials science
- Phase diagrams in materials science
- Synthesis of functional materials, CVD processes, plasma chemistry

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PLENARY LECTURES

Novel methods for predicting exotic compounds and new materials

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Until mid-2000s it was thought that crystal structures are fundamentally unpredictable. This has changed, and a special role in this was played by our evolutionary method/code USPEX (http://uspex-team.org). This method can be viewed as a type of artificial intelligence, and routinely allows one to predict stable crystal structures for a given chemical composition], predict all stable compounds formed by given elements, and even predict among all possible compounds the structure and composition that have desired combination of properties. Here I will discuss:

1. Discovery of novel chemical phenomena at high pressure: transparent non-metallic allotrope of sodium, counterintuitive novel sodium chlorides, chemical reactivity of helium, prediction and discovery of new high-temperature superconducting polyhydrides, approaching room-temperature superconductivity.
2. Recent extension of crystal structure prediction to finite temperature, and first results.
3. Development of coevolutionary methods – COPEX (to predict all stable compounds in very complex systems) and Mendelevian search (navigating the chemical space to find the material with desired properties).

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Combined method for precise electronic-structure modeling of compounds of lanthanides and actinides based on the compound-tunable embedding potential

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A combined method (periodic+cluster) for modeling materials using compound-tunable embedding potential (CTEP) [1-3], which is formulated on the basis of the generalized relativistic effective core potential (GRECP) theory [4], is discussed.

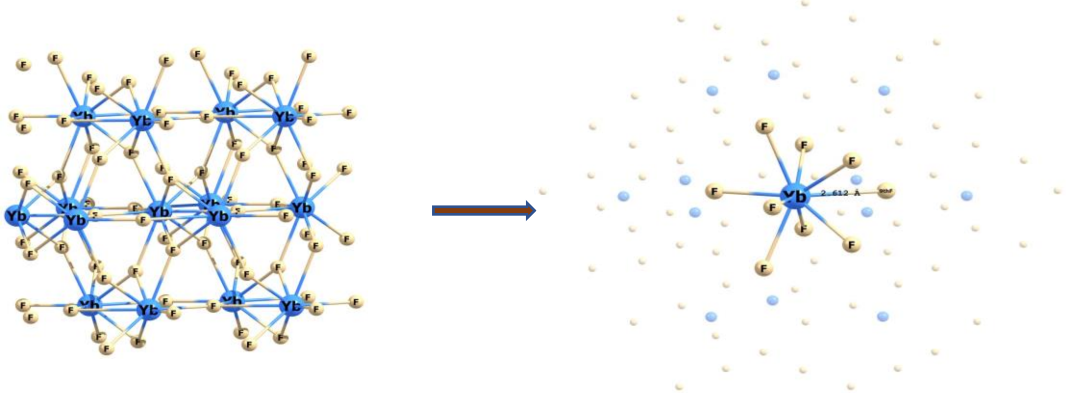
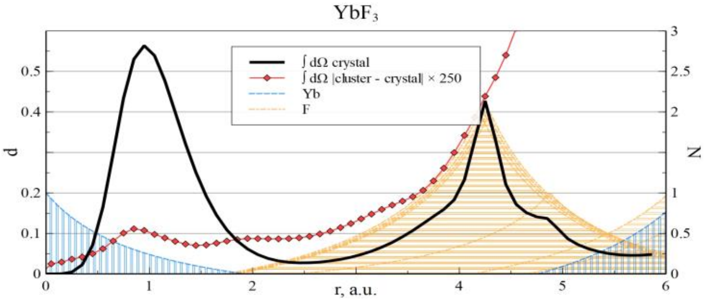


Fig. 1. Periodic study followed by cluster study with CTEP.

Prospects of this approach for studying materials both with point defects containing transition metals (*d*-elements), actinides & lanthanides (*f*-elements) [1–2] and with periodically arranged *d,f*-elements [3] are discussed as a tool for analyzing experimental data describing local characteristics of such materials [5-7], and for predicting the properties of materials at the level of accuracy of molecular studies.



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SECTION 1. PHYSICS OF MATERIALS

X-ray diffraction studies of single crystal triglycine sulphate deformation behavior under uniaxial compression

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Crystalline materials play an important role in the development of micro- and optoelectronic industry. The reliability of the devices depends on materials behavior under various influences, such as the temperature, vibrational and mechanical load, pressure, radiation exposure, etc. Previously, a method was developed to study the dynamics of the structure of crystalline materials with time resolution under conditions of external mechanical and ultrasonic effects using double-crystal X-ray diffractometry [1,2]. The technique proposed in this paper is for studying deformation characteristics and defect structure of single crystals under uniaxial compression using the X-ray diffraction topography (XRDT) with a laboratory X-ray source.

This technique is based on the registration of X-ray diffraction patterns in the transmission geometry using a two-dimensional detector during a controlled uniaxial mechanical load created with a compact hydraulic press. X-ray topography refers to direct methods for studying the real structure of crystals and is sensitive to deformations and defects that affect the periodic structure of the crystal structure. This makes it possible to study the dynamics of a crystal structure with localization over the volume at different values of uniaxial load.

For the model experiment, a single crystal of triglycine sulfate (TGS) was chosen as a sample. TGS consists of light chemical elements and has a relatively low X-ray absorption, which makes it possible to study rather thick samples (up to several mm thick). During the experiments, a sample 7 × 6 × 3 mm in size was subjected to an increasing elastic uniaxial load (up to 5 MPa). At the same time, a series of topograms was recorded using a detector with a pixel size of 55 μm. Deformation behavior of TGS crystals under mechanical compression along the [100] and [010] crystallographic directions were established. Topograms from mutually perpendicular crystallographic planes with the same direction of compression show a fundamentally different pattern of strain distribution and have different sensitivity to macrodefects.

This work has been supported by the Russian Foundation for Basic Research, grant No. 19-29-12037 (to MK), and by the Ministry of Science and Higher Education of the Russian Federation, grant No. 075-15-2021-1362, as a part of the development of X-ray techniques and in the framework of the work on the state assignment of the Federal Research Center for Crystallography and Photonics, Russian Academy of Sciences.

Water absorption behavior of composite materials based on agro waste and polyolefin

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The interest in agricultural waste as a reinforcing agent in polymer matrix has grown rapidly in the last decade. But nevertheless, there are some disadvantages in using agricultural waste as filler. Since the chemical composition of agricultural waste is rich in cellulose, which is hydrophilic in nature, they are susceptible to water absorption and, therefore, their use as a reinforcing agent is limited. As a result of water absorption, the fibers swell, microcracks appear in the fiber-matrix space, and this can lead to a decrease in the mechanical and dimensional properties of the composites. The degree of water absorption of composites reinforced with natural filler depends on temperature, filler concentration, filler orientation, filler permeability, void content, hydrophilicity of individual components, etc. [1, 2]. In this regard, a study was carried out on the water absorption of composites based on low density polyethylene and peanut shells. The study of water absorption of composites was carried out in accordance with ASTM D-570. The results of the study of water absorption of composites showed that water absorption gradually increases with increasing filler concentration, reaching a saturation point at which the moisture content remains almost constant. Thus, a higher concentration of filler leads to a greater absorption of water. It is worth noting that water molecules can easily wet the peanut shell/LDPE composites, as well as penetrate the composites through voids, resulting in a higher water absorption index in a short exposure time. This phenomenon can be explained by considering the mechanisms of water diffusion in polymer composites based on natural fibers. Usually, water diffuses into polymer composites in three ways [3]. First, water molecules diffuse into small spaces between polymer chains. Secondly, water molecules diffuse through the pores and slots at the interface between the filler and the matrix. Thirdly, water molecules diffuse through microcracks in the matrix, which appear when the filler of plant origin swells. Peanut shells are naturally hydrophilic. On the one hand, peanut shells contain a large number of hydroxyl groups. On the other hand, it is a fibrous substance with many capillaries and a large surface area, so it easily absorbs water. Thus, natural fibers are very promising materials that can be used in the development of polymeric biocomposites using various fiber surface modification methods to improve the water absorption of the composites.

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Resonant properties of PMN-PZT-PG solid solutions on a microstrip line in the microwave range

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One of the topical areas of application of functional materials is microwave technology. In this paper, $0.98(xPbTiO_3 - yPbZrO_3 - zPbNb_{2/3}Mg_{1/3}O_3) - 0.02PbGeO_3$ solid solutions are considered as a promising material for dielectric resonators or filters.

The dependence of the resonant frequencies and the absorption band width of cylindrical samples 10 mm in diameter and 1 mm thick on the concentration of $PbTiO_3$ in the frequency range 10 MHz – 20 GHz was studied. The measurements were carried out using a P4M-18 «Mikran» vector network analyzer, while the samples were placed on a segment of a microstrip line (MSL). After obtaining the frequency dependences of the S-parameters, the absorption coefficient of the material was calculated as the difference between the scattering coefficient of the MSL with the sample and the empty MSL, which were calculated taking into account S_{11} and S_{12}. Studies have shown that compositions with an $PbTiO_3$ concentration (ferroelectric phase) ranging from 0,4 to 0,5 mole fractions exhibit the weakest resonance behavior, but at the same time have the widest absorption band (Fig. 1).

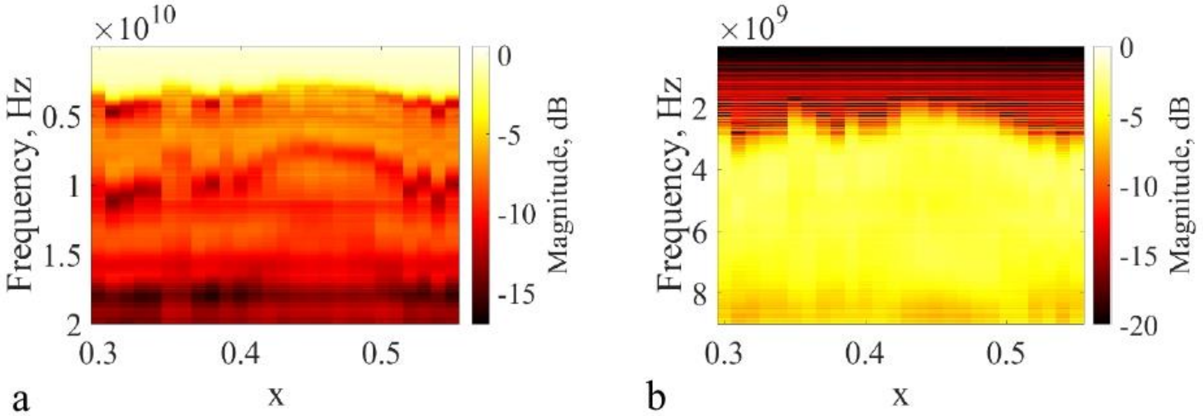

Fig. 1. Dependences of dispersion of transfer coefficient (a) and absorption coefficient (b) on $PbTiO_3$ concentration

The results obtained will help in future research and selection of compositions for further development of microwave devices.

The study was carried out on the equipment of the Shared Research Facility Centre of SFedU, Research Institute of Physics with the financial support of the Ministry of Science and Higher Education of the Russian Federation (State task in the field of scientific activity, scientific project No. (0852-2020-0032)/(BAZ0110/20-3-07IF)).

Effect of temperature on the effective viscosity of polymer composites based on polypropylene/ $Mg(OH)_2$ blend and oligopropylene ester of salicylic acid

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The viscosity of polymer melts is called the effective viscosity. It depends on temperature and decreases with increasing temperature. The effect of temperature on the effective viscosity of polymer melts is usually expressed in terms of the activation energy of viscous flow [1]. According to the Frenkel-Eyring theory, the viscosity of the melt depends exponentially on temperature. The activation energy of a viscous flow is determined in accordance with the dependence $\lg\eta = f(1/T)$. In the case of a nonlinear dependence of the logarithm of viscosity on the inverse temperature, the so-called apparent activation energy of the flow is calculated.

In this regard, in Fig. 1 presents the results of studying the effect of the inverse temperature on the effective viscosity of a mixture of PP/$Mg(OH)_2$ and composites based on it in Arrhenius coordinates. From a comparative analysis of curves (fig. 1a), it can be seen that within the limits of loads from 3.8 to 21.6 kg, the dependences of viscosity on temperature are predominantly linear, and at loads of 5 and 12.5 kg, the dependences of viscosity on temperature are presented in the form of curves. And since the dependence of viscosity on temperature is expressed as a curve, the activation energy of a viscous flow will be a variable. In such cases, the “apparent” activation energy of the viscous flow is usually determined. The apparent activation energy of the viscous flow of the PP/$Mg(OH)_2$ mixture varies in the range of 40.7–42.8 J/mol. It is clearly seen from curves of 1b and 1c that in the region of non-Newtonian flow of polymers, the dependence of viscosity on temperature is presented as a curved line. The nonlinear dependence of $\lg\eta$ on 1/T, in our opinion, confirms the assumption about a certain process of decomposition of macrochain associates.

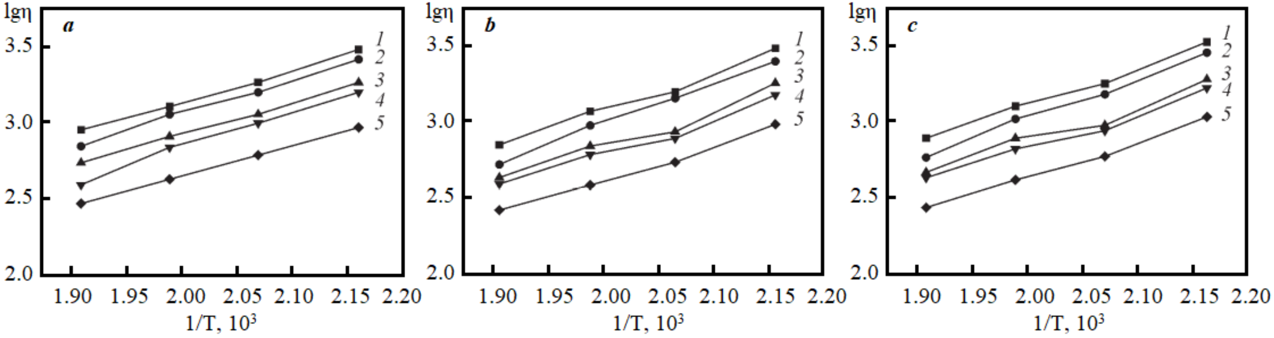

Fig.1. Dependence of melt viscosity of: a – PP/$Mg(OH)_2$ (30/70); b – PP/$Mg(OH)_2$ + 1.66 wt. % OPESA; c – PP/$Mg(OH)_2$ + 3.33 wt. % OPESA, on the inverse temperature at different loads, kg: 1 – 3.8; 2 – 5.0; 3 – 10.0; 4 – 12.5; 5 – 21.6

Apparent viscous flow activation energy for PP/$Mg(OH)_2$+1.66 wt.% OPESA and PP/$Mg(OH)_2$+ 3.33 wt.% OPESA composites varies within 55.6–59.9 kJ/mol.

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Production of Si_2N_2O-based ceramics by spark plasma sintering using Si_3N_4 – Y_2O_3 – Al_2O_3 nanopowder compositions

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Previously, it has been reported that Si_2N_2O ceramics could be obtained from the pre annealed in an atmosphere of air Si_3N_4 nanopowder mixture with a precursor oxide sintering additive [1]. It is assumed that the reason for the oxynitride formation, is the oxygen adsorption on the surface of Si_3N_4 nanoparticles during the annealing at 1000°C.

The work considers the production of Si_2N_2O ceramics by spark plasma sintering (SPS) of powder composition based on Si_3N_4 (99.5%, average crystallite size ~15 nm) with a sintering additive Y_2O_3 – Al_2O_3 in an amount not exceeding 5% wt. The components were mixed in molar ratios: 3:5 (sample 1), 1:2 (sample 2), 1:1 (sample 3), which corresponds to $Y_3Al_5O_{12}$, $YAlO_3$, $Y_4Al_2O_9$ phases. The additive was added into the Si_3N_4 powder by co-precipitation from the gel in the presence of citric acid.

SPS was carried out on a Dr. Sinter model SPS-625 equipment at 70 MPa, the heating rate was 50°C/min until the end of shrinkage, at the end of shrinkage no exposure was performed. The temperature at the end of shrinkage was 1640-1770°C. The relative density of samples 1-3 was 94.8%, 95.5% and 96.4%, respectively.

The phase composition of the ceramic samples was investigated by X-ray diffraction analysis (XRD) on a Shimadzu XRD-7000 diffractometer (CuKα, $\lambda = 1.5406$ Å). The microstructure was studied by scanning electron microscopy (SEM) on a JEOL JSM-6490 microscope.

According to XRD and SEM investigations it was found that the Si_2N_2O crystal phase prevails in the studied ceramics with the presence of a small amount of β-Si_3N_4 (about 5% wt.). The average size of crystallites estimates is about 0.7 μm according to XRD and SEM. Phases containing Y and Al were not detected, which is probably due to the amorphous sintering additive phase in the ceramic sample.

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Influence of epoxidized extender oil on properties of natural rubber compounds

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The selection of the best components for the rubber compounding process is essential for obtaining rubber products that meet the requirements of the market. For product properties, rubber process oil is, like reinforcing fillers and other additives, highly significant blending component. Due to the toxicity of commonly used mineral extender oils, there is a demand for usage of environmentally friendly oils in rubber compounding. Although eco-friendly, vegetable oils have some less desirable properties compared to mineral oils, such as lower thermal stability and lower solubility parameter. These issues may be overcomed by chemical modifications of vegetable oils such as epoxidation transesterification, etc.

The influence of epoxidized soybean oil on the natural rubber compounding process is determined in this study. Properties of epoxidizes soybean oil as rubber process oil, , which were experimentally determined or calculated, have been compared to properties of soybean oil. The mixing phase of the rubber compounding process was performed on a laboratory internal batch mixer, at 90°C and a rotor speed of 60 rpm. The rheological properties of rubber compounds and rubber hardness were determined. Power consumption during the rubber compounding mixing phase was calculated on the basis of experimental data for voltage and amperage changes. Power consumption and parameters related to compounding process, as well as parameters of obtained rubber compounds, were determined for different content of epoxidized soybean oil.

The results showed that rubber compounds obtained with epoxidized soybean oil were softer, while, as expected, power consumption during the mixing phase was higher compared to soybean oil. Epoxidized soybean oil can be used as rubber process oil during the compounding process at 90°C or above, to obtain rubber with desired properties and prevent separation of unmixed extender oil from the product.

The authors are thankful to the Ministry of Education, Science and Technological Development of the Republic of Serbia for their financial support, Project No. 451-03-68/2022-14/200134.

Effect of zinc oxide nanoparticles on physico-mechanical properties of hyperbranched polyester coatings

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The application of hyperbranched resins, as binders in environment-friendly coatings, has an advantage due to less organic solvent content and lower viscosity than conventional resins. The second generation of hyperbranched (HB) resin was synthesized based on ditrimethylolpropane and dimethylol propionic acid. In order to improve the properties of the coating, zinc oxide nanoparticles (average size 20 nm) were added to HB resin. Three samples were prepared with ZnO nanoparticles in an amount of 0, 1, and 3 wt% of the total weight of the resin. After homogenization, HB resin with zinc oxide nanoparticles is crosslinked using commercial melamine resin. A wet film layer of the resin mixture thickness of 100 ± 2 μm was applied on the steel panel. The coatings were crosslinked in an oven for 30 minutes at a temperature of 120 °C. The thickness of the dry coating film was 60 ± 2 μm, measured according to ISO 2360, using the Defelsko PosiTector 6000 FSN2. The Cross-Cut Test was applied to assess the resistance of the coating to separate from the substrate. Adhesion has been assessed following ISO 2409. The edges of the cuts are completely smooth, none of the lattice squares is detached. The gloss of the coated film was determined at an angle of 60° using a BIK-Gardner gloss meter. With the increase of the content of zinc oxide nanoparticles in the system, there is a slight decrease in the value of the gloss of the coating (from 98 % to 88 %, ISO 2813). At low concentrations of zinc oxide (below three weight percent), it can be concluded that the well-dispersed particles in the coating do not protrude above the surface and therefore do not have a significant effect on surface gloss. Hardness was measured using a Konig Pendulum hardness tester according to DIN 53157 standard. Impact resistance of the coating film was measured following ISO 6272 standard. The hardness of the coating and the impact resistance increases slightly with the amount of zinc oxide nanoparticles in the system. It is assumed that this is the result of improved coating curing in the presence of ZnO nanoparticles.

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Computational search and plasma dynamic synthesis of tabtalum-hafnium high-entripy carbides

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High-entropy carbides (HEC) of refractory metals are some of the most intriguing compounds studied around the world having unique properties like high hardness, high melting temperature, low thermal conductivity. Stabilization of such materials mainly comes from the entropic contribution minimizing the Gibbs free energy [1–6]. Spark plasma sintering techniques requiring presence of vacuum for synthesis of HEC are the most widely used methods [1,2]. Here we demonstrate a unique plasma dynamic technique to synthesize high-quality ternary Hf–Ta–C compounds both as powders and coatings that can be easily applied to various substrates. To discover new ternary Hf–Ta–C compounds, we used the evolutionary algorithm USPEX [7–9]. After study of thermodynamic stability of predicted phases, we selected 10 compounds for plasma dynamic synthesis and comprehensive characterization. The application of the plasma dynamic technique for the synthesis of Hf–Ta–C compounds results in formation of both high-quality powders and protective coatings composed of nonstoichiometric hafnium–tantalum carbides.

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Influence of Features of Specimens Produced by Spark Plasma Sintering on Final Ballistics Processes

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Currently, a popular method for sintering ceramics is Spark Plasma Sintering (hereinafter referred to as SPS). The advantages of this technology are improved mechanical properties, homogeneous and high-density nanostructure of products, and reduced sintering time.

In this work, we studied the phenomenon observed in experiments on the ballistic resistance of ceramic barriers made by the SPS method. There are experimental data obtained at the NIFTI UNN, which show that for such materials it is important which end the barrier is located relative to the striker. Depending on the side on which the impact will fall, the data obtained can vary greatly. The effect was observed on samples having the same chemical composition and also made under the same temperature conditions.

Such a strong influence on the results of ballistic tests can be associated with the microstructure of the obtained samples, or with the occurrence of residual stresses in the process of ceramics manufacturing. The influence of both factors was tested using mathematical modeling.

It was found that the phenomenon under study is not related to the heterogeneity of the structure observed in the samples under study. However, there is a significant asymmetry in the cooling rate of the sample upon completion of the sintering process. The unevenness of the temperature fields leads to residual stresses, which can significantly affect the processes of the final ballistics.

The method of taking into account the influence of internal residual stresses for brittle materials under dynamic problems is associated with the representation of a homogeneous material by a heterogeneous model, in which some areas with different stress levels are introduced.

The hypothesis about the influence of internal residual stresses on the processes of final ballistics, obtained as a result of the technological features of the technique of electric pulse plasma sintering (asymmetric temperature distribution pattern), is confirmed by calculations in the simulation process and correlates with the available experimental data.

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Tungsten carbide creep behavior at elevated temperatures

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The aim of the work is to study the high-temperature deformation behavior of sintered tungsten carbide ceramics.

Powders of tungsten monocarbide α-WC with an initial particle size were studied: nanopowder No. 1 with an initial particle size of ~95 nm, as well as powders No. 2 and No. 3 of industrial production of the Kirovograd Hard Alloy Plant with an initial particle size according to Fischer of 0.8 μm and 3 μm, respectively. Nanopowder No. 1 was obtained by plasma-chemical synthesis followed by reduction annealing in hydrogen at a temperature of 1050°C (3 hours).

The compaction of cylindrical samples with a diameter of 12 mm and a height of h = 12 mm was carried out by the SPS method using the Dr. Sinter model SPS-625. Samples were baked from powder compacts weighing 22.5 g in continuous heating mode at a set speed of 50 °C/min to a baking temperature T_s, followed by cooling in free mode. Sintering was carried out under conditions of uniaxial pressure of 70 MPa, which was applied to the sample simultaneously with heating.

High-temperature deformation of sintered samples was carried out using the Dr. Sinter model SPS-625. For creep tests, they were placed in a graphite mold with an internal surface of 20 mm, which was larger than the diameter of the sintered ceramic specimens.

To take into account the contribution of thermal expansion of molds, an experiment was carried out on heating empty molds. The true shrinkage value (L) was obtained by subtracting the thermal expansion of the mold from the experimentally measured "effective" value $L_{eff}(T, t)$.

It is shown that the magnitude of the creep activation power in ultrafine-grained (UFG) tungsten carbide with a particle size of ~0.15 μm, sintered from plasma-chemical nanopowders, is ~31 kTm. This value is 1.5-2 times higher than the creep activation power in fine-grained samples of tungsten carbide, by the method of obtaining SPS from submicron (~0.8 μm) and micron (~3 μm) industrial powders. It has been established that the value of the coefficient of change varies from 2.4 to 3.1, which corresponds to the appearance of lattice dislocations in the field of probability of occurrence of point phenomena. It has been suggested that one of the reasons for the increased creep activity during testing of UFG samples of tungsten carbide is an increased volume fraction of W2C carbide particles formed during high-speed sintering of plasma-chemical α-WC nanopowders with an increased concentration of absorbed oxygen.

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Nanocomposite Based on the Single-walled Carbon Nanotubes Filled with the Fluoride-ion Conductor $CsSn_2F_5$

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The crystallization of cesium pentafluorodistannate $CsSn_2F_5$ was performed using SnF_2 (Sigma-Aldrich), CsF (pure) from an aqueous solution by the reaction $CsF + 2SnF_2 = CsSn_2F_5$. Cesium fluoride was pre-dried at 80ºC. The plastic test tubes with the fluorides weighted in a molar ratio were heated to 70°C in an ultrasonic bath to obtain a concentrated solution and achieve supersaturation during cooling. An ice bath was used to increase the crystallization product yield.

A novel nanocomposite $CsSn_2F_5$@SWCNT was synthesized by capillary wetting technique from the melt. A test charge of $CsSn_2F_5$ with a mass ~200 mg and ~5 mg of SWCNT (OCSiAl) was ground in a jasper mortar and placed in a quartz ampoule. The ampoule was subjected to thermo-vacuum treatment (250ºC, 2.5 Pa) during 30 min. Then the ampoule was sealed under the vacuum and placed in a muffle furnace, where was heated at the temperature 380ºC during five days with the subsequent cooling. The sample obtained was investigated by means of transmission electron microscopy (TEM), powder X-Ray diffraction analysis (XRD). TEM was carried out with the FEI Osiris electron microscope, accelerating voltage 200 kV. XRD was carried out with XRD-6000 Shimadzu diffractometer with Cu$K\alpha$ radiation. Powder diffraction pattern was recorded in the 2θ angle range 10°–60° in 0.02° steps.

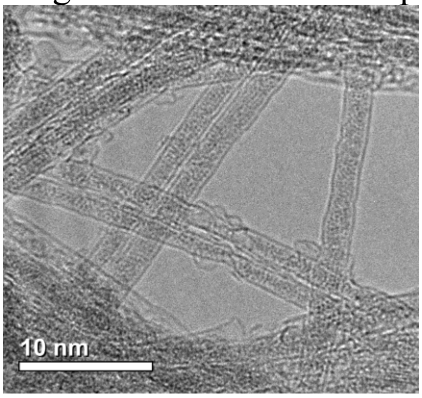

Fig. 1. TEM microphotograph of $CsSn_2F_5$@SWCNT nanocomposite.

There are bundles of SWCNT with diameter varying from 1.3 to 1.9 nm continuously filled with ordered packing of atoms are observed on the TEM-microphotograph (fig.1). Analysis of the XRD pattern proved the presence of single phase: $CsSn_2F_5$ (a = 10.03(4) Å, b = 5.92(7) Å, c = 11.96(9) Å, β = 107.4(5)°).

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Analytical method for predicting a binary crystal properties

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An analytical method has been developed for calculating the properties of binary crystals of the type of AB substitution solid solutions [1]. The method makes it possible to predict properties at any (corresponding to the solid phase) temperature (T), specific volume ($v = V/N$) and pressure (P). The four–parametric Mie–Lennard-Jones potential is used to describe the interatomic interaction. When determining the parameters for the interaction of dissimilar A-B atoms, the "average atom" method was used [2], which takes into account the deviation of the interatomic distance A-B in solid solution from the Vegard rule. The method allows calculating both the state equation $P(v, T)$ and P-T-v dependences of the following properties: Debye temperature, three Gruneisen parameters, elastic modulus ($B_T = -V(\partial P/\partial V)_T$), isochoric and isobaric heat capacities, thermal expansion coefficient ($\alpha_p = (\partial \ln V/\partial T)_P$), and specific surface energy. The method also allows calculating the derivatives of these properties both by temperature along the isobar and by pressure along the isotherm. The method was tested when calculating the properties of Si-Ge, Au-Fe, and Mo-W solid solutions. Both isothermal-isobaric concentration dependences of the properties and the dependences of the properties of a binary crystal of equiatomic composition on P-T arguments were studied. The results obtained showed good agreement with the experimental and theoretical data of other authors. It was shown that there is a certain temperature T_B, in which the product $\alpha_p \cdot B_T = (\partial P/\partial T)_V$ does not change during isothermal compression of the crystal. At $T > T_B$, the $\alpha_p \cdot B_T$ function increases, and at $T < T_B$, the $\alpha_p \cdot B_T$ function decreases with an isothermal increase in pressure. It has been shown that, at a certain pressure P_B, the isotherms of the baric derivative of modulus ($B'(P) = (\partial B_T/\partial P)_T$) intersect. At this pressure, the $B'(P)$ function does not depend on temperature. At $P < P_B$, the $B'(P)$ function increases, and at $P > P_B$, the $B'(P)$ function decreases with an isobaric increase in temperature. Using the RP model of a nanocrystal from Ref. [3], isothermal-isobaric changes in the properties of FCC-$Au_{0.5}Fe_{0.5}$ were studied both with an isomorphic (with an unchanged shape) decrease in the nanocrystal size, and with an isomeric (at N = const) deviation of the nanocrystal shape from the most energy-optimal shape (for the RP model it is a cube). It was shown that size dependences are more noticeable the higher the temperature, or than more noticeable the nanocrystal shape is deviated from the energy-optimal shape.

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$1/f^2$ noise as precursor of structure reconstruction in ionic crystals near the melting point

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Nonequlibrium fluctuations nonlinear Brownian noise type have been occurred in different systems near the phase transition points. As a rule, such nonequlibrium processes appeared as precursors of materials fracture and degradation. Observation near the melting point of transient premelting effect and anomalous behavior of temperature dependence of some physical parameters indicate a change of solid state structure and properties, which have nonlinearly dependence on heating rate. In present work analysis of KCl premelting phases dynamic structuring has been carried out in different kinetic regimes (dynamic – v=5,10 K/min; quasistatic – v=1 K/min). As it revealed, premelting is nonequlibrium fluctuating processes, which is accompanied by dissipative state formation and characterized by systems of thermodynamic and structure parameters with nonlinear character of the heating rate. On X-ray data the average size of coherent scattering region of KCl peremelting phases are calculated, it varies between 65-90 nm [1]. Nonmonotonic peak intensity has been revealed in KCl premelting phase, which connected with heat fluctuations in temperature area $T \geq 0.85\ T_m$. Spectral analysis of fluctuation processes KCl in premelting phase was carried out using continuous wavelet transform. As it revealed, heat fluctuations in KCl premelting states are $1/f^{\ 2}$ type noisee (nonlinear Brownian noise), i.e., random process with independent increments. At analyzing complex fluctuation signals, it is possible to evaluate the degree of their randomness using such stochastic characteristic as Hurst parameter (H). Hurst parameter is the measure of the process towards trend tendency (in contrast to the usual Brownian motion). Evaluation of Hurst parameter of heat fluctuations in KCl premelting states at dynamic regimes provides the values H ~ 0.4. This indicates a system which is more prone to reconstructions when its development tendency changes. Such fluctuation signals have been characterized by a lack of stability (antipersistency). Their growth in the past means a decrease in the future, and tendency to decrease in the past makes an increase in the future likely. Evaluation of Hurst parameter at quasistatic regime gives H ~ 0.6. This indicates that this time dependence has stable tendency to change (persistence). In other words, the presence of $1/f^2$ type fluctuations in the system indicate strucrural changes near the melting point. In such case, as a rule, oscillatory change of “stability-instability-stability” type occurs. This important phenomenon is known as ordering through fluctuations.

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Microcumulation at impact loading as a method of comparative evaluation of dynamic plasticity of metallic materials: Case of copper

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A novel experimental laboratory technique for evaluating the dynamic plasticity of materials, under the conditions of cumulative flow and without using explosives, is described. To perform the microcumulative tests, miniature cylindrical specimens with conical pits were used. The dynamic loading of the specimens was performed using a gas gun with a striker accelerated up to speeds in the range of 600–800 m/s. The optimal specimen geometry and testing regimes, including the focal distance during microcumulation testing, were then determined. The flow speed of the microcumulative jet was found to be equal to its theoretical value calculated within the framework of the Lavrent'ev hydrodynamic theory. The novel technique was demonstrated to enable the study of the relationship between the initial specimen microstructure and the dynamic plasticity magnitude at the cumulative flow using high-purity copper as an example. The penetration depth of the cumulative microjet into a steel barrier was shown to depend on the parameters of the copper microstructure. A preliminary analysis of the effects of copper purity and processing regimes on the dynamic plasticity characteristics was performed.

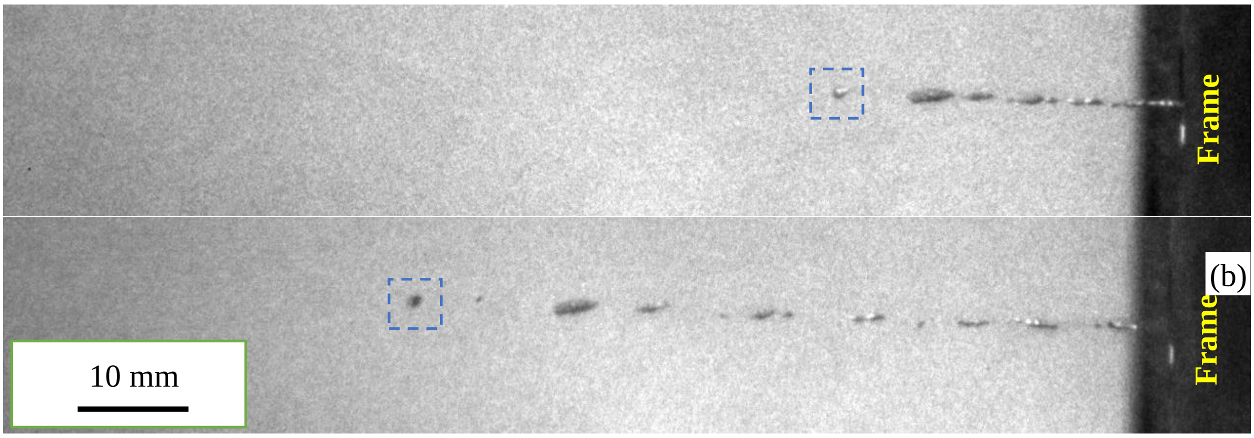

Fig.1. High-speed filming of the cumulative jet. The experimental scheme is shown in Figure 2. The steel barrier was not installed while filming, and the jet was able to expand freely until destruction. The head element of the CJ is marked by the blue dashed line

Numerical investigation of thermal fields and melt pool behaviors for laser surface treatment of aluminium

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Laser surface treatment (LST) is a complex process in which the surface of a material is melted with a laser, thereby changing its microstructure and properties. Due to the features of the LST process, it is difficult to directly observe thermal fields and predict the melt pool behavior, since they strongly depend on the laser process parameters, such as scanning speed, laser power, hatch spacing, coating thickness, etc. Therefore, numerical modeling is used to predict thermal fields and microstructures.

The objective of this study is to create a model that can be used to investigate thermal fields and study the dimensions of the melt pool during LST process. The Comsol Multiphysics 5.4. package and 3D finite element method are used to model thermal effects.

In general, heat transfer can be described by the heat conduction equation. The laser source is represented by a heat source with a Gaussian distribution. When the laser interacts with the material, heat losses due to convection and radiation are taken into account. The phase transition of melting and evaporation is considered in the equation of heat capacity.

In the process of heating and cooling, the physical properties of materials change, since they are temperature dependent. The model has the ability to set such properties as thermal conductivity, heat capacity, density, as a function of temperature. Also, before starting the calculation, it is possible to change the values of process parameters, such as power, scanning speed, laser beam diameter, hatch spacing, sample dimensions and coating thickness.

As a result of the study, a model that can be used to obtain a non-stationary temperature distribution in the entire volume of the sample was created. Ten laser beam passes were simulated for samples made of ST3 steel with different thickness of aluminum coating. It is established that at a laser speed of 400 mm/s, 800 mm/s and a power of 180 W, there is no mixing of components in the heat affected zone, since energy input is insufficient. At a scanning speed of 100 mm/s and a power of 180 W for a coating thickness of 20 μm and 40 μm, the components are mixed in a ratio of 2:1 and 1:2, respectively. These modes will ensure high-quality adhesion of the coating to the sample material and will not create strong composition gradients after mixing the components.

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Study of the effect of high-temperature annealing on the resistance of fine-grained titanium alloy PT-3V to corrosion-fatigue fracture

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The object of study is industrial pseudo-α titanium alloy PT-3V (Ti-4.73 wt.% Al-1.88 wt.% V). The ultrafine-grained (UFG) structure in the alloy was formed by rotational forging (RF). Fatigue tests were carried out on cylindrical specimens according to the "bending with rotation" scheme in a 3% NaCl aqueous solution. Short 30-minute high-temperature annealings were carried out at temperatures of 500, 550, 600, and 700°C. Long-term (500, 1000, 1500, 2000 h) high-temperature annealings were carried out at a temperature of 250°C.

Studies of the microstructure have shown that, after RF, an UFG structure with an average fragment size of ~0.2–0.5 μm is formed in the PT-3V alloy. After prolonged annealing at 250°C and short annealing at 500, 550°C, the structure of the alloys does not change; the first recrystallized grains are observed after annealing at 600°C.

It is shown that at annealing temperatures of 500 and 550°C the microhardness does not change and amounts to ~2980 MPa. A significant drop in microhardness is observed after annealing at temperatures above 600°C. The microhardness of the UFG titanium alloy PT-3V after long-term annealing at a temperature of 250°C remains unchanged and amounts to ~3100 MPa.

Carrying out corrosion-fatigue tests of fine-grained titanium alloy PT-3V showed that short annealings at temperatures of 500, 550, 600, 700°C lead to a significant decrease in the corrosion-fatigue strength of the UFG titanium alloy PT-3V.

An analysis of the results of corrosion-fatigue tests after long-term annealing at a temperature of 250 °C shows that after 500 hours of annealing, there is a slight decrease in the corrosion-fatigue strength of the UFG titanium alloy PT-3V, and after annealings of 1000, 1500, 2000 hours there is a slight increase in corrosion resistance - fatigue characteristics.

A fractographic analysis of fractures of samples of annealed UFG titanium alloys after their corrosion-fatigue tests at various stress amplitudes has been carried out. The main stages of crack initiation and growth are revealed.

Physical and mechanical properties of phenolic plastics for technical purposes using fibrous organic production waste

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One of the promising directions for the utilization of fibrous organic waste from various industries is the production of polymer composite materials (PCM). A wide range of technical phenolic products gives grounds for the possibility of their production using these wastes and phenol-formaldehyde resins [1]. As the main components of PCM, crushed wastes of fibrous cellulose fibers (fiber length 20÷160 µm, fiber diameter 5÷30 µm) and solid phenol-formaldehyde resins of the resole (RF-342) and novolac (RF-010) types were used. Chemical substances were used as technological additives: magnesium oxide, kaolin, calcium stearate, urotropine, pigments. Chemical substances were used as technological additives: magnesium oxide, kaolin, calcium stearate, urotropine, pigments. The main technological processes for obtaining PCM were: grinding, mixing, plasticizing the mixture by rolling, obtaining a press powder (with a particle size of 1÷2,5 mm) and thermal pressing with isothermal exposure of the product at a speed of 0,8÷1 mm of its thickness per minute at temperature 170°C and pressure 20 MPa.

Physical and mechanical properties (ultimate tensile strength σ_r , and bending σ_i, impact strength a_n, degree of moisture absorption ε_w , and mineral oil absorption ε_m) of the obtained composites were determined taking into account the content of fibrous cellulose filler (FCF). The most optimal characteristics of the properties of composites were obtained at 40-50% filler content (table 1).

Table 1. Physical and mechanical properties of composites

Resin	FCF, %	σ_r, MPa	σ_i, MPa	a_n, MJ/m^2	ε_W, %	ε_M, %
RF -342	40-50	5,7-5,9	62,3-54,1	10,9-11,3	0,3-0,8	0,1-0,25
RF -010	40-50	5,9-6,2	56,2-48,5	13,9-13,1	0,4-1,1	0,16-0,24

The obtained experimental data have quite acceptable values for polymer composite products (phenolic plastics) for technical purposes [1].

It should be noted that during the molding of products, a good fluidity of the press powder and uniformity of coloring the structure of the obtained PCM samples with powder inorganic pigments in black, raspberry, green colors are observed to obtain a smooth shiny texture of their surface.

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Investigation of the strain aging effect in U8 steel subjected to various types of loading

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The aim of the work was to study the tendency of carbon steel to strain aging after various types of deformation.

The object of the study was U8 steel in a normalized state. The samples were studied in the initial state, after quasi-static and dynamic compression for a given degree of deformation. Impact loading was carried out with a steel flat impactor on the test sample. The structure of the steel was studied by the methods of metallography and scanning electron microscopy; the microhardness technique was used to certify the mechanical properties. To visualize the changes in physical and mechanical quantities in the process of high-grade deformation, modeling was carried out in the Ansys Workbench.

Metallographic studies have shown that U8 steel in the initial state has the microstructure of lamellar pearlite. After quasi-static and dynamic compression, the microstructure of U8 steel does not undergo significant changes. It has been established that dynamic compression causes a slight increase in hardness in the central part of the specimens. The results obtained are consistent with the results of finite element modeling, where the maximum value of the yield strength is reached in the central region of the rear side of the sample.

It has been established that low-temperature annealing (150-500 °C) of the non-deformed steel U8 leads to a monotonic decrease of hardness. Samples of steel U8 subjected to quasi-static compression and dynamic loading during annealing exhibit the effect of strain aging, which consists in an increase in hardness during annealing in the temperature range of 200-300 °C. An increase in the degree and rate of deformation is accompanied by an increase in the hardness of the annealed steel. The maximum microhardness for steel after dynamic compression is observed at a lower annealing temperature than in the case of specimens subjected to quasi-static upsetting.

The strain aging effect in U8 steel after quasistatic compression and dynamic loading was suggested to originate from an increasing of the lattice dislocation density, the long-range internal stress fields from which lead to the dissociation of the cementite Fe_3C plates and to increasing of the concentration of carbon atoms in the ferrite crystal lattice. During annealing, the formation of Cottrell atmospheres occurs, blocking the free slip of dislocations in the crystal lattice.

The work was carried out within the framework of project No. 0729-2020-0060 of the Russian Ministry of Education and Science.

X-ray diffraction analysis of ceramics irradiated with high-energy ions

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Two series of ceramic samples obtained by spark plasma sintering (SPS) $NaNd(WO_4)_2$ (NNW) and $NaNd(MoO_4)_2$ (NNMo) were investigated. Previously, the samples were subjected to radiation resistance tests by irradiating them with high energy Ar (E = 46 MeV), Kr (107 MeV) and Xe (160 MeV) ions with a fluence between $6 \cdot 10^{10} - 2 \cdot 10^{12}$ cm^{-2}.

X-ray studies were performed on a Bruker D8 Discover diffractometer (CuKα-radiation). The diffractometer uses a parabolic Goebel mirror and a 1 mm collimator to form a parallel beam, and Soller slits with a 0.2° angle aperture are positioned in front of the detector. The angle of incidence of the X-ray beam α varied from 1° to 10°, and the scanning was performed by rotating the detector by an angle of 2θ. The imaging was carried out in the vicinity of the high-intensity reflection (112) of the NNW and NNMo phases.

The analysis of X-ray diffraction experiments revealed an increase in the degree of amorphization with increasing irradiation dose from 20% at a dose of $6 \cdot 10^{10}$ for NNMo ceramics to 85% at a dose $2 \cdot 10^{12}$ for NNW ceramics. NNMo ceramics, at lower densities, showed greater resistance of the crystalline phase to external radiation exposure compared to NNW at the same irradiation doses. The depth of the amorphized layer was greater than the depth of X-ray penetration into the samples (2 μm). The disturbed layer is homogeneously amorphized within this depth range. The result of modeling in the SRIM software package of the irradiation process of the materials in question is consistent with the results of experimental studies.

X-ray diffraction studies of the samples before and after irradiation were carried out at the laboratory for diagnostics of radiation defects in solid-state nanostructures at the IPM RAS with the support of the Ministry of Science and Higher Education (g/z № 0030-2021-0030).

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Structure, thermal stability and mechanical properties of ultrafine-grained bimetallic aluminum wires

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Small-sized (with a diameter of less than 0.5 mm) composite wires are one of the key elements of modern aircraft electric systems, they are thereby subject to stricter requirements concerning electric conductivity, strength, and thermal stability. One of the biggest challenges of modern electrical engineering is to replace copper wires with aluminum ones while ensuring the same level of thermal stability, high electrical conductance and strength at elevated temperatures. The research focused on the structure of small-sized wires with a diameter of 0.2-0.5 mm. The aluminum alloys with a varying content of REE and transition metals (TM) (Sc, Zr, Hf, Er, Yb) were used as base materials. The cast alloys were subjected to Equal Channel Angular Pressing (ECAP) and Rotary Swaging followed by recrystallization annealing in order to eliminate the heterogeneity microstructure. The annealing conditions were selected individually for each alloy to ensure a homogeneous recrystallized structure with a SER (no more than 2.8-2.9 μΩ·cm). The annealing at 320 °C leads to a fairly noticeable increase in SER for most of alloys. This goes to prove that solid solution decomposition begins, and Al_3(REE,TM) precipitation starts. It should also be noted that solid solution decomposition in scandium-containing alloys begins at a lower temperature (275 °C) than in alloys with higher zirconium content. This result shows that Al_3Sc and Al_3(Zr,REE,TM) precipitates form independently in the alloys under consideration. The workpieces were then scalped to remove oxides and subjected to multistage cold rolling in grooves. Rolling was performed on copper-coated workpieces. As a result, samples of composite aluminum wires with a diameter of 0.26 mm and a copper coating approx. 10 μm thick were produced. Mechanical tensile tests of wires at room temperature demonstrate that they are quite strong – after rolling, the tensile strength of wires made of the new alloys exceeds 500 MPa. Thermal stability of the structure and mechanical properties of wires made of microalloyed fine-grained aluminum alloys has been studied. It has been shown that the alloys have high thermal stability at isothermal exposure within a temperature range of 100-500 °C. It has been confirmed that annealing is accompanied by recrystallization processes that impair the mechanical properties of the wire. The rate of copper diffusion into the surface layers of the aluminum wire is negligible. The fracture analysis has shown that the annealed samples after tensile tests demonstrate ductile failure. No detachment of the copper buffer layer from the aluminum wire surface was observed.

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Hot salt corrosion of fine-grained α- and near-α titanium alloy Ti-Al-(V,Zr)

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The α- and near-α-titanium alloys are extensively used today in nuclear engineering and nuclear power industry to produce heat exchange equipment for nuclear engineering. The hot salt corrosion (HSC) is considered to be one of the most dangerous types of decay in titanium alloys.

The research has been conducted into the impact that structural-phase state of grain boundaries in α-titanium alloy Ti-2.5%Al-2.6%Zr (Russian industrial name PT-7M) near-α-titanium alloy Ti-5%Al-2%V (Russian industrial name PT-3V) and has on strength, plasticity and susceptibility to intercrystalline corrosion (ICC). Ultrafine-grained (UFG) structure was formed using the Equal Channel Angular Pressing (ECAP) technology and Rotary Swaging (RS) technology.

Autoclave HSC tests were carried out in a mixture of NaCl and KBr salts at the ratio of 300:1 at 250 ºC. Corrosion electrochemical studies were performed using R-8 potentiostat-galvanostat in an aqueous solution of 0.2%HF+10%HNO_3.

It is found that increased resistance to ICC in UFG alloy PT-3V is related to diffusion redistribution of vanadium on grain boundaries. It is found that a decrease in average grain size along with a decrease in vanadium local concentration during high-temperature ECAP leads to a reduction in the depth of intercrystalline hot salt corrosion defects from ~500-700 μm to 100-150 μm.

It is shown that there are two types of corrosion defects observed on the surface of a coarse-grained near-α-titanium alloy PT-7M after HSC tests: defects related to stitched β-phase particles (defects of type I) and ICC defects (defects of type II) related to higher concentration of corrosive doping elements (zirconium, aluminum) along grain boundaries. The nature of HSC-driven decay that occurs in UFG alloys depends on testing time and changes from pit corrosion to ICC when testing time increases from 270 h to 500 h. Changes in the nature of corrosion decay affecting a UFG alloy PT-7M occur when recrystallization starts, during which intensively migrating grain boundaries bring forth corrosive alloying elements distributed in the crystal lattice of a PT-7M titanium alloy.

Formation of a UFG structure is found to increase the resistance of a titanium alloy PT-7M to electrochemical corrosion and hot-salt corrosion. During electrochemical testing, corrosion damage to the surface of a coarse-grained specimen occurs through etching interphase (α-β)-boundaries; active corrosion etching of localized deformation bands is observed in a UFG alloy.

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Study of the effect of small additives (ppm) of Y_2O_3 and MgO on the strength of aluminum oxide grain boundaries

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In this work, we investigated the crack resistance of grain boundaries as the most vulnerable structural components for crack propagation.

The methodology presented in this work is based on measuring the fraction of crack propagation along the grain boundary using scanning electron microscopy. This approach allows a more detailed study of the crack propagation pattern, and it responds more accurately to small additions of impurities segregating at the grain boundary. Also, this method allows us to relate macro parameters, such as intergranular crack fraction or boundary crack resistance, to the grain boundary energy, and use the grain boundary as an additional tool in improving the strength of the ceramic product.

The addition of yttrium oxide improves grain boundary crack resistance by forming stronger Y-O bonds and filling in the septagonal rings in the aluminum oxide grain boundaries. Filling of the selective rings leads to a decrease in the relative free volume of Al_2O_3 grain boundaries, hence, the boundary energy decreases, which leads to an increase in the crack formation energy in the grain boundary.

The addition of magnesium oxide reduces the width distribution of dihedral angles in Al_2O_3, the reduction of the dispersion of dihedral angles has a favorable effect on the grain growth during sintering and the homogeneity of the final microstructure. A more homogeneous grain boundary energy of Al_2O_3 avoids the preferential vulnerable orientation for crack propagation.

This approach will further improve the ballistic resistance of ceramic barriers by influencing fragmentation and abrasion processes. Also, these studies will assess how much hardening additives should be added to Al_2O3 in fractions of ppm to increase the strength of the grain boundaries.

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Phase transitions in intercalated titanium diselenides

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Layered titanium dichalcogenides exhibit interesting fundamental [1,2] and practically important properties [3]. The crystal structure of such objects is a titanium layer surrounded on both sides by chalcogen layers. Such association of three layers is called a "sandwich" and the bond between the atoms in a "sandwich" is strong covalent. "Sandwiches" are separated by interlayer space approximately equal to them in thickness. This allows to consider such material as quasi-two-dimensional. Atoms and even molecules can be intercalated into interlayer spaces. For most transition metals, equilibrium with the metal is reached at 65 mol% of the intercalated metal per formula unit. Such high concentrations of the intercalant lead to its ordering in the form of monoatomic chains of intercalant and a decrease in symmetry from trigonal to monoclinic. Chains are stabilized by chemical bonding between the atoms that make up them.

In current work we systematically study the transition associated with the formation of chains and their thermal destruction depending on the degree of filling of the 3d shell of the intercalant. The homologous series $TM_{0.5}TiSe_2$ (TM=Ti, V, Cr, Fe, Co, Ni) was studied during in-situ heating. The experiment was carried out on the MCX [4] beamline of the Elettra synchrotron in the range of 50-1000 ^oC with a step of 25 ^oC or less. It is established that the transition is described in the Ising model with the order parameter depending on the electronic configuration of the intercalant. Increasing the filling of the 3d shell changes the order parameter from the typical 2D case to the 3D case. A systematic change in the ordering temperature as a function of the filling of the 3d shell is found. The results obtained are discussed together with previously obtained data on the electronic structure of intercalated compounds.

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The phase composition features of tungsten carbide ceramics produced by spark plasma sintering

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Spark plasma sintering (SPS) of powders is one of the most promising technologies for obtaining high-density and fine-grained materials. SPS takes place in a graphite mold. It has been shown that carbon diffusion from mold parts into the sample surface layers can take place during sintering. It can lead to an inhomogeneous distribution of crystal phases in different sample sections.

The aim of the work is to investigate the phase composition homogeneity in depth of samples obtained by SPS of tungsten carbide (WC) powders. The study objects were four WC ceramics prepared from powders of different phase composition and average particle size. Powder 1 was obtained by plasma-chemical synthesis in Baikov IMET RAS and contained 2.6% wt. of W (except for α-WC). Powders 2-4 were produced by JSC «KZTS». Powder 2 (0.8 µm) contained 1.7% wt. of W_2C (except for α-WC), powder 3 (3 µm) – 2.5% wt. of W_2C, powder 4 (14 µm) – 1.0% wt. of W_2C. The error of the phase composition estimation is 0.2% wt. Each powder was sintered in a graphite mold (12 mm inner diameter) until shrinkage was complete. SPS was carried out on a Dr. Sinter model SPS-625 in vacuum. P=70 MPa, V=50°C/min. The phase composition homogeneity of the samples was investigated by layer-by-layer X-ray diffraction (XRD) analysis. The layers (up to 50 µm thick – 1-7 stage of surface treatment, at least 200 µm thick – subsequent stages) were removed by successive mechanical grinding and polishing of the sample surface. XRD experiments were performed on a Shimadzu XRD-7000 diffractometer (CuKα) after each layer removal. Quantitative phase analysis was carried out by the reference intensity ratio method. The height of the cylindrical samples did not exceed 6 mm. A total of 700-800 µm was removed from the surface of each sample. It has been demonstrated that the near-surface layer (80-100 µm) is graphite paper. W_2C was detected in samples 1-3 at 100-150 µm from the surface and at 250 µm from the surface in sample 4. This is probably due to the fact that the carbon diffuses from the mold surface and reacts with W (in sample 1): $2W + C \rightarrow W_2C$ and W_2C (in all samples): $W_2C + C \rightarrow 2WC$. In addition, the W_2C fraction in each sample increases with distance from the surface. It is assumed that this is caused by decarbonization of α-WC particles to W_2C because of the adsorbed oxygen presence on the α-WC particle surface. Thus, the phase composition of the studied WC ceramics changes with the distance from the surface. The change consists in the W_2C absence in the surface layers and its presence at a depth of at least 100 µm from the sample surface.

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Temperature-dependent phase transition in $TiZrNbHfTaC_5$. A computational study

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Recently, high-entropy alloys have attracted significant attention owing to their exceptional mechanical strength, corrosion resistance and stability at high temperatures. As a result, the number of theoretical and experimental research of high-entropy materials increased dramatically over a past few years. Among them, a dozen of studies is dedicated to a separate class of materials, known as high-entropy carbides (HEC), which are based on group IV and V transition metals and form equimolar solid solutions, where 4-6 metals occupy NaCl-type crystal structure. Usually, synthesis of single- and multi-phase HEC requires a temperature regime which is not known a priori. The aim of this work is to determine optimal temperature regime for HEC synthesis theoretically, using materials modeling methods.

For modeling HEC phases at different temperatures, we used canonic Monte Carlo (CMC) simulations combined with low-rank potential, which is a type of machine-learning interatomic potential trained on density functional theory (DFT) calculations. Simulations were performed within temperature range 300 – 2000 K on 865 atom (10 × 12 × 15) supercell with fixed face-centered cubic lattice. After computational experiment phase transition between single- and multi-phase HEC was observed at 900 K. Specifically, purely single- and multi-phase structures were obtained at 2000 K and 500 K respectively. Calculated lattice parameters of both phases are 0.45 nm. Experimental HEC synthesis was conducted accounting for the temperature regime obtained with CMC simulations. As a result, our findings perfectly matched experiment. Thus, single- and multi-phase HEC were obtained at 2200 K and 400 K, respectively, and measured lattice parameters of corresponding phases are 0.45 nm and 0.46 nm.

The developed method, based on machine-learning potentials, allows to predict phases at different temperatures at much lower computational cost than any quantum mechanical model and can be employed for selection of temperature regime during experimental synthesis of HEC.

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The influence of zinc oxide particle sizes and content on the crosslinking process of composites based on natural rubber

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Zinc oxide plays a significant role in the rubber industry for the vulcanization of rubber with the help of sulfur. By improving the kinetics of the crosslinking process and promoting short sulfide bridging between rubber macromolecules, zinc oxide is an essential activator in the rubber industry. However, soluble zinc compounds are classified as toxic to aquatic species, and from an ecological point of view, reducing the ZnO content in rubber products is advisable. The release of zinc from rubber into the environment occurs during the production, decomposition, and recycling of rubber products and the use of rubber products because these products are prone to wear. Given the great importance of zinc oxide for the sulfur vulcanization process, it is necessary to investigate and study the possibilities of a reasonable reduction in ZnO levels in rubber compounds. One solution may be to replace macro ZnO particles with ZnO nanoparticles.

This paper aims to examine the influence of the size (macro and nano) and content of nano zinc oxide particles on the crosslinking process of composites based on natural rubber. Conventional micro ZnO is dosed in an amount of about 4 phr into a mixture based on natural rubber. In addition to the standard macro ZnO used in the rubber industry, mixtures with different nano ZnO content (0.5; 1 and 2 phr) were prepared. All samples were mixed in a laboratory mixer at 90 °C. The crosslinking processes of the rubber compounds were monitored using a rheometer at 150 °C for 15 minutes. It was concluded that with the increase of the share of nano ZnO in the rubber mixture, the value of the minimum torque increases, which tells us that the physical interactions of filler-filler and filler-rubber in the system before the crosslinking process are more pronounced. The maximum torque values, Mmax, increase with increasing ZnO content, which indicates that the degree of crosslinking increases with increasing zinc oxide content. Nano ZnO particles are more efficient than macro ZnO due to their larger specific surface area, so 2 phr nano ZnO is enough to achieve relatively close Mmax values in the system with 4 phr macro ZnO. The differences in the start time of crosslinking are not significant.

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Composite materials based on intercalate compounds of titanium dichalcogenides.

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The intercalation compounds M_xTiX_2, where M–intercalated metal, X = S, Se, Te, may be considered as solid solutions with a limited stability range. When the boundary of stability is exceeded, the decay of homogeneous state with extraction of intercalated metal as an individual phase is observed. These layered intercalated compounds have a notable feature - high anisotropic intercalant diffusion coefficients D. In the temperature interval 400-800 °C the ratio $D_{\|}/D_{\perp}$ is in order of 10^5–10^3, where $D_{\|}$ and $D_{\perp}$ are diffusion coefficients along and across the basal planes of the lattice, respectively. This circumstance causes the entire extracted metal remains within the same interlayer space. Moreover, the host lattice dictates a specific flat shape for inclusions with a few angstrom thickness within the interlayer space.

Anisotropy D also leads to anisotropy of the crystal growth rate along and across the basal plane. This opens up the possibility of forming a “dynamic” composite consisting of nanoinclusions of intermediate compounds trapped in the interlayer space of the layers of the growing crystal of the host lattice.

In this work, variants of the formation mechanism of nano-composites obtained by the decomposition of a solid solution and "dynamic" composites are considered. The results of studying such composites by scanning and transmission electron microscopy, spectral microscopy (SPEM), and time-resolving X-ray diffraction analysis (diffraction cinema) are presented. The results of a study of the macrophysical properties, first of all, the magnetic susceptibility of the described composites, are presented.

As an example, the formation of highly coercive $Fe_3Se_4/TiSe_2$ composites, superconducting $FeSe/TiSe_2$ composites, and "dynamic" $CrSe_2/ZrSe_2$, $Ni_5Se_4/(Fe,Ni)_{0.25}TiSe_2$ composites is considered.

High performance n$^+$-Ge/p$^+$-Si(001) junction for near-infrared Light Sensing formed using HW CVD

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In the present abstract we report on the growth of the n$^+$-Ge:P layers on p$^+$-Si(001) substrates on fabrication of phototype LED's based on these ones. The n$^+$-Ge/p$^+$-Si(001) heterestructures were grown by Hot Wire CVD. The Si(001) substrates heavily doped with B were annealed at~1000°C for 10 min. After wards, the p$^+$-Si buffer layer of ~0.2μm in thichness heavily doped with B were deposited at the substrate temperature $T_S \approx 700$°C. The B concentration in the Si buffer layer was $\approx 2 \cdot 10^{19}$ cm^{-3}.

The n$^+$-Ge:P layers were grown at $T_S \approx 325$°C letting monogermane (GeH_4) into the growth chamer up to the partial pressure of $\approx 4 \cdot 10^{-4}$ Torr. GeH_4 was cracked pyrolytically on the surface, of Ta strip hearted up to 1400°C. This way, a flow of Ge atoms onto the substrate was formed. The Ge layers the thickness 0.6-1.0μm were doped with P from P_2 molecular beam obtained by the sublimation from the surface of a GaP bulk placed inside a effusion cell.

The prototype mesa light emitting diode (LED) with rectangular mesas of 1800×1200μm^2 in size windows for the light were fabricated. The mesa-LED's demonstrated the room-temperature electroluminescence with the pick emission photon energies ≈0.61 eV related to the indirect (photon- assisted) interband optical transitions in the n$^+$-Ge:P layers. The EL intensity increased with increasing P concentration in the n$^+$-Ge:P layers. The low-temperature of depolisition of the n$^+$-Ge:P layers in the HW CVD process (325°C) favors the Si-based QEIC's monolithic integration of such EDS.

Electric and magnetic states of $PrBaMn_2O_6$ double manganite under high pressure

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Double manganites RBaMn$_2$O$_6$ (R – rare earth) are built as a sequence of RMnO$_3$ and BaMnO$_3$ cubic perovskite cells in *c*-direction forming resulting tetragonal cell. In spite of ordinary manganites the temperatures of magnetic phase transition are much higher; that makes these materials perspective magnetoresistors, sensors, magnetocalorics *etc.* As for ordinary manganites the properties of double manganites are formed as a result of competition between the AFM superexchange and the FM double interaction in Mn-O subsystem. The temperatures of magnetic and electric phase transitions changes when type of R-element varies, so some size effect is present. The size effect may by tuned by applying of the external pressure. We performed neutron diffraction in temperature range 50 – 320 K and pressure range 0 – 5.2 GPa for $PrBaMn_2O_6$ as magnetic and electric phase transitions at ambient pressure for this compound were studied previously [1].

Only without external pressure single phase ferromagnetic state was observed. External pressure leads to AFM insulating state already at 320 K. For the same sample we measured ac-specific heat, magnetic susceptibility and electric conductivity in the pressure range 0 – 5 GPa. The results show the presence of ferromagnetic conducting state at high temperature for all pressure values. We explain the results as a presence of ferromagnetic conducting clusters in antiferromagnetic insulator matrix at external pressure.

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Production of high-density ceramics based on aluminum oxide by free sintering

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The structure of powder blanks is always heterogeneous, which is due to the presence of a certain proportion of agglomerated particles in the initial powder. When sintering such workpieces, various types of heterogeneity of the structure lead to selective compaction, the development of internal stresses and the appearance of crack-like defects that reduce the strength properties of the manufactured ceramics.

The aim of the study was to obtain ceramics based on Al_2O_3 containing a minimum number of structural defects. Ceramics were obtained by free sintering of blanks obtained by uniaxial pressing of the initial powder and blanks obtained by deposition of electrostatically stabilized suspensions. The sintering temperatures were 1100 °C, 1250 °C, 1400 °C, 1550 °C, the heating rate was 2.5 °C/min, there was no isothermal exposure. For the preparation of suspensions, HNO_3 solution and Al_2O_3 powder with a dispersion of 200 nm were used. The resulting suspension was subjected to ultrasonic treatment followed by centrifugation. The microstructure of ceramics was studied by the SEM method using a Jeol JSM-6490 microscope, microhardness measurements were carried out on an automatic Qness 60A+ hardness tester, density was measured by hydrostatic weighing.

It is shown that the relative density of ceramics obtained by uniaxial pressing does not exceed 97,02%, while the density of ceramics obtained by precipitation of suspensions is 99,2% At different sintering temperatures, the density of the colloidal sample is higher than the density of the pressed sample by 10,14% at 1100 °C and by 1,94% at 1550 °C.

The microhardness value of the sample obtained by uniaxial pressing is 18.2 GPa, and that of the sample obtained by precipitation of suspensions is 18.9 GPa.

Thus, the removal of agglomerated powder particles by stabilization makes it possible to achieve high uniformity of structure and high density values under free sintering conditions.

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$Sr_{0,61}Ba_{0,39}Nb_2O_6$/MgO (001) film: determination of the refractive index and thickness from the transmission spectrum

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This paper presents the spectrophotometric results for barium-strontium niobates $Sr_{0.61}Ba_{0.39}Nb_2O_6$ (SBN-61) thin films deposited on MgO (001) crystalline substrates.

To determine the optical parameters of transparent films, such as thickness, refractive index and its dispersion, optical transmission spectra are used. SBN-61 films were grown by RF-cathode sputtering of a ceramic target with a stoichiometric composition of SBN-61 on single-crystal MgO (001) substrates. The deposition time of SBN-61 on MgO was 115 min. The optical transmission spectra of the films were recorded in the wavelength range 350–1000 nm on a ELLIPS-1991 spectrophotometer at room temperature. The optical transmission spectra of SBN-61 thin films, which demonstrate the possibility of determining the order of interference at a wavelength $\lambda = 633$ nm ($m = 3$), are shown in Fig. 1. At the points of maxima, the value of the refractive index was estimated after finding the average value of the film thickness.

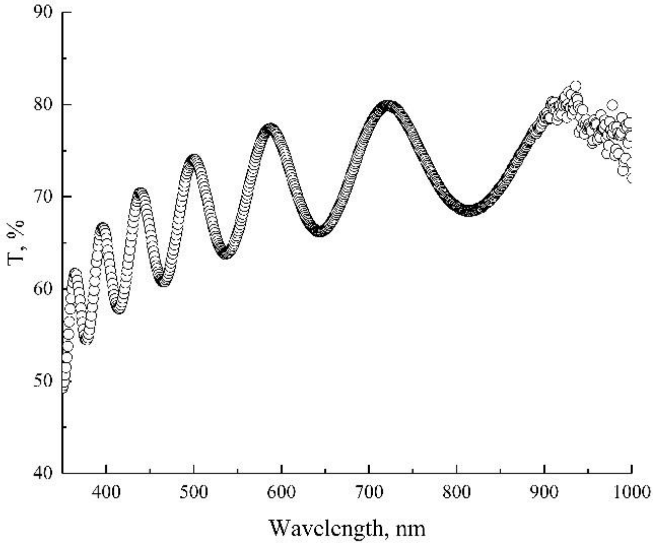

Fig. 1. Film transmission spectra for deposition time 115 min

The refractive index value obtained from the transmission spectrum is 2.3, and the film thickness is about 600 nm.

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Исследование коррозионной стойкости ультрамелкозернистой аустенитной стали 08Х18Н10Т полученной методом РКУ-прессования

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Исследована микроструктура, механические свойства и коррозионная стойкость при комнатной и повышенной температурах образцов ультрамелкозернистой (УМЗ) стали 08Х18Н10Т, полученной методом равноканального углового прессования (РКУП) при температурах 150 и 450 °С. В результате исследований методом Тафеля определяли значения плотности тока коррозии ($i_{кор}$), потенциал коррозии ($E_{кор}$) и рассчитывали скорость коррозии ($V_{кор}$). Испытания на стойкость против межкристаллитной коррозии (МКК) проводили электрохимическим методом по ГОСТ 9.914-91, а также стандартным методом кипячения по ГОСТ 6232-2003. УМЗ сталь обладает высокими значениями предела текучести и предела прочности, а также хорошей пластичностью. Показано, что в УМЗ стали наблюдается снижение коэффициента Холла-Петча, обусловленное фрагментацией частиц δ-феррита при РКУП. РКУП приводит к повышению скорости общей коррозии, при этом образцы УМЗ сталей обладают высокой стойкостью к МКК (см. табл. 1). Установлено, что снижение коррозионной стойкости УМЗ стали обусловлено увеличением объемной доли мартенсита деформации при РКУП.

Таблица 1. Результаты электрохимических коррозионных испытаний образцов крупнозернистой и УМЗ стали

Режим обработки стали методом РКУП		Результаты испытаний по методу Тафеля			Испытания методом потенциодинамической реактивации по ГОСТ 9.914-91		Испытания на МКК по ГОСТ 6232-2003
		$E_{кор}$, мВ	$i_{кор}$, мА/см^2	$V_{кор}$, мм/год	$K_{мкк}$, 10^4	Характер коррозии	Характер коррозии
Исходное состояние		-403	0.073	0.58	0.93	МКК	МКК или питтинги
T=150°C	$N_{ркуп}$=1	-402	0.072	0.56	1.64	Общая коррозия	Питтинги
	$N_{ркуп}$=2	-403	0.083	0.64	1.96	Общая коррозия	Питтинги
	$N_{ркуп}$=3	-404	0.084	0.65	2.07	Общая коррозия	-
	$N_{ркуп}$=4	-404	0.084	0.65	2.34	Общая коррозия	-
T=450°C	$N_{ркуп}$=1	-404	0.092	0.71	2.78	Общая коррозия	Питтинги
	$N_{ркуп}$=2	-406	0.084	0.64	3.25	Общая коррозия	-
	$N_{ркуп}$=3	-406	0.099	0.77	2.41	Общая коррозия	-
	$N_{ркуп}$=4	-403	0.097	0.75	2.22	Общая коррозия	-

Работа выполнена при поддержке Минобрнауки России (проект Н-498-99_2021-2023 в рамках Программы «Приоритет-2030» ННГУ).

Перовскиты как база синтеза комнатнотемпературных сверхпроводников

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Вскоре после открытия явления сверхпроводимости (1911 г.) в металле (Hg) при $T \sim 4$ K, встала проблема поиска материалов с более высокой (вплоть до комнатной $T \sim 300$ K) температурой сверхпроводящего перехода $T_{c,}$, Эта проблема рассматривалась акад. В.Л.Гинзбургом как вторая по важности после термоядерного синтеза, т.к. ее решение дало бы возможность передавать энергию через линии электропередачи без тепловых потерь, вследствие отсутствия сопротивления у таких проводов. Хотя предпринимались экспериментальные попытки найти такие материалы, однако теория этого явления появилась только в середине 1950-х (Бардин, Купер, Шриффер (БКШ)). Оказалось, что электроны проводимости, обеспечивающие проводимость металла в нормальном состоянии ($T > T_c$), объединяются в куперовские пары при $T < T_c$ за счет взаимодействия с колебаниями атомной решетки (фононами), что приводит к исчезновению сопротивления металла – сверхпроводимости (СП). Такая картина позволила Литтлу (1964 г.) выдвинуть идею о синтезе органического сверхпроводника с высокой T_c за счет взаимодействия электронов проводимости с волнами поляризации (экситонами), характерная энергия которых существенно больше температуры Дебая при фононном механизме (БКШ). Эта идея была основана на структуре молекулы ДНК – проводящая нить, окруженная сильно-поляризующейся изолирующей оболочкой. Эта идея привлекла внимание многих химических лабораторий в мире. Первым органическим сверхпроводником стало соединение tetramethyl-tetraselenafulvalene-hexafluorophosphate (TMTSF)2PF6, открытое в 1979 г. Однако, несмотря на большие усилия, появление нового журнала «Synthetic metals», величина T_c в органических металлах к 1986 г. оставалась невысокой (~ 15 K). Появление в том же году СП в неорганических соединениях типа перовскита при $T_c > 40$ K (LSCO) (а затем и 77 K (YBCO)) определило интерес большинства лабораторий. Тремя годами позже нами были получены свидетельства того, что сверхпроводящему переходу при высокой температуре (ВТСП) в этих слоистых материалах предшествует магнитный (АФ ВСП) фазовый переход, приводящий как к частичной диэлектризации поверхности Ферми, так и к формированию периодической страйп-наноструктуры в проводящих CuO_2-плоскостях. Первый механизм приводит к умеренному росту T_c за счет роста плотности состояний на краях диэлектрической щели (псевдощели) на поверхности Ферми (механизм Келдыша-Копаева, 1964). Второй механизм обеспечивает резкий рост T_c за счет реализации экситонного механизма Литтла-Гинзбурга в страйп-наноструктуре оксидов меди (планарный «сэндвич Гннзбурга). Представлена возможность комнатнотемпературной сверхпроводимости в перовскитах с более высокой температурой Нееля. Проведено сравнение последовательности магнитного и только затем сверхпроводящего перехода в органических сверхпроводниках и оксидах меди.

Экспериментальное исследование термической стабильности проводниковых алюминиевых сплавов Al-0.5Mg-Sc

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В качестве объектов исследования выступали сплавы Al-0.5вес.%Mg-XSc (X = 0.2, 0.3, 0.4 вес.%), полученные методом индукционного литья (литейная машина INDUTHERM VTC-200) с последующей деформацией методом ортогонально-углового прессования (ОУП) при температуре 225°C и путем комбинации метода равноканального углового прессования (РКУП) и ОУП. В процессе исследования определяли средний размер и объемную долю рекристаллизованных зерен, микротвердость и удельное электросопротивление в зависимости от температуры 30-минутного отжига.

Показано, что увеличение содержания Sc в сплавах приводит к увеличению микротвердости с 350±10 МПа (0.2вес.%Sc) до 370±10МПа (0.4вес.%Sc). Установлено, что ОУП приводит к повышению микротвердости в 1.5-2 раза. Микротвердость образцов после РКУП в пределе погрешности совпадает с микротвердостью сплавов после ОУП.

Исследования УЭС показывают, что при увеличении содержания Sc величина УЭС повышается от 3.40 мкОм·см (0.2вес.%Sc) до 3.82 мкОм·см (0.4вес.%Sc). Установлено, в процессе отжига наблюдается уменьшение удельного электросопротивления, что связано с распадом твердого раствора Sc и выделением частиц.

Проведены экспериментальные исследования процесса рекристаллизации при отжиге (30 мин.) данных деформированных алюминиевых сплавов. Обнаружено, что температура начала рекристаллизации данных сплавов весьма высока и составляет 425-450°C. После отжига (30 мин.) при температуре 475°C средний размер рекристаллизованного зерна порядка 3 мкм, объемная доля рекристаллизованного зерна не превышает 5%. Отметим, что это достаточно неожиданный результат, поскольку температура начала рекристаллизации в мелкозернистых сплавах Al-Mg-Sc обычно не превышает 300 °C.

Были проведены исследования однородности макроструктуры и H_V по длине заготовки. Обнаружено, что края заготовки ~20 мм имеют крупнозернистую структуру.

Для объяснения полученных результатов проведен анализ механизмов распада твердого раствора при отжиге литых и мелкозернистых алюминиевых сплавов.

Работа выполнена при поддержке гранта РНФ №20-19-00672.

SECTION 2. CHEMISTRY OF MATERIALS

Creation of new biomaterials based on biogenic collagen from fish skins

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Collagen is one of the most common fibrillar proteins and performs a large number of mechanical functions, in particular in animals, as well as in representatives of marine fauna, such as fish. It consists of the main part of tendons and ligaments, most of the organic matrix in bones and dentin, is contained in the skin, arteries, cartilage and, in general, in most tissues in the extracellular space. [1]. Despite the rather large amount of experimental data, the technology of obtainig of fish products requires the deepening and expansion of scientific data substantiating the functional and technological properties of collagen substances, the conditions for obtaining various forms and varieties of application in various sectors of the economy [2].

Fish collagen hydrolysate was isolated by pouring pre-cleaned skins with sodium hydroxide, followed by neutralization with acetic acid. The collagen dispersion was subjected to freeze-drying process for 24 hours at -70 C. As a result, collagen sponges with high porosity were obtained.

A physicochemical study of the obtained samples was carried out using X-ray diffraction and IR spectroscopy. A comparative analysis with a commercial sample showed that the obtained collagen is not inferior in chemical properties to the products presented on the market. In the future, it is planned to use fish collagen to produce biocomposite materials with various inorganic compounds.

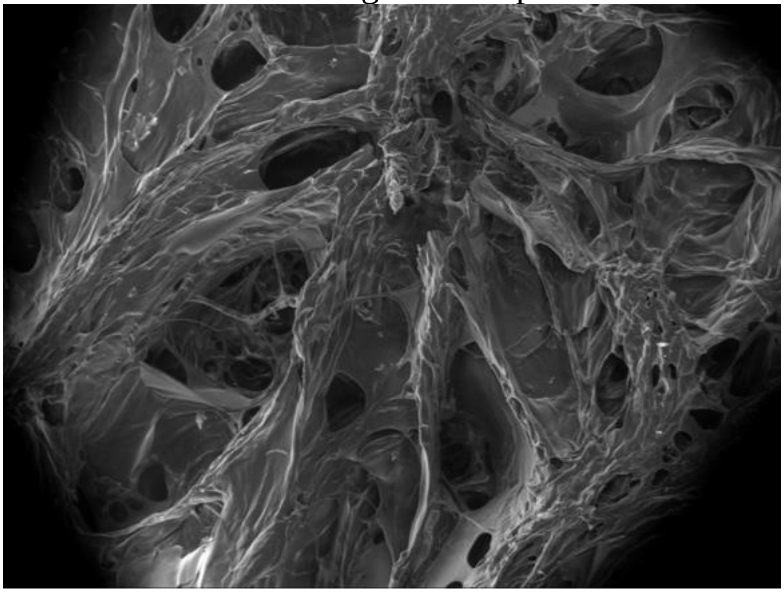

Fig. 1. Microphotograph of collagen sponge obtained from fish skins.

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Hydrolytic stability of ceramics based on $CsZr_2(PO_4)_3$ in various environments. Study of the influence of the contact environment on the composition and microstructure of the near-surface layer of ceramics

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One of the important tasks of modern radiochemistry is the management of high-level waste accumulated over many years of nuclear power operation. The structure of kosnarite is one of the most promising and studied matrices for the immobilization of various high-level waste fractions. It is stable over a very wide range of cationic substitutions in all crystallographic positions. In addition, compounds with the kosnarite structure have high hydrolytic and radiation stability.

The aim of this work was to study the hydrolytic stability of ceramics based on $CsZr_2(PO_4)_3$ phosphate with the kosnarite structure at 90°C in various environments.

The $CsZr_2(PO_4)_3$ compound was obtained by the sol-gel method. The final synthesis temperature was 900°C. Powder sintering was carried out in graphite molds in vacuum (6 Pa) using the Dr. Sinter model SPS-625 at a temperature of 1200°C and a pressure of 70 MPa without isothermal exposure. The phase composition of the resulting powders and ceramics was studied by XRD using a Shimadzu LabX XRD-6000 diffractometer. A JEOL JSM-6490 scanning electron microscope was used to evaluate the ceramic microstructure parameters before and after testing. The near-surface layer of ceramics before and after hydrolytic tests was studied using the SIMS method on a secondary ion mass spectrometer TOF.SIMS 5 (Germany).

The hydrolytic stability of ceramics was studied in a static mode at 90°C in distilled and mineralized water, as well as in slightly acidic and slightly alkaline media. The content of elements that passed into solution during leaching was determined by ICP-MS on an ELEMENT 2 high-resolution mass spectrometer (Thermo Scientific, Germany) using external calibration. In the course of the work, the influence of the contact environment on the rate of cesium leaching, as well as on the composition and microstructure of the near-surface layer of ceramics was studied, and the mechanisms of cesium leaching were determined.

The study of the surface of the samples before and after hydrolytic testing was carried out in the laboratory for diagnosing radiation defects in solid-state nanostructures of the IPM RAS with the support of the Ministry of Science and Higher Education of the Russian Federation (state assignment No. 0030-2021-0030). The equipment of the Central Collective Use Center of the IPM RAS "Physics and Technology of Micro- and Nanostructures" was used.

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Thermodynamics parameters of complex formation between rutin and quercetin with 2-hydroxypropyl-β-cyclodextrin in water-ethanol solvents

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Natural polyphenolic compounds-flavonoids have antioxidant properties, which mainly explains their biological significance and the importance of studying their properties as well as widespread use in medicine. Rutin (Rut) belongs to the class of flavonoids and, being a non-toxic and non-oxidizable molecule, has a number of advantages when used in pharmaceuticals over other flavonoids similar in structure. The low solubility of rutin in water imposes restrictions on its use. Such limitations can be removed due to complexation with macrocyclic oligosaccharides – cyclodextrins (CD). Unique solubilizing and selective properties, low toxicity and commercial availability determine their large and promising use in pharmaceuticals, cosmetics, and textile productions, bioorganic and analytical chemistry. The thermodynamic parameters of the complexation between rutin (Rut) and hydroxypropyl-β-cyclodextrin (HP-β-CD) in water-ethanol solvents ($\lg K$, $\Delta_r H$, $\Delta_r G$, $T\Delta_r S$) were calculated from isothermal titration calorimetry data in water-ethanol solvents with a content of ethanol 0.05 and 0.10 mol. fractions. Calorimetric experiments were carried out on a TAM III calorimeter system (TA Instruments) with a 20 mL reaction cell (microcalorimeter) and a titration module at T = 298.15 K. The values of $\lg K$ [Rut⊂HP-β-CD] obtained in this work decrease with an increase in the ethanol content in the solvent: $\lg K = 3.3$ ($X_{\mathrm{EtOH}} = 0.05$ mol.fr), $\lg K = 2.7$ ($X_{\mathrm{EtOH}} = 0.1$ mol.fr). The obtained enthalpy values are: $\Delta_r H = -16.0$ kJ/mol ($X_{\mathrm{EtOH}} = 0.05$ mol.fr), $\Delta_r H = -11.0$ kJ/mol ($X_{\mathrm{EtOH}} = 0.1$ mol.fr). The comparison of obtained data with thermodynamic parameters of complex formation between flavonoid quercetin (QCT) with HP-β-CD was carried out. The stability of the [QCT⊂HP-β-CD] complex varies from $\lg K$ 3.8 in water to $\lg K$ 3.3 in a solvent of 0.2 mol. fr. ethanol [1]. A decrease in the stability of both [QCT⊂HP-β-CD] and [Rut⊂HP-β-CD] was observed with an increase of EtOH concentration in the solvent and it is controlled by the enthalpy factor. The increase in the entropy contribution to the change in the Gibbs energy of the complex formation reactions is probably caused by an increase in the number of free water molecules as a result of the desolvation of Rut, QCT and HP-β-CD in aqueous ethanol solvents.

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Research of Ho^{3+} coordination compounds with amino acids

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The interaction of lanthanide ions with biologically active ligands is of great importance for the understanding and development of new organometallic frameworks (MOFs). In general, hybrid compounds can be used as sensors, gas storages, luminescent materials, catalysts, drug delivery systems, wireless charge transfer systems, and in thin film devices [1]. The success of lanthanide-amino acid complexes depends on stability, which is critical to ensure that the complex can reach the target point without change. Secondly, the structure of the complex is very important in determining the behavior of the agent in vivo. For example, the coordination number, the presence of coordinated water, and the formation of multinuclear particles can drastically change the usefulness of a compound. Significant progress has been made recently in the coordination chemistry of lanthanides. In particular, our group obtained a complex of holmium perchlorate with glycine with the formula $[Ho(Gly)_3 \cdot 2H_2O](ClO_4)_3$ (fig.1) in the form of a single crystal, which crystallized in the triclinic system with the space group $P\bar{1}$. The crystal was obtained by isothermal evaporation of a saturated aqueous solution of Ho_2O_3 oxide.

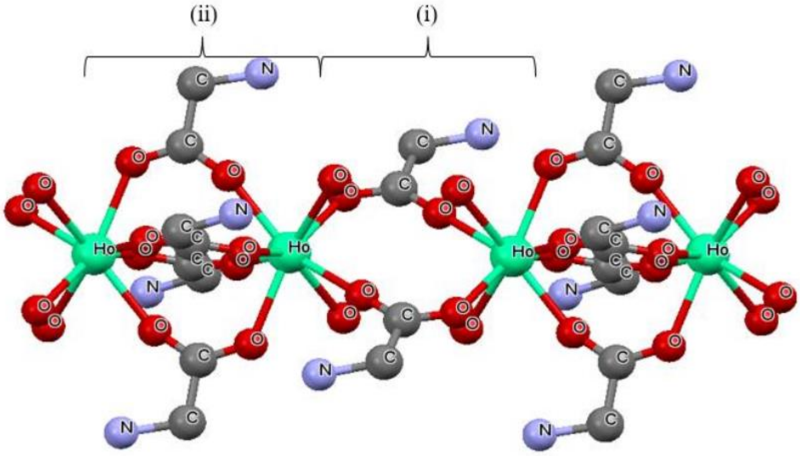

Fig. 1. Structure of $[Ho(Gly)_3 \cdot 2H_2O](ClO_4)_3$, (i) - double bidentate bridge $(\mu_2\text{-}\eta^1\eta^1)_2$, (ii) - quadruple bidentate bridge $(\mu_2\text{-}\eta^1\eta^1)_4$

In the future, it is planned to synthesize the complex of holmium chloride with aspartic acid $[Ho(Asp)(H_2O)_5]Cl_2 \cdot H_2O$, obtained earlier [2], to study the thermal stability in the temperature range $150 \leq T \leq 500$ K in order to study the stability of Ho3+ crystals. The obtained data will expand theoretical and experimental knowledge in the field of obtaining and behavior of complexes based on lanthanides.

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The effect of carbon contamination and temperature gradient on the phase composition of ceramics produced by spark plasma sintering

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The temperature gradient and overheating of the contact surfaces of the graphite mold and the sample is possible during spark plasma sintering (SPS) due to rapid heating.. It can lead to the carbon contamination from the surface of the mold into the sample, which can cause significant changes in the phase composition and degradation of the obtained material properties.

Ceramic samples produced from Si_3N_4 powder (purity: 99.6%, 90% wt. α-Si_3N_4, dispersity <5 μm, Alfa Aesar, Germany) with Y_2O_3 – Al_2O_3 additive (molar ratio 3:5) in the amount of 3 (sample 1), 5 (sample 2), 10 (sample 3) and 15% wt. (sample 4) have been studied.

Ceramic samples were obtained by SPS method on Dr. Sinter model SPS-625 under 70 MPa and at heating rate 100°C/min until the end of sample shrinkage. It was reached at 1900, 1890, 1710, 1630°C for samples 1-4 respectively. The relative density of all obtained samples exceeded 95.5%.

The phase composition of the ceramic samples was studied layer-by-layer using X-ray phase analysis (XRPA) on a XRD-7000 diffractometer (Shimadzu, Japan) (CuKα, $\lambda = 1.54$ Å). Investigation of each layer was performed in the range of 2θ from 15° to 70°, scanning step was 0.04°, exposure time was 2s. Each surface layer was formed by sample grinding with diamond disks on a Secotom-10 (Struers, Denmark). The thickness of the removed layer (not less than 60 μm) exceeded the depth when the X-ray beam intensity decreases by *e* factor (~40 μm for Si_3N_4).

SiC phase was detected in the near-surface layers of the ceramics, which is probably due to the carbon diffusion from the mold. Si phase was also detected, which is probably related to the overheating near the contact sample surface with the mold, which caused the decomposition of Si_3N_4 (> 1600°C) [1].

Only β-Si_3N_4 phase was detected in layers exceeding 140 μm in depth in samples 1 and 2/. In addition to β-Si_3N_4 phase, α-Si_3N_4 phase was detected in samples 3 and 4.. The α/β ratio for each sample is constant, which indirectly suggests an insignificant temperature gradient.

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Three-phase region with a change of metatectic reaction for the peritectic one in the system Cu-Ni-Mn

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Three-phase equilibrium in the isobaric ternary system could be either a eutectic type – with the both solid phases mass increasing, or a peritectic type – with the one solid mass decreasing. First method to check the terms for the change of three phase transformation type (Fig. 1) was named as a tangent method [1, 2]. Though it's correctness was restricted for the cases with the solubility in solids yet in 1945 [3], for the long time this method was preferable [4-8]. Some attempts were made to improve the tangent method [8, 9].

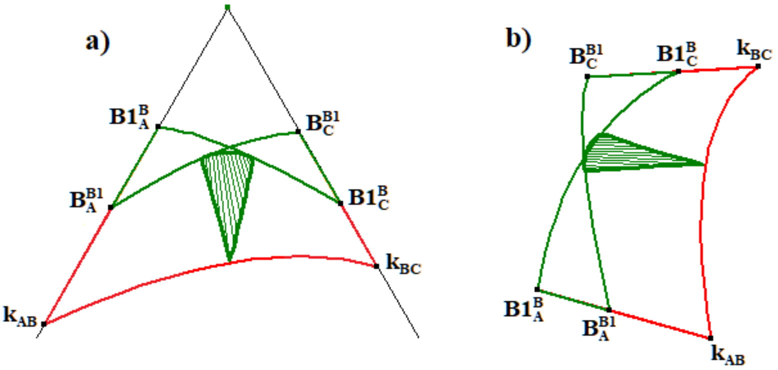

Fig. 1. 3-Phase region with a change of metatectic reaction for the peritectic one (in green – a surface of 2-phase reaction) in the system Cu-Ni-Mn = A-B-C: x-y projection - a), axonometry - b)

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Synthesis and properties of phosphate-based ceramic materials of alkali, 2-valent metals and zirconium

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The development of materials with certain characteristics is an important branch of inorganic chemistry and contributes to the success in the development of modern materials science. Among them are compounds having the structure of the mineral kosnarite $KZr_2(PO_4)_3$ (synthetic analogue - $NaZr_2(PO_4)_3$, NZP) and $Sc_2(WO_4)_3$ (SW), forming large families of structural analogues due to the inclusion of various cations in their composition in various crystallographic positions. Materials based on them have high ionic conductivity, chemical and radiation resistance, low coefficient of thermal expansion.

In the present work, we have studied the phase formation, thermal expansion, and electrical conductivity of the phosphates $A_{1+2x}M_xZr_{2-x}(PO_4)_3$ (A – Li, Na; M – Zn, Mg, Ni, Mn, Co). The compounds were synthesized by sol-gel method and studied by powder X-ray diffraction, including studies in wide temperature range (298 - 473 K). The electrical conductivity was studied by the impedance method in the interval 423 - 773 K.

The results obtained indicate the formation of limited solid solutions in the studied systems. Li-containing phosphates $Li_{1+2x}M_xZr_{2-x}(PO_4)_3$ (M – Zn, Mg) obtained at the temperatures of 873 - 973 K, had SW structure, and the increase of temperature up to 1073 - 1373 K leaded to their transition to NZP structure. In the $Na_{1+2x}M_xZr_{2-x}(PO_4)_3$ (M – Zn, Mg, Ni, Mn, Co) system, limited solid solutions of the NZP structure were obtained. Temperatures of their synthesis were 873 - 1073 K. Solid solution limits were established.

Thermal expansion of the phosphate $Na_{1.8}Zn_{0.4}Zr_{1.6}(PO_4)_3$ was studied using X-ray diffraction. The temperature dependences of its unit cell parameters were described by linear functions. Significant expansion of the structure along the c axis upon heating is characteristic of NZP compounds containing small cations in the cavities of the framework. With increasing temperature, a decrease in cell parameters a is observed. According to the value of the average coefficient of thermal expansion, the studied compound belongs to the class of medium expanding substances.

The ionic conductivity of the $Na_{1+2x}Zn_xZr_{2-x}(PO_4)_3$ solid solution in the temperature range 423–773 K changes in accordance with the Arrhenius law. The ionic conductivity due to the transfer of sodium cations in interconnected cavities increases with an increase in the carrier concentration.

Synthesis of ball-type и clam-shell magnesium phthalosyanines with oxy-benzene fragments as a bridge substitutes and study of fluorescence properties

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Phthalocyanines have a unique structure that includes four isoindole fragments, due to which these complexes exhibit linear and nonlinear optical properties. Based on the above, compounds of this class can be used to create nonlinear optical materials that protect human eyes and optical devices from laser radiation. Compared to their monomeric counterparts, ball-type phthalocyanines show greater interaction between macro rings, which is reflected in the properties [1]. Compounds of this structure absorb light in the long-wave region of the spectrum, so they can be considered as promising complexes for photodynamic therapy [2]. In addition, their absorption is shifted to the red region of the spectrum, where the transparency of biological tissues is higher, which expands the therapeutic possibilities of the method. However, the compounds of this structure are prone to uncontrolled aggregation, which makes it very difficult to work with these compounds, since most studies are performed in organic and aqueous solutions. In this work we present methods for the synthesis of phthalocyanines with complex structures, such as clam-shell and ball-type phthalocyanines, and study their fluorescent properties. The synthesis was carried out in iso-amyl alcohol solution at the boiling temperature of the solvent using a reflux condenser. Nitriles of various structures and four-water magnesium acetate were used as starting compounds.

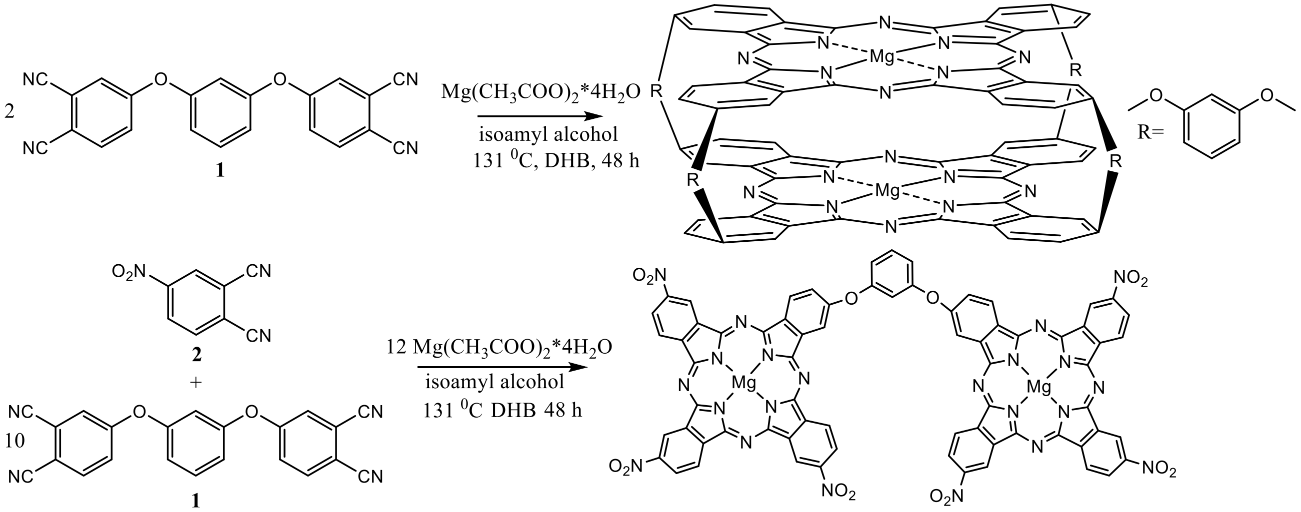

Fig. 1. Sunthesis ball-type and clam-shell magnesium phthalocyanines

This work was supported by the Russian Science Foundation project No 17-73-20017

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Photocatalytic desulfurization of hydrocarbons in the presence of Bi-containing layered perovskites

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The conventional technique to remove sulfur from fuel is hydrodesulphurization (HDS), but this process requires harsh conditions (P = 3–6 MPa, T = 200–450 °C). Another disadvantage is associated with the fact that HDS catalysts have difficulties in the removal of some sulfur compounds, such as dibenzothiophene (DBT) and its derivatives [1]. In this regard, the photocatalytic oxidation of sulfur compounds in mild reaction conditions (ambient temperature and atmospheric pressure) is considered as one of the promising methods to obtain fuels with sulfur content less than 50 ppm. Nowadays, a significant number of photocatalysts, including TiO_2, WO_3, g-C_3N_4, *etc.*, have been proposed for the photocatalytic desulfurization [2].

In this work, the photocatalytic desulfurization of hydrocarbons was investigated in the presence of layered perovskites Bi_2WO_6 and Bi_2MoO_6 as well as their solid solutions $Bi_2W_xMo_{1-x}O_6$ (x = 0.25, 0.50, 0.75). The photocatalysts were prepared by hydrothermal method (160 °C, 12 h) using stoichiometric amounts of $Bi(NO_3)_3\cdot5H_2O$, $Na_2WO_4\cdot2H_2O$, and $Na_2MoO_4\cdot2H_2O$. The model mixture for the desulfurization reaction contained 200 ppm of DBT in *n*-dodecane (10 mL of the mixture, ambient temperature, molar ratio H_2O_2/DBT of 10, catalyst amount of 10 $g\cdot L^{-1}$, 30 W LED lamp as the visible light source). Experimental results are shown in Figure 1. The best desulfurization degree after 120 min of the reaction was obtained using solid solutions $Bi_2W_xMo_{1-x}O_6$ (x = 0.25 and 0.50) as photocatalysts.

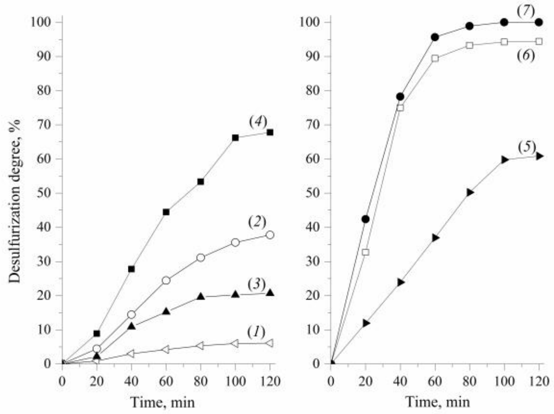

Fig. 1. Photocatalytic activity of Bi-containing perovskites: (*1*) no photocatalyst; (*2*) Bi_2WO_6 (no light); (*3*) Bi_2MoO_6; (*4*) Bi_2WO_6; (*5*) $Bi_2W_{0.75}Mo_{0.25}O_6$; (*6*) $Bi_2W_{0.5}Mo_{0.5}O_6$; (*7*) $Bi_2W_{0.25}Mo_{0.75}O_6$.

This work was financially supported by the Ministry of Education and Science of the Russian Federation (assignment 0729-2020-0053).

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Influence of epoxidized extender oil on properties of natural rubber compounds

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The selection of the best components for the rubber compounding is essential for obtaining rubber products that meet the market requirements. Like reinforcing fillers and other additives, rubber process oil is a highly significant blending component. Due to the toxicity of commonly used mineral extender oils, there is a demand for environmentally friendly oils in rubber compounding. Although eco-friendly, vegetable oils have some less desirable properties compared to mineral oils. They have lower thermal stability and lower solubility parameter. Chemical modifications of vegetable oils, such as epoxidation or transesterification, may help to overcome these issues.

The influence of epoxidized soybean oil on the natural rubber compounding process is determined in this study. Properties of epoxidizes soybean oil as rubber process oil, which were experimentally determined or calculated, have been compared to the properties of soybean oil. The mixing phase of the rubber compounding process was performed on a laboratory internal batch mixer at 90°C and a rotor speed of 60 rpm. The rheological properties of rubber compounds and rubber hardness were determined. Power consumption during the rubber compounding mixing phase was calculated based on experimental data for voltage and amperage changes. Power consumption, parameters related to the compounding process, and properties of obtained rubber compounds, were determined for different contents of epoxidized soybean oil and soybean oil.

The rubber compounds obtained with epoxidized soybean oil were softer, while, as expected, power consumption during the mixing phase was higher compared to soybean oil. Epoxidized soybean oil can be used as rubber process oil during the compounding process at 90°C or above, to obtain rubber with desired properties and prevent separation of unmixed extender oil from the product.

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The influence of hempseed extender oil on natural rubber compounding process

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To obtain a product that meets the requirements of the market, proper selection and ratio of natural rubber compounds are substantial in the rubber industry. Properties of finished products based on natural rubber depend upon blending components, such as additives, antioxidants, vulcanization agents, other reinforcing fillers, and especially the nature of extender oil.

The potential use of hempseed oil as an environmentally friendly extender oil and its influence on the rubber compounding process was examined. Blending was performed by an internal batch mixer at the constant temperature of 90°C and the speed of 60 rpm. Rubber compounds were prepared with a broad range of extender oil content. Their hardness was determined according to ISO 7619-1 standard method. The power consumption of the rubber compounding effective mixing phase was calculated from the experimentally measured voltage and amperage. For the sake of comparison, rubber blends with commonly used naphthenic process oil were prepared under the same conditions.

Power consumption during the mixing process decreases with the increase of extender oil content for hempseed and naphthenic oil. The results showed that hempseed oil could be used in a wide range of oil content as extender oil in rubber blending, even though it shows remotely higher power consumption than naphthenic extender oil during the effective mixing phase. Rubber hardness was decreased by adding extender oils, where samples with hempseed extender oil showed significantly lower hardness at any content oil applied. The statistical method was applied to obtain the equations for the reliable prediction of power consumption and rubber hardness.

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Phosphate-sulfate of eulytite structure as host materials for the immobilization of radionuclides

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The issue of managing spent nuclear fuel and other wastes from the nuclear fuel cycle is an urgent and important task. The study of forms of immobilization of fractionated components of radioactive waste, their use in the form of inorganic crystalline mineral-like compounds is carried out by many scientific groups [1]. Silicates, germanates, phosphates and vanadates with the structure of the eulytite mineral $Bi_4(SiO_4)_3$ are used as the basis for promising Low Temperature Co-Fired Ceramic devices for high-frequency electronic devices, optical isolators − essential components of modern lasers, matrices for solid-state phosphors, their use as crystalline materials for localization of nuclear technology waste is also investigated.
We carried out a targeted synthesis of phosphate-sulfates $MeSr_2Eu(PO_4)_2SO_4$ (Me = K, Rb, Cs) and $Ba_xSr_{4-x}(PO_4)_2SO_4$ ($0 \le x \le 4$) with the structure of the mineral eulytite, including fission products, lanthanides (imitators actinides) and technological elements. The phase formation of phosphate-sulfates was studied, the structure was refined, and thermal expansion was investigated. Phosphate-sulfates were obtained by coprecipitation of salts from aqueous solutions followed by heat treatment. The synthesis temperatures were 1173–1473 K. Phosphate-sulfates $MeSr_2Eu(PO_4)_2SO_4$ and $Ba_xSr_{4-x}(PO_4)_2SO_4$ were characterized by X-ray diffraction (Shimadzu XRD-6000 diffractometer), microprobe analysis (JEOL JSM-7600F microscope with energy dispersive spectrometer), IR- spectroscopy (FTIR-8400 spectrophotometer). Thermal expansion was studied on the same diffractometer using a temperature attachment with a discrete mode of temperature change in the range from 173 to 523 K with a step of 50–100 K. According to XRD data, individual $MeSr_2Eu(PO_4)_2SO_4$ compounds and an continuous $Ba_xSr_{4-x}(PO_4)_2SO_4$ solid solution with the eulitytite structure (sp. gr. $I\bar{4}3d$) are formed. Their neutral framework is formed by wavy chains of distorted MeO_6 octahedra connected by edges, and $(P,S)O_4$ tetrahedra connected to octahedra through vertices. Samples do not undergo polymorphic transitions. The IR-spectra of the phosphate-sulfates by the position and shape of the absorption bands are typical of sulfates and phosphates crystallizing in the eulytite structural type with sp. gr. $I\bar{4}3d$ and indicate the absence of X-ray amorphous impurities. Ceramics $MeSr_2Eu(PO_4)_2SO_4$ and $Ba_xSr_{4-x}(PO_4)_2SO_4$ with the eulytite structure expand isotropically with changing temperature and have thermal linear expansion coefficients $\alpha_a = (11 \div 18) \cdot 10^{-6}$ K^{-1}.

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On the role of phosphate minerals in abiogenic reproducible peptide synthesis

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As part of the research, the properties of organophosphate particles characterized by the presence of nitrogen-containing heterocyclic compounds included in the surface layer were obtained and studied. It is expected that such surface-modified particles will have the ability to selectively bind amino acids (including those with polar side chains) of a certain stereochemical class on their surface, as well as the ability to subsequently reproducibly polymerize bound amino acids into oligomeric macromolecules - peptides with a certain sequence of amino acid residues.

Particles of phosphate minerals (whitlockite $Ca_{2.5}Mg_{0.5}(PO_4)_2$, meryllites $Ca_9MgNa(PO_4)_7$ and $Ca_9MgK(PO_4)_7$) with a branched internal structure providing increased surface porosity and pronounced adsorption properties were obtained by solid-phase synthesis. To study the binding processes of nitrogenous bases (guanine, uracil, adenine) by phosphate particles, their interactions in solvents simulating the abiogenic environment of the Earth's volcanic geolocations of the early Archean era (formamide, NH_3) were considered, as well as the result of direct solid-phase coexistence in the form of a homogenized mixture (with mass ratio phosphate/base = 20/1), pressed at p= 3.5 atm under isothermal conditions (100°C).

The control was carried out by IR spectroscopy (Shimadzu FTIR 8400s). The study of the obtained objects in liquid media did not lead to the discovery of any effects due to the significantly higher intensity of the absorption bands of the solvent. The spectra of dry mixtures recorded in KBr under standardized conditions showed a change in the relative intensity of the absorption bands of nitrogenous bases with time, which can be considered as an indirect confirmation of adsorption processes on the phosphate matrix.

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Creation of a composite material based on marine collagen and methyl methacrylate by photopolymerization in the presence of complex oxides $CsTeMoO_6$ and $RbTe_{1.5}W_{0.5}O_6$

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The development of new biomaterials to replace damaged or lost organ tissues is one of the urgent problems of regenerative medicine. The creation of composite materials based on natural polymers and synthetic monomers solves the dilemma that arises when developing biomaterials: the use of biopolymers leads to good biocompatibility of materials, but to low strength characteristics, while synthetic materials are characterized by good physical and mechanical properties, but do not have biological activity. Photocatalytic reactions under the influence of visible light attract attention due to compliance with the principles of green chemistry and a wide range of possibilities for their use, namely the possibility of carrying out the reaction at room temperature, the absence of fragments of an organic initiator in the system, etc. Recently, oxides of a number of metals have become the most widespread, capable of catalyzing reactions when irradiated with visible light, rather than ultraviolet [1]. The purpose of this work is to implement MMA grafting on the surface of cod collagen under visible light irradiation of a complex oxide $CsTeMoO_6$ and to compare the characteristics of the most important properties of the resulted graft copolymer with those for the graft copolymer MMA-collagen obtained earlier $RbTe_{1.5}W_{0.5}O_6$ [2]. Graft copolymerization was carried out in an aqueous emulsion. Grafting onto a natural polymer is carried out due to the reaction of radical substitution with a hydroxyl radical, which is formed when irradiated with visible light (λ=400-700 nm) of a complex oxide. The obtained results of GPC and CHNS analysis, along with an increase in the polymer mass after grafting in the aqueous phase of the emulsion by 5-7%, indicate the production of the graft copolymer MMA-collagen in the case of using both complex oxides. By scanning electron microscopy, when comparing lyophilically dried sponges of samples, a similar structural and relief organization of composites was established.

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A brief study for monocrystal structure of lanthanides with alanine compounds

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Lanthanides are widely used in different fields of medical treatment and diagnostics. They are considered to be the best contrast enhanced agents in medical Magnetic Resonance Imaging and the Gd-complexes especially are routinely used in clinics [1].

A group of lanthanides complexes with alanine where prepared by dissolving lanthanides oxides (La_2O_3, Gd_2O_3, Dy_2O_3, Ho_2O_3, Tm_2O_3, Yb_2O_3) under stirring with heating in a mixture containing concentrated aqueous solution of perchloric acid (0.5 mL) and deionized water.

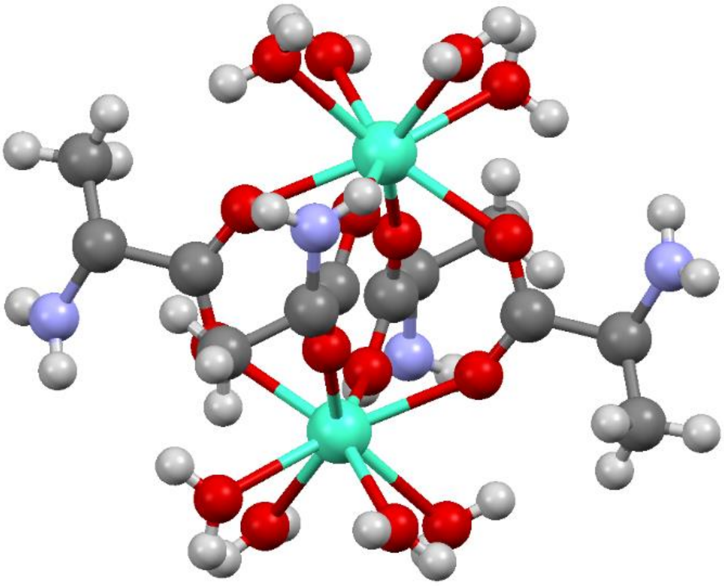

Fig. 1. Molecular structure of $[Gd(Ala)_2{\cdot}4H_2O)]_2(ClO_4)_3$.

The primary structure of gadolinium complexes was determined by structurally invariant direct methods using SHELX. The position of the remaining atoms was determined by differential electron density syntheses and refined by $|F|^2$ by the least squares method.

Single X-ray examination of monocrystals of gadolinium complex $[Gd(Ala)_2{\cdot}4H_2O)]_2(ClO_4)_3$ which was obtained in the monoclinic system at a temperature of 100 k and crystallized in the C 2/c space group, showed that the structure has four bridges between two neighboring gadolinium atoms, and every atom of lanthanide has a coordination number equals to 8, the four bridges are consisting of two atoms of oxygen and one carbon atom by the order (-O-C-O-) formed form the carbocyclic group of alanine.

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Formation enthalpies of common anions of ionic liquids

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Ionic liquids are one of the most promising materials for various branches of industry due to combination of unique properties and ability of fine tuning by selection different types of cations and anions. However the implementation of these compounds in industrial processes needs the knowledge of their thermodynamic properties. The latters are still very scanty, especially ion properties. This work is devoted to theoretical determination of formation enthalpies of common anions of ionic liquids.

Bis(trifluoromethane)sulfonylimide [NTf_2^-], trifluoromethanesulfonate [TfO^-], ethyl sulfate [ES^-], and dicyanamide [DCA^-] anions were chosen as the objects under study. Isodesmic reaction approach was applied to evaluate the formation enthalpies. Both DFT (B3LYP, B98, M06, M06-2X) and composite G4 methods were used. Basis set used in DFT calculations was Dunning’s aug-cc-pVTZ. All values were calculated at 298.15 K. Results of calculation are summarized in Table 1.

Table 1. Calculated formation enthalpies, $\Delta_f H°$, and its standard deviations, σ. All values in kJ·mol^{-1}

Method	NTf_2^-		TfO^-		ES^-		DCA^-	
	$\Delta_f H°$	σ	$\Delta_f H°$	σ	$\Delta_f H°$	σ	$\Delta_f H°$	σ
B3LYP	-1983	94	-1287	52	-845	32	71	21
B98	-2037	89	-1320	45	-878	26	90	16
M06	-2027	63	-1357	43	-915	27	63	20
M06-2X	-2092	58	-1329	80	-1117	85	78	22
G4	-2127	62	-1401	27	-957	11	109	17
Ref.	-2103 [1]		-1346±49 [2]					

It was found that DFT/M06-2X gave the best agreement between our calculations and literature data. However this method has the largest uncertainties of values found. Taking into account high accuracy of G4 the $\Delta_f H°$ obtained by this approach can be chosen as recommended.

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Biphenyl as a liquid organic hydrogen carrier: study of the hydrogenation process on supported Pt and Pd catalysts

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Aromatic compounds, such as toluene, diphenyl, naphthalene, etc., are considered as the most promising hydrogen carriers capable of chemically binding it by catalytic hydrogenation. This concept of hydrogen binding and storage has been actively studied in recent decades and is called liquid organic hydrogen carriers (LOHC) [1-2]. To ensure a stable cycle based on LOHC, it is necessary to develop an effective "LOHC-catalyst" system that will be stable for many hydrogenation-dehydrogenation cycles without loss of activity. The diphenyl-based system has a number of advantages, the main of which are low volatility (compared to toluene) and higher stability (compared to heterocycles like N-ethylcarbazole). It is well known that the properties of the catalyst support directly affect its interaction with the metal, the dispersion of the active component, which largely determines the properties of catalysts based on precious metals. In this work, we studied Pt- and Pd-containing catalysts supported on SiO_2, Al_2O_3 and mesoporous silicates SBA-15 and MCM-48. The synthesized catalysts were investigated by the methods of low-temperature nitrogen adsorption, temperature-programmed reduction, and high-resolution transmission electron microscopy. The catalytic properties of the prepared catalysts were tested in liquid-phase hydrogenation of biphenyl in a flow reactor. The results of the study showed that the nature of the carrier has a significant effect on the dispersion, size and location of metal particles. The use of mesostructured silicates (SBA-15 and MCM-48) as carriers makes it possible to increase the dispersion of the active phase in comparison with traditional silica and alumina. Apparently, the diphenyl hydrogenation reaction is structurally sensitive and the higher dispersion of the active phase allows platinum and palladium catalysts to show higher activity in the deep hydrogenation reaction of diphenyl to bicyclohexyl. Pt-containing catalysts exhibit significantly higher activity than Pd catalysts.

This research was funded by the Ministry of Science and Higher Education of the Russian Federation (theme No. AAAA- A12-1111100072-9) as part of the state task of the Samara State Technical University (creation of new youth laboratories).

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Ultrafast Melting Properties of Natural Cyclodextrins

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Natural cyclodextrins (CDs) are a class of cyclic oligosaccharides having molecular cavities. CDs are widely used in pharmaceutics, cosmetics, food and textile industry, catalysis, chromatography. Undoubtedly, such important substances as cyclodextrins require accurate knowledge of fundamental thermodynamic properties: melting points and corresponding enthalpies. Such data are essential for understanding and predicting of properties based on structure-property relationships; for calculations on the energy of the crystal lattice, which has a crucial effect on inclusion properties; for evaluation of the limiting temperatures during the modification of drug complexes by fast heating and cooling. At the same time, the melting points and corresponding enthalpies cannot be measured by conventional methods, since solid CDs decompose without melting at temperatures less than 300 °C.

The present study is focused on the determination of the melting parameters and high-temperature behavior of natural cyclodextrins using fast scanning calorimetry (FSC). Melting points of α-, β- and γ-cyclodextrin were determined for the first time using FSC with heating rates up to 40000 $K \cdot s^{-1}$, also as melting enthalpy of γ-cyclodextrin. The activation energies of thermal decomposition of cyclodextrins were calculated from the temperature dependence at wide range of heating rates.

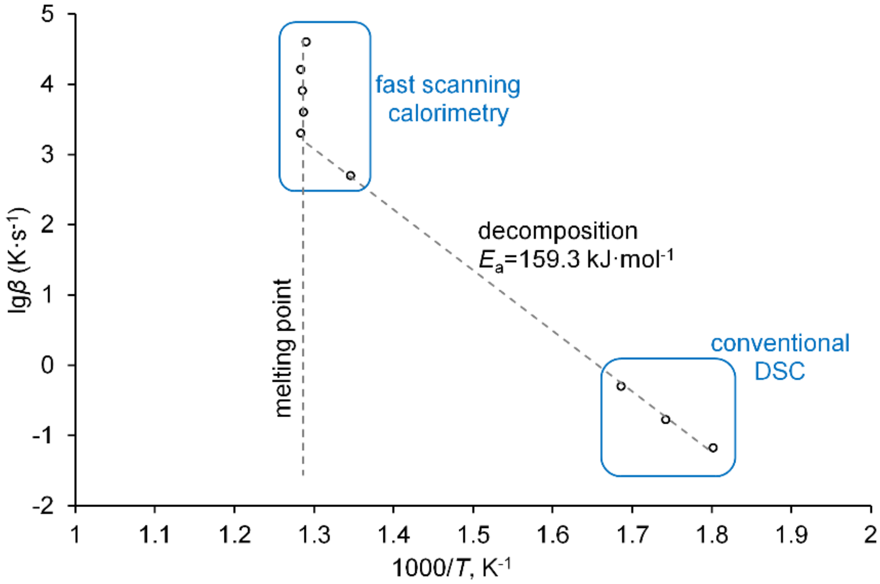

Fig. 1. Dependency of onset temperatures (T) of main exothermic peak for anhydrous α-cyclodextrin on heating rate (β) in Flynn–Wall–Ozawa analysis coordinates.

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Properties of the material of interfacial formations synthesized in the field of mechanical vibration

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Receiving materials with desired properties is the most important area of research and development in nanotechnology. When receiving such materials, an important role belongs to self-organization and self-assembly, which can be controlled by acting on the system with an external force field. The interfacial layer of a heterogeneous liquid system can be considered as an assembler, the possibilities of which for the synthesis of structures with desired properties are great.

This report presents the results of studies on the effect of local vibration on the properties of the material of interfacial formations (MIF) based on di-(2-ethylhexyl)phosphates of *d*- and *f*-elements.

The method of material synthesis, its taken and determination of properties are described in [1]. Synthesized in the field of mechanical vibration of the resonant frequency, MIF has a higher density, melting point, and magnetic susceptibility. With the local supply of mechanical energy of the resonant frequency, the primary contacts between the particles of metal di-(2-ethylhexyl)phosphate are destroyed, which immediately appear due to the thermodynamic instability of the disperse system. The adhesion of smaller particles leads to the formation of a denser material. The x-ray phase analysis data show that a material with a higher degree of crystallinity and a finer crystallite size is synthesized in the vibration. The melting temperature, density, and magnetic susceptibility of MIF based on *f*-elements are higher than in the case of systems with *d*-elements, and for REE of the yttrium group they are higher than in the case of cerium. Apparently, this is due to an increase in the proportion of crystallinity and a higher molar mass of MIF. The electrical conductivity of the material of interfacial formations based on lanthanide di-(2-ethylhexyl)phosphate is mainly due to the presence of water in their composition.

Thus, the spontaneously arising material of interfacial formations based on metal di-(2-ethylhexyl)phosphates, when exposed to vibrations on the interfacial layer, has changed properties, namely, lower electrical conductivity and higher density, magnetic susceptibility, and melting point.

Microscopic study of the structure MIF was carried out with the financial support of 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" number FSSM-2021-0013.

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The In–In_2O_3 system as a low-temperature source of gaseous indium oxide In_2O

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In_2O_3-based nanomaterials are in high demand in modern industry, especially electronics, due to In_2O_3 electrophysical properties. The conjunction of visible light transparency and electrical conductivity makes In_2O_3 thin films a key material for the production of electronic devises. When such materials are required to be of high purity, methods of physical vapor deposition are used. Evaporation techniques involve heating of a target to transfer its material into the gas phase followed by deposition of the film on a substrate. Thus, the thermodynamics of vaporization of the deposited substance is very important for producing of functional materials using evaporation methods. The In–In_2O_3 system was proposed as a low-temperature source of gaseous indium oxide In_2O by analogy with other metal-oxide systems [1]. In the present work, vaporization thermodynamics of the system was investigated by Knudsen effusion mass spectrometry in the temperature range 930–1210 K. The system does not form any compounds and there is a heterogeneous phase field [In(l)+In_2O_3(s)] in the composition range between phases In(l) and In_2O_3(s). An original approach was developed to interpret the mass-spectrum of the vapor over the system and the composition of the equilibrium gas phase was determined. The main vapor species in the [In(l)+In_2O_3(s)] heterogeneous phase field were In(g) and In_2O(g) with the gaseous oxide predomination. Partial pressures of the vapor species in the system and their temperature dependences in the temperature range under study in the whole composition range were found. The oxygen partial pressure in the vapor over the [In(l)+In_2O_3(s)] heterogeneous phase field occurred to be extremely low for experimental determination and was calculated from the equilibrium constant of a gas-phase reaction $2In + 1/2O_2 = In_2O$, obtained from vaporization study of pure In_2O_3 oxide. The enthalpies of several reactions accompanying evaporation of the system were calculated by the second- and the third-law of thermodynamics. The results of these two ways of calculation were in good agreement. The standard enthalpy of formation of the gaseous oxide In_2O at 298.15 K was found to be –31.3 ± 8.7 kJ/mol. A *p-x*-section of the system phase diagram at 1060 K was constructed. The vapor over the [In(l)+In_2O_3(s)] heterogeneous phase field consists of 95% In_2O at 1060 K. Consequently, the In–In_2O_3 system can be used as a low-temperature source of highly concentrated vapor of In_2O.

This work was supported by the Russian Science Foundation (project No. 21-13-00086).

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Phase formation and properties of phosphate ceramics with a high alkali metal content

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An intensive study of framework and layered phosphates is associated with the prospects for their use as ceramics for the immobilization of toxic (including radioactive) wastes. Their important advantage is the possibility of strong fixation of alkali metals in a hardly soluble stable structure.

The purpose of this work is to study the phase formation, crystal structure, thermal and hydrolytic stability of complex iron phosphates and various alkali metals of the form $Na_{3-x}A_xFe(PO_4)_2$ and $Na_{3-x}A_xFe_2(PO_4)_3$ (A – K, Rb, Cs).

The samples were synthesized by coprecipitation of salts from aqueous solutions (final annealing temperatures were 400–750°C) and studied by X-ray diffraction, electron microscopy and microprobe analysis, IR spectroscopy, and differential thermal analysis.

According to the results of the study, limited solid solutions with a structure similar to the mineral glaserite (layered structure) were obtained in the $Na_{3-x}A_xFe(PO_4)_2$ series. The limits of isomorphic miscibility decreased with increasing difference in the ionic radii of alkali metals and amounted to $0 \leq x \leq 0.4$ for the Na–K system and $0 \leq x \leq 0.3$ in the series of Na–Rb phosphates. For samples with A - Cs, isodimorphism was observed with the formation of two rows of solid solutions in the intervals $0 \leq x \leq 0.2$ and $2.5 \leq x \leq 3$. Phosphates $Na_{3-x}A_xFe_2(PO_4)_3$ crystallized in the kosnarite structural type, framework-type solutions in all studied systems were almost the same ($0 \leq x \leq 0.3$).

The crystal structure of the individual compound $Cs_3Fe(PO_4)_2$ obtained for the first time was studied by the Rietveld method using X-ray data (sp. gr. $P\bar{3}m$, $\chi^2 = 1.21$, $a = 5.832(1)$ Å, $c = 7.136(1)$ Å, $V = 210.2(1)$ Å^3). Two types of columns can be distinguished in the crystal lattice of the compound under study: columns of alternating phosphate tetrahedra and cesium ten-vertex columns and columns of FeO6 octahedra and twelve-vertex structures built around the cesium atom.

Thermal expansion and hydrolytic stability of $Cs_3Fe(PO_4)_2$ (glaserite type) and $Na_{2.7}Cs_{0.3}Fe_2(PO_4)_3$ (kosnarite type) samples were studied. It is shown that the studied phosphates are characterized by sufficiently high average thermal expansion coefficients (25–200°C), however, a low degree of expansion anisotropy makes it possible to ensure a uniform increase in the dimensions of finished ceramics. The steady-state rates of cesium leaching from phosphate samples (dynamic mode, Soxhlet extractor, 90°C) amounted to 10^{-3}–10^{-4} g/(cm^2·day), which corresponds to the requirements for matrix materials for immobilization of the radioactive cesium.

Crystal structure of $EuErCuTe_3$

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The compound $EuErCuTe_3$ were prepared by mixing the elements copper, europium, erbium and tellurium in stoichiometric amounts (1:1:1:3 molar ratios) along with CsCl as flux according to the following scheme:

$$Eu + Er + Cu + 3\ Te \rightarrow EuErCuTe_3$$

The crystal structure of $EuErCuTe_3$ telluride synthesized for the first time was determined using single-crystal diffraction data. Compound is of the orthorhombic system space group *Cmcm*. The compound belongs to the $KZrCuS_3$ structural type with unit cell parameters a = 4.3069 (2) Å, b = 14.3093 (8) Å, c = 11.1943 (7) Å. The crystal structure was refined by the Rietveld method using the SHELXL-93 software package. The confidence factors were $wR_2 = 0.0724$ and $R_1 = 0.0291$. Data for the isostructural compound $EuErCuS_3$ were used as the initial model. The Eu^{2+}, Er^{3+}, Cu^{+} ions occupy independent crystallographic positions (Fig. 1). Distorted tetrahedrons (pI) $CuTe_4$ jointed by apical Te1 atoms form chains in a string along the *a* axis, between which the octahedra's $ErTe_6$ are located. The $ErTe_6$ connecting by the ribs along the *a* axis and by the peaks along the *c* axis form a two-dimensional grids in the *a*-*c* plane. The $ErTe_6$ and the $CuTe_4$ pL, connecting by the ribs form parallel $[ErCuTe_3]$ layer-blocks perpendicular to the *b* axis. Trigonal prisms (TP) $EuTe_6$, connected by edges, form chains along the *a* axis. Thus, the connection structure of the $EuErCuTe_3$ compound is described by two-dimensional layers $[EuErCuTe_3]$ in the *a*-*c* plane between which the Eu^{2+} ions are located.

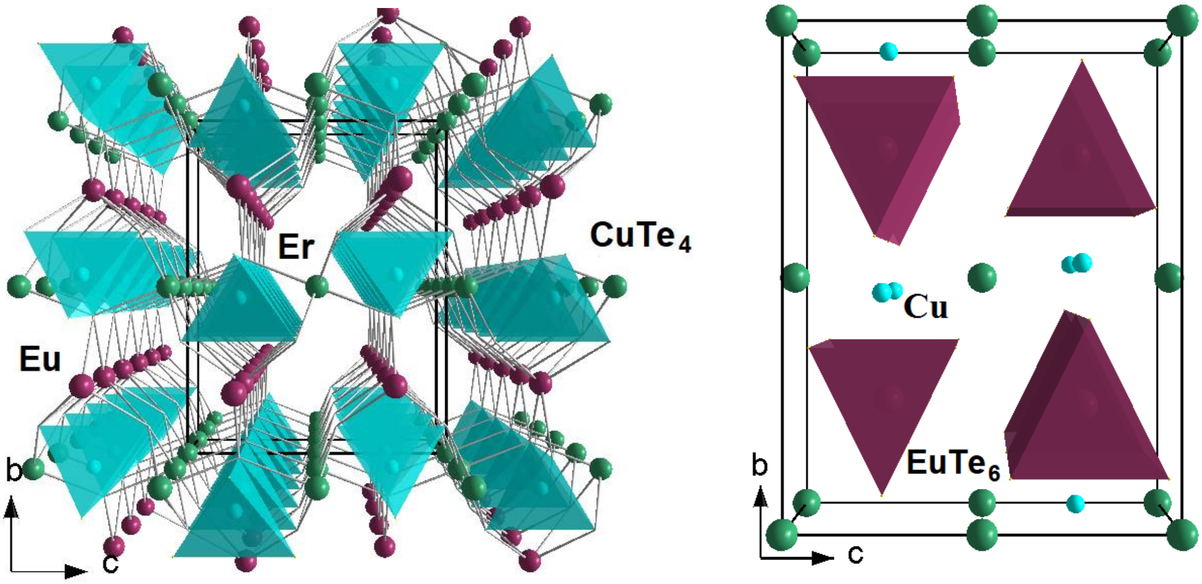

Fig.1. Structure $EuErCuTe_3$ projections

Crystal structure of $EuScCuSe_3$

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Selenides of the $ALnBSe_3$ type can be used as optoelectronic, thermoelectric, semiconductor, magnetic materials. The crystal structure of $EuScCuSe_3$ selenide synthesized for the first time was determined using single-crystal diffraction data. Compound is of the orthorhombic system space group *Cmcm*. The compound belongs to the $KZrCuS_3$ structural type with unit cell parameters a = 3.9883 (2) Å, b = 13.2776 (10) Å, c = 10.1728 (9) Å. The crystal structure was refined by the Rietveld method using the SHELXL-93 software package. The confidence factors were $wR_2 = 0.1040$ and $R_1 = 0.0442$. Data for the isostructural compound $EuScCuS_3$ were used as the initial model. The Eu^{2+}, Sc^{3+}, Cu^+ ions occupy independent crystallographic positions. Distorted tetrahedrons (pI) $CuSe_4$ jointed by apical Se1 atoms form chains in a string along the a axis, between which the octahedra's $ScSe_6$ are located. The $ScSe_6$ connecting by the ribs along the a axis and by the peaks along the c axis form a two-dimensional grids in the a-c plane. The $ScSe_6$ and the $CuSe_4$ pL, connecting by the ribs form parallel [$ScCuSe_3$] layer-blocks perpendicular to the b axis. Trigonal prisms (TP) $EuSe_6$, connected by edges, form chains along the a axis. Thus, the connection structure of the $EuScCuSe_3$ compound is described by two-dimensional layers [$EuScCuSe_3$] in the a-c plane between which the Eu^{2+} ions are located.

The research was supported by the Tyumen region within the framework of the grant agreement in the form of a grant to non-profit organizations no. 89-don dated 07.12.2020.

Morphology of gelatin and polymethylmethacrylate copolymers synthesized in the presence of tributylborane

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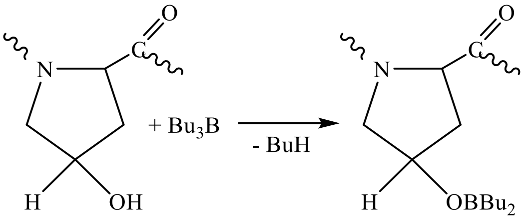
Started in the 1950s, studies of organoboron compounds in radical (including grafting) polymerization of a wide range of monomers have developed in recent years. Interest in organoboron compounds is due to their ability to participate in all steps of radical polymerization: initiation, chain growth, chain termination, and chain transfer. The following initiating systems were used for the synthesis of copolymers: azobisisobutyronitrile (AIBN) – tributylborane (TBB); AIBN – TBB – 2,5-di-tert-butyl-*p*-quinone (2,5-DTBQ); TBB – 2,5-DTBQ. The obtained copolymers have different compositions and molecular weight characteristics. These differences are caused by different copolymer formation mechanisms. The common stage is the interaction of gelatin with TBB:



The resulting borated gelatin acts in further transformations as an organoboron compound. IR spectra of copolymers include absorption bands characteristic of gelatin and polymethylmethacrylate, and UV spectra indicate the embedding of 2,5-DTBQ into the polymer chain.

The obtained copolymers were lyophilized and then examined by scanning electron microscopy (SEM). The morphology of copolymers depends on the composition of the initiator and consequently the mechanism of the formation of macromolecules (Fig. 1). The most differences are observed for the product obtained in the presence of the TBB - 2,5-DTBQ system.

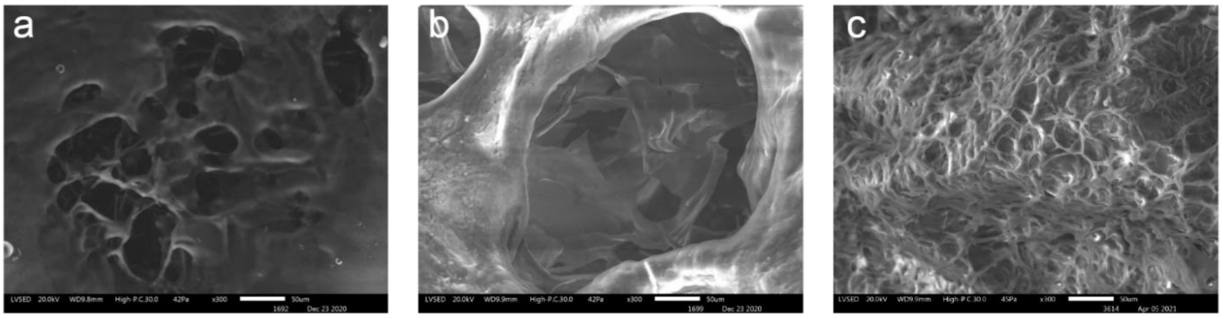


Fig. 1. SEM images of copolymers obtained by grafted polymerization of methylmethacrylate to gelatin initiated by AIBN – TBB (a); AIBN – TBB – 2,5-DTBQ (b) and TBB – 2,5-DTBQ (c)

This study was funded by the Russian Science Foundation (research project № 22-23-20091).

Preparation and characterization of high-purity isotopically enriched $^{28}SiO_2$

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Obtaining and studying the properties of materials based on isotopically modified quartz glass is promising for various fields of science and technology [1, 2]. In particular, the possibility of manufacturing quartz optical fibers is indicated, in which $^{28}Si^{16}O_2$ and $^{30}Si^{18}O_2$, respectively, are used as the shell and core material to ensure the difference in refractive indices. However, information about obtaining and studying the properties of optical fibers based on such glasses in the literature is very limited. When working with scarce and expensive isotopically enriched substances, it is necessary to operate with small amounts of substances, which can provide the sol-gel method, which is one of the promising methods for obtaining quartz glass. Isotopically enriched $^{28}SiF_4$ was used as the initial silicon compound. The conversion of silicon tetrafluoride to silicon tetrachloride was carried out under static conditions using $AlCl_3$. To obtain $^{28}SiO_2$ by the sol-gel method, the reaction of $^{28}SiCl_4$ (degree of enrichment 99.99 by ^{28}Si) with dried ethyl alcohol and hydrolysis of the formed $^{28}Si(OC_2H_5)_4$ with an aqueous alcohol solution in the molar ratio $^{28}Si(OC_2H_5)_4$:C_2H_5OH:H_2O=1:4 was carried out:4. Next, the solution was placed in molds and kept until a xerogel was formed, which was then calcined. Determination of the impurity and isotopic composition of the samples was carried out by the MS-ISP method. As a result, transparent samples of $^{28}SiO_2$ (light transmission >90% in the visible region) with a content of ^{28}Si at the level of 99.99 at. % were obtained. According to X-ray phase analysis, the samples are amorphous and do not contain crystalline inclusions. The spectra of silicon dioxide samples of different isotopic compositions were obtained and characterized by IR spectroscopy. To study the process of gelation and the formation of monolithic samples, a study was conducted on the selection of a catalyst (HF, HCl, HNO_3) and the temperature regime of drying. The kinetics of the sol particle size growth was determined by the DLS method (NanoBrook 90Plus Zeta). By the method of hydrostatic weighing, the densities of the obtained images were determined, the values of which ranged from 1.172 to 1.950 g/cm^3. According to the data obtained, HCl and HNO_3 catalysts are the most promising for these purposes.

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Effect of zinc oxide nanoparticles on physico-mechanical properties of hyperbranched polyester coatings

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The application of hyperbranched resins, as binders in environment-friendly coatings, has an advantage due to less organic solvent content and lower viscosity than conventional resins. The second generation of hyperbranched (HB) resin was synthesized based on ditrimethylolpropane and dimethylol propionic acid. In order to improve the properties of the coating, zinc oxide nanoparticles (average size 20 nm) were added to HB resin. Three samples were prepared with ZnO nanoparticles in an amount of 0, 1, and 3 wt% of the total weight of the resin. After homogenization, HB resin with zinc oxide nanoparticles is crosslinked using commercial melamine resin. A wet film layer of the resin mixture thickness of 100 ± 2 µm was applied on the steel panel. The coatings were crosslinked in an oven for 30 minutes at a temperature of 120 °C. The thickness of the dry coating film was 60 ± 2 µm, measured according to ISO 2360, using the Defelsko PosiTector 6000 FSN2. The Cross-Cut Test was applied to assess the resistance of the coating to separate from the substrate. Adhesion has been assessed following ISO 2409. The edges of the cuts are completely smooth, none of the lattice squares is detached. The gloss of the coated film was determined at an angle of 60° using a BIK-Gardner gloss meter. With the increase of the content of zinc oxide nanoparticles in the system, there is a slight decrease in the value of the gloss of the coating (from 98 % to 88 %, ISO 2813). At low concentrations of zinc oxide (below three weight percent), it can be concluded that the well-dispersed particles in the coating do not protrude above the surface and therefore do not have a significant effect on surface gloss. Hardness was measured using a Konig Pendulum hardness tester according to DIN 53157 standard. Impact resistance of the coating film was measured following ISO 6272 standard. The hardness of the coating and the impact resistance increases slightly with the amount of zinc oxide nanoparticles in the system. It is assumed that this is the result of improved coating curing in the presence of ZnO nanoparticles.

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The influence of hempseed extender oil on natural rubber compounding process

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In the rubber industry, to obtain a product that meets the requirements of the market, proper selection and ratio of natural rubber compounds are substantial. Properties of finished products based on natural rubber depend upon blending components, such as additives, antioxidants, vulcanization agents, other reinforcing fillers, and especially upon the nature of extender oil.

The potential use of hempseed oil as an environmentally friendly extender oil and its influence on the rubber compounding process was examined. Blending was performed by an internal batch mixer, at the constant temperature of 90°C and the speed of 60 rpm. Rubber compounds were prepared with broad range of extender oil content. Their hardness was determined according to ISO 7619-1 standard method. The power consumption of rubber compounding effective mixing phase was calculated from the experimentally measured voltage and amperage. For the sake of comparison, rubber blends with commonly used naphthenic process oil were prepared under same conditions.

Power consumption during the mixing process decreases with the increase of extender oil content, for hempseed as well as naphthenic oil. The results showed that hempseed oil can be used in a wide range of oil content as extender oil in rubber blending, even though it shows remotely higher power consumption than naphthenic extender oil during the effective mixing phase. Rubber hardness was decreased by adding extender oils, where samples with hempseed extender oil showed significantly lower hardness at any content oil applied. The statistical method was applied to obtain equation for reliable prediction of power consumption and rubber hardness.

The authors are thankful to the Ministry of Education, Science and Technological Development of the Republic of Serbia for their financial support, Project No. 451-03-68/2022-14/200134.

Block copolymers on the base of N,N-[(dialkylamino)alkyl](meth)acrylamides and alkoxy(oligoethylene glycol)methacrylates

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In the last decade, studies in the field of targeted and controlled drug delivery using polymer nanocontainers have received much attention from researchers around the world. One of the promising options for drug delivery to diseased human organs and tissues is the use of stimuli-responsive polymer micelles with a drug loaded into a hydrophobic core. The ongoing research is aimed at developing thermo- and pH-responsive polymers based on N,N-[(dialkylamino)alkyl](meth)acrylamides (DAA) and alkoxy(oligoethylene glycol)methacrylates (AOEGM), promising for use as micellar drug delivery vehicles. The study has been carried out on the synthesis of copolymers of block structure, the general formula of which is shown in Fig. 1.

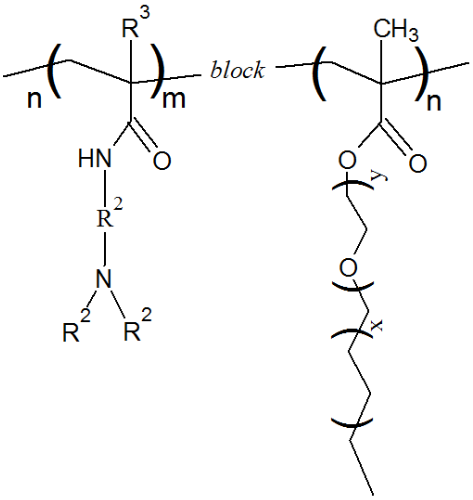

Fig. 1. Copolymer structure.

Synthesis of block copolymers of DAA and AOEGM was carried out using reversible addition−fragmentation chain-transfer polymerization (RAFT-polymerization). 4-Cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoic acid was used as a chain transfer agent and 2,2-azobis(2-methylpropionitrile) was used as an initiator. In the course of the study, the influence of the composition of the solvent (toluene, tetrahydrofuran) and the order of synthesis of copolymer blocks on the characteristics of the obtained copolymers was evaluated.

The presented results were financially supported in the form of a scholarship of the President of the Russian Federation to young scientists and graduate students carrying out promising research and development in priority areas of modernization of the Russian economy (СП-4129.2021.4).

Direct synthesis of Cu, Cu@Cu_2O and CuO nanoparticles from a bulk sample by induction flow levitation

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Currently, nanotechnology related to nanoparticles is one of the most important interests in the world. This is due to the fact that such materials have new unique properties compared to bulk materials, this is due to the high ratio between specific surface area and volume (the smaller the size, the higher this ratio). Metal nanoparticles have become of particular interest, since their application is possible in many areas of science and technology. Such nanoparticles are mainly used as catalysts, creation of biosensors, information storage, optics, in medicine for the treatment and diagnosis of diseases, etc. In many areas of science and technology, copper nanoparticles are attractive due to their low cost compared to precious metals and a wide range of applications.

In this work, Cu, Cu@Cu2O, and CuO nanoparticles were obtained by induction flow levitation (IFL) from a bulk sample. This method has a number of advantages, such as high productivity and continuity of the process of obtaining nanoparticles (NPs), the ability to control the size of the obtained NPs in a wide range, non-contact heating, which leads to high purity. Nanoparticles with a core-shell structure and copper oxide were obtained depending on the area of oxygen supply to the quartz reactor. The resulting nanoparticles were characterized by the following methods: TEM (including electron diffraction on a selected area - SAED), XRF, BET, STSA, BJH, DLS.

It was shown in the work that with a decrease in the gas pressure in the reactor, there is a sharp decrease in the average size of the nanoparticles synthesized by the IFL method, thus the copper oxide obtained at a pressure in the reactor of 0.5 atm had an average particle size of 5 nm. This work shows that the IFL method can be used to obtain high-purity NPs in the mode of continuous synthesis of copper NPs and their oxides with controlled morphology.

The study was financially supported by the Russian Science Foundation (grant no. 20-79-10097) and the Ministry of Science and Education of the Russian Federation within the framework of the scientific laboratory of the project "Laboratory of "smart" materials and technologies" project no. FSSM-2021-0013.

An effect of the mixture composition on the CO_2 absorption capacity, density and viscosity in mixtures monoethanolamine + ethylene glycole + choline chloride

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In the present study a systematic investigation of an influence of an amine and salt concentration on the CO_2 absorbing capacity (m_{CO2}), moles of CO_2 absorbed by 1 kilo of a solution) and amine efficiency (c_{CO2}), moles of CO2 absorbed by 1 mole of amine) of the ternary mixtures composed of monoethanolamine (MEA), ethylene glycol (EG) and choline chloride (ChCl) was carried out. We demonstrate that, in general, the presence of a fixed amount of ChCl in a mixed {MEA+EG} solvent cannot improve m_{CO2} over an entire range of the solvent composition and weakly decreases c_{CO2} with an effect more pronounced for the mixtures containing greater amount of MEA (Fig.1a). An influence of ChCl concentration on the above properties was analyzed for the mixtures with a fixed MEA/EG mole ratio but varying ChCl concentrations. It was shown that a decrease in m_{CO2} observed with an increase of ChCl, again, is rather caused by an overall decrease of MEA content in a mixture as its efficiency c_{CO2} does not change when ChCl concentration increases (Fig.1b).

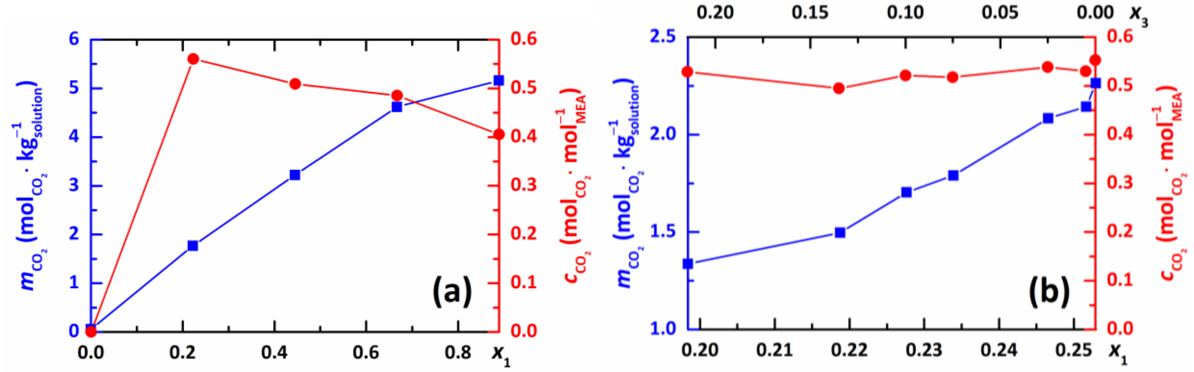

Fig. 1. CO_2 absorption capacity (m_{CO2}, blue) and MEA efficiency (c_{CO2}, red) of the ternary {MEA(1) + EG(2) + ChCl(3)} mixtures containing constant mole fraction of ChCl (x_3 = 0.1111, a) and a fixed x_1/x_2 molar ratio of 0.3386 (b) as a function of MEA (x_1 and ChCl (x_3) mole fraction at T = 313.15 K.

In addition, such properties as density (ρ) and viscosity (η) of the binary {MEA+EG} and ternary {MEA+EG+ChCl} mixtures were obtained within a wide range of temperatures for both neat and CO_2-loaded samples. We show that regardless of the {MEA+EG} mixed solvent composition the presence of ChCl increases both ρ and η. For CO_2-loaded samples both properties increase significantly with a greater contribution for the mixtures containing greater amount of MEA.

This work was supported by the Russian Science Foundation (Project No. 21-73-00167).

Synthesis and catalytic properties of double perovskites Sr_2NiWO_6 and Ba_2NiWO_6

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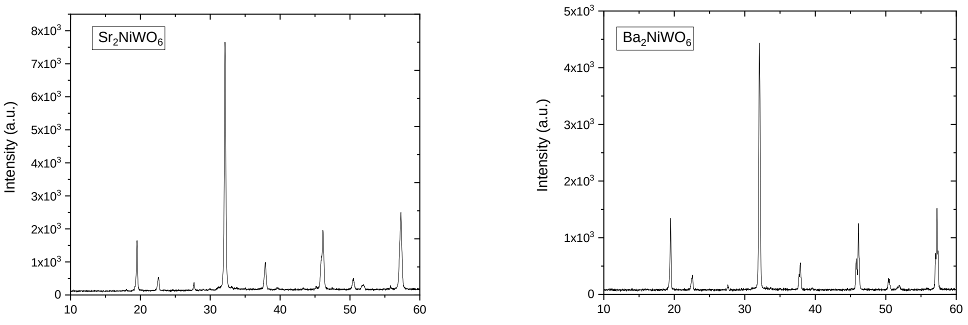
Analysis of the literature data [1,2] showed that some compounds with the structure of double perovskite A_2BWO_6 are stable in a reducing atmosphere, have mixed electron-ion conductivity and demonstrate high catalytic activity for the oxidation of hydrocarbons. So, they can be used as alternative anode materials for SOFC. The samples A_2NiWO_6 (A=Ba, Sr) were synthesized by solid-phase method at 1250°C. The elemental composition was confirmed using a JEOL JSM-IT300LV electron scanning microscope with EDX attachment.



a b

Figure 1 - X-ray patterns of A_2NiWO_6 (a)A=Sr, (b)A=Ba

The temperature dependence of the total conductivity of the samples was determined by the four-contact method at constant current on the Zirconia- M device in the temperature range of 500 - 900 °C. The catalytic properties of Sr_2NiWO_6 and Ba_2NiWO_6 were studied in a flow-through tubular quartz reactor with a fixed catalyst layer in the temperature range of 500 - 900 °C. The composition of the gas mixture was analyzed using a chromatograph Chromatek "Crystal-5000.2". Additionally, the samples were sintered together with YSZ and CeY at 900°C. During the X-ray phase analysis, the presence of new phases was not detected. Thus, this work will demonstrate the prospects for the use of double perovskites A_2NiWO_6 (A=Ba, Sr) as anode SOFC materials with internal hydrocarbon reforming. The study was carried out on the equipment of the Collective Usage Center “New Materials and Resource-saving Technologies” (Lobachevsky State University of Nizhny Novgorod).

This work was financially supported by the Ministry of Science and Higher Education of the Russian Federation (Contract No. 0729-2020-0053)

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Electrochemical behavior of 2,2'-bipyridine and 4,4'-bipyridine in the hydrogen evolution reaction in the presence of various acids

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Due to declining prices for electricity generated by alternative energy sources water electrolysis can be suggested as a digestible way to produce hydrogen on an industrial scale. One of the main obstacles to the active implementation of water electrolysis in industry is the low efficiency of this process and the lack of available catalysts for the hydrogen evolution reaction from water [1].

Studies conducted in recent decades suggest that catalysts based on organic compounds, in particular those containing a heterocyclic fragment, can provide a significant reduction in the costs arising in the process while maintaining high economic efficiency in the production and storage of hydrogen [2, 3]. In addition, the use of synthetic catalysts containing polyaromatic groups will allow efficient immobilization of the catalytic system due to strong physical sorption on the surface of carbon supports in order to obtain stable and highly efficient heterogeneous electrocatalysts for the production of molecular hydrogen.

In the presented report, the electrochemical characteristics of organic heterocyclic molecules, which are promising materials for the creation of electrocatalysts for the production of molecular hydrogen - 2,2'-bipyridine and 4,4'-bipyridine, are considered. Based on the results obtained using the method of cyclic voltammetry. Probable mechanisms of the ongoing electrocatalytic reduction of molecular hydrogen, including the possibility of realizing a synergistic effect, were proposed.

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Evaluation of the efficiency of the electrocatalytic process of molecular hydrogen reduction in the presence of 2,2'-bipyridine and 4,4'-bipyridine

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It is known that the rapid growth of the Earth's population contributes to the natural growth of needs in the field of heat and electricity. An equally rapid decline in the reserves of fossil fuels that are actively used today poses a challenge for the scientific community in the search for alternative energy sources, and molecular hydrogen is rightfully considered a promising option [1].

The main method for obtaining environmentally friendly hydrogen is water electrolysis, however this technological process is associated with many disadvantages, such as high energy consumption and high cost of the resulting product, which questioning the active introduction of electrolysis into industry. It is important to note that the largest contribution is made by the cost of catalysts - platinum and platinum group metals. Thus, their replacement with fully synthetic analogues will help reduce the price of molecular hydrogen.

It should be noted that in recent years, significant progress has been made in the development of electrocatalysts for the production of molecular hydrogen, however out of the whole variety of molecular complexes, none of them combines sufficient efficiency, stability under the conditions of the experiment, and low overvoltage values [2,3].

To evaluate the efficiency of the catalytic process, it is necessary to calculate the TON and TOF parameters, and within the framework of the presented report, the calculated parameters for catalytic systems consisting of 2,2'-bipyridine and 4,4'-bipyridine in the presence of acids of various strengths will be considered and compared. The calculations were carried out according to the results of experimental data obtained using preparative potentiostatic electrolysis.

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Structural and thermodynamic study of biologically active substances

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Nucleobases, vitamins and hormones - one of the most important representatives of biologically active substances. They are vital and necessary compounds, each of which plays an indispensable and very important role in the vital activity of the organism. Vitamins - organic compounds that are necessary for the normal functioning of almost all processes in the body. Most vitamins are involved in biochemical reactions as coenzymes or their precursors. Hormones are the products of internal secretion, which are produced by special glands or individual cells, are secreted into the blood and spread throughout the body, causing a certain biological effect. These substances have always been of interest to chemistry in terms of their synthesis. However, not only the preparation of the compound is important, but also information on its physicochemical properties and structural characteristics. The investigation allowed a comprehensive study of the physicochemical properties and structure of B vitamins, such as riboflavin (B_2), nicotinic acid (B_3), myo-inositol (B_8), folic acid dihydrate (B_9), L-carnitine (B_{11}) and cyanocobalamin (B_{12}), and steroid hormones such as hydrocortisone acetate, methylprednisolone, and methylprednisolone aceponate. The calorimetric determination of the temperature dependences of the heat capacity of these compounds in the range from 6 to 350 K is carried out and standard thermodynamic functions are calculated: heat capacity, enthalpy, entropy and the Gibbs function of heating in the temperature range of 0 - 350K. The type of topology structure is determined according to the data of multifractal processing of low-temperature heat capacity. The combustion energies of the studied samples were determined at $T = 298.15$ K. Thermodynamic modeling of some biochemical processes was carried out with the participation of these compounds. The enthalpies of sublimation of the studied samples were determined using the Quartz-crystal microbalance (QCM) technique. The thermal properties and features of thermal expansion of compounds by differential scanning calorimetry and low-temperature X-ray diffraction have been studied. Structural studies of steroid hormones and solvates based on them were carried out by X-ray analysis. Recently, an ambitious task was set to develop methods for the isolation and methodology for the study of crystalline proteins from natural objects. For the first time, a low-temperature thermodynamic study of crystalline protein was carried out using hevein as an example. Thus, a practical and theoretical base has been prepared for the study of protein-peptide hormones.

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Chemoresistive materials for "electronic nose"

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An electronic sense of smell (electronic nose) is a device that can detect and recognize smells and tastes using an array of sensors. In the last decade, the development of chemoresistive materials for such a device has attracted considerable interest, because it is necessary in such vital segments of the functioning of modern society as health care, environmental monitoring, detection and prevention of man-made threats, transport safety, storage and preparation of food products, and also timely warning of chemical and biological threats during counter-terrorism and military operations.

The goal of this study is to develop the scientific foundations for creating a new generation of functional nanostructured polymer-inorganic chemoresistive materials for further use as a sensor matrix in an electronic nose device. As universal inorganic matrices will be complex oxide materials with a branched surface have been obtained - double and ternary oxide systems - TeO_2-ZnO, TeO_2-Bi_2O, TeO_2-ZnO-Bi_2O, TeO_2-ZnO-Cu_2O doped with both optical and electroactive impurities.

Speaking about sensitive materials and their properties, it should be noted that the synthesis method is a determining factor, since it significantly affects their structure, stoichiometry, the number of defect states, chemical purity and the possibility of changing their physicochemical properties by doping. As part of the work on the project, it is planned to develop a fundamentally new unparalleled universal direct one-stage method of plasma chemical vapor deposition (PECVD) for the synthesis of nanostructured complex oxide materials from the corresponding high-purity elements, to achieve the best purity and, ultimately, the highest electron mobility in material. Potentially, plasma initiation always has an advantage over thermal, since, other things being equal; it provides two additional tools for influencing the process - the temperature of electrons and their concentration. In addition, plasma initiation does not require heating the substrate to any significant temperatures, which makes it possible to use thermosensitive, for example, polymer substrates. In plasma initiation, the substrate temperature plays an important role as an additional factor that sets the required relaxation mode for excited particles, allowing additional control of the growth process, achieving a particular phase composition of the final material. At the same time, at pressures of 0.1-1 Torr, the temperature of the reactor wall, as a rule, does not exceed 150-200°C, which excludes contamination of the final product by the materials of the apparatus.

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Thermolysis of RAFT-Synthesized Poly(Alkyl Methacrylate)

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Reversible Addition–Fragmentation Chain Transfer (**RAF**T) radical polymerization is one of the most versatile processes for Reversible-Deactivation Radical Polymerization in displaying superior flexibility with respect to monomers and reaction conditions. A key feature of RAFT polymerization is that the thiocarbonyl groups, present in the initial RAFT agent, are retained in the polymeric products [1, 2]. The retention of these groups is responsible for the polymers' living character. However, the presence of the thiocarbonyl functional groups also means that the polymers are usually colored and their performance may deteriorate.

Synthesis of polymers based on alkyl methacrylates (**C_{10}-C_{18}**) was carried out in the presence of azobisisobutyronitrile and 2-cyano-2-propyl benzodithioate. The course of thermolysis of poly(alkyl methacrylate) (**PAMA**) prepared with dithiobenzoate RAFT agents was followed by thermogravimetric analysis (**TGA**) in inert atmosphere, thermo-oxidative degradation in the presence of atmospheric oxygen and gel permeation chromatography (**GPC**). The weight loss profile TGA observed depends strongly on the nature of polymers. Thus, the effect of the chain end on the temperature T2%, at which polymer thermolysis begins is most pronounced in the case of stearyl methacrylate. The end group is lost at ~180°C (table.1).

Table 1. The results of thermogravimetric analysis

№.	Polymer	RAFT–agent, mol×l^{-1}	M_n ×10^{-3}	M_w/M_n	$T_{2\%}$,°C	$T_{90\%}$,°C
1	PAMA (C_{10}-C_{14})	-	109	2.3	261	353
2	PAMA (C_{10}-C_{14})	0.01	46	1.2	263	376
3	PAMA (C_{18})	-	33	2.3	216	391
4	PAMA (C_{18})	0.01	64	1.3	176	381

In the case of polymer degradation under isothermal conditions in the presence of atmospheric oxygen, the effect of end groups is even more pronounced. In this case, the molecular weight of the polymers decreases.

Thus, it was found that the end groups of RAFT agents have a significant effect on the thermal stability of PAMA. These results must be taken into account in the application of polymers in various fields.

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Low-temperature heat capacity of zinc gallate

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In the current work, a method for the preparation of zinc gallate was proposed and an experimental study of its low-temperature heat capacity was carried out. The $ZnGa_2O_4$ powder was synthesized by gel combustion method using PVA as a fuel. Phase purity and chemical composition of the powder obtained were confirmed using X-Ray diffraction analysis and X-Ray fluorescence spectrometry.

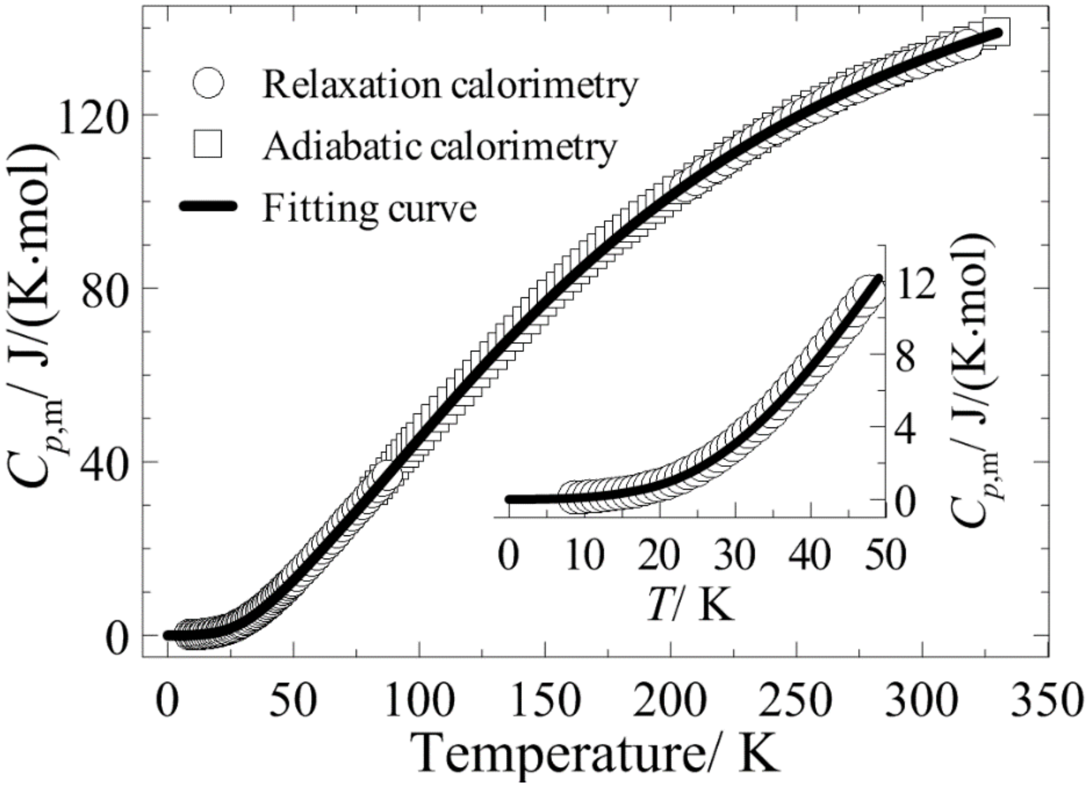

Fig. 1. Heat capacity of zinc gallate as a function of temperature.

The temperature dependence of the heat capacity of $ZnGa_2O_4$ was measured using relaxation and adiabatic calorimetry in the range from 8 K to 329 K. It was found that the experimental heat capacity curve has no anomalies in the temperature range studied (Fig. 1). Using the measured heat capacity values, the temperature dependences of the standard thermodynamic functions of $ZnGa_2O_4$ were calculated in the range from 0 to 329 K.

Synthesis of verdazylium tetrafluoroborates and verdazyl radicals containing an acridinyl fragment

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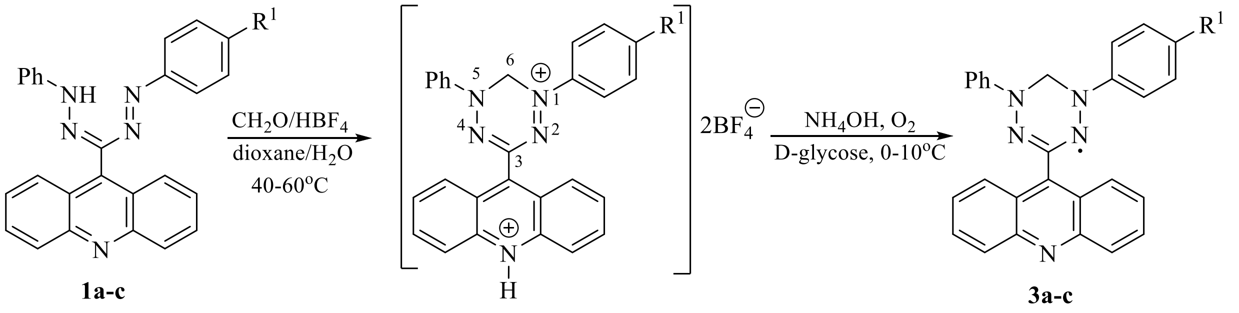
Verdasyl (tetrazinyl) radicals were first described in 1964 by Kuhn and Trishman [1]. Since then, numerous works devoted to the synthesis, study of properties, and application of verdasyls have appeared.

According to the reaction of acridine-9-carbaldehyde phenylhydrazone with arenediazonium salts obtained from p-substituted anilines the corresponding formazans **1a-c** were synthesized. By the action of formalin in the presence of tetrafluoroboric acid, formazans were converted into the corresponding bis-tetrafluoroborates of the binuclear cation of verdazylium-acridinium **2a-c**. When salts **2a-c** are treated with D-glucose in a weakly alkaline medium (NH_4OH), stable verdazyl radicals **3a-c** are formed.



R^1 = H (**a**), CH_3 (**b**), Br (**c**)

Formazans **1a-c** and tetrazinium tetrafluoroborates **2a-c** were isolated in the individual form and characterized by elemental analysis, IR, UV, ^1H and ^{13}C NMR spectroscopy. Thus, formazans **1a-c** have two absorption maxima in the UV-spectra in the region of 375-390 nm and 475-495 nm; IR-spectra confirm the presence of chelate structures with an intramolecular hydrogen bond – absorption band 1500-1510 cm^{-1} (C=N), weak absorption band 3020-3050 cm^{-1} (N-H). In the UV-spectra of tetrafluoroborates **2a-c**, a bathochromic shift is observed in the region of 405-420 nm and 567-590 nm; In the IR-spectra, there is a wide intense band ~1080 cm^{-1}, corresponding to vibrations of the tetrafluoroborate anion. Benzene solutions of radicals **3a-c** give time-stable EPR-spectra containing 9 broad lines caused by the interaction of an unpaired electron with four nitrogen atoms of the tetrazine ring.

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Synthesis and investigation of $Rb_{0.9}Nb_{1.625}Mo_{0.375}O_{5.62}$ complex oxide doped SnO_2

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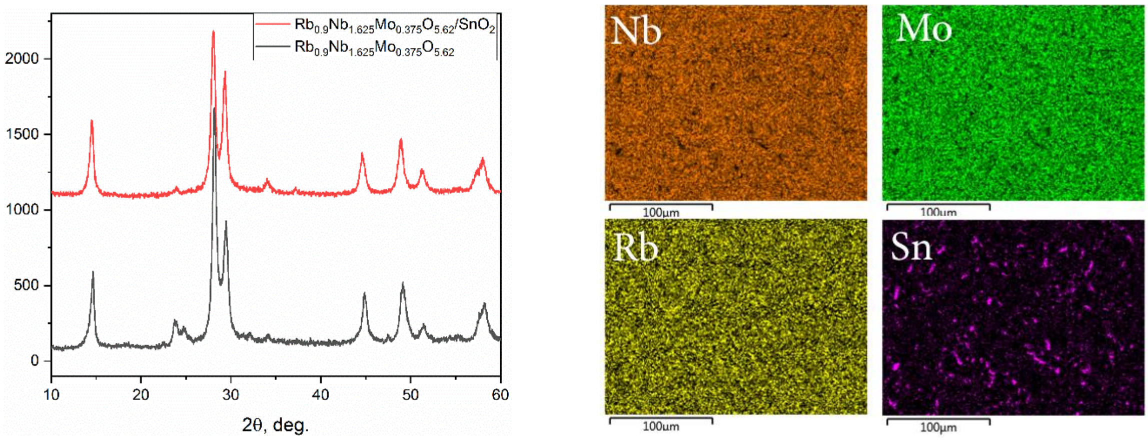
Search for photocatalytic materials with a band gap value of 2.0-2.2 eV, which corresponds to the maximum intensity of solar radiation, is an urgent task; however, the most oxides have the light absorbance in UV range. Such promising $Rb_{0.9}Nb_{1.625}Mo_{0.375}O_{5.62}$ compound with β-pyrochlore structure leads to almost 100% methylene blue decomposition under UV irradiation for 10 hours. One of the ways to improve the photocatalytic activity of complex oxides is to reduce the band gap value by creating heterostructures [1,2]. In this work, the $Rb_{0.9}Nb_{1.625}Mo_{0.375}O_{5.62}/SnO_2$ heterostructure was prepared by hydrothermal method. The obtained sample was characterized using scanning electron microscopy, X-ray microanalysis and X-ray powder diffraction analysis (Fig.1a). We have found fine particles of amorphous SnO_2 appear on the $Rb_{0.9}Nb_{1.625}Mo_{0.375}O_{5.62}$ surface (Fig.1b). The photocatalytic activity was measured using decomposition of a methylene blue dye. The initial sample does not show any photocatalytic activity on the visible light irradiation, whereas the heterostructure begins to exhibit photocatalytic properties in the visible region of the spectrum. The conversion of methylene blue using $Rb_{0.9}Nb_{1.625}Mo_{0.375}O_{5.62}/SnO_2$ under visible light was 30% in 3 hours.



(a) (b)

Fig. 1. Comparison of XRD patterns $Rb_{0.9}Nb_{1.625}Mo_{0.375}O_{5.62}$ and $Rb_{0.9}Nb_{1.625}Mo_{0.375}O_{5.62}/SnO_2$ (a) and EDX elemental map of $Rb_{0.9}Nb_{1.625}Mo_{0.375}O_{5.62}/SnO_2$ (b)

This work was supported by the Ministry of Education and Science of the Russian Federation (0729-2020-0053) on the equipment of the Collective Usage Center "New Materials and Resource-saving Technologies" (Lobachevsky State University of Nizhnii Novgorod).

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Electrosurface properties and aggregative stability of biocompatible tantalum oxide nanodispersions

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The electrosurface properties and aggregative stability of nanoparticles (NPs) are key factors that determine their performance and biological or environmental fate. However, there is still a lack of data on the stability of aqueous dispersions of some important NPs for biomedical applications, such as tantalum oxide. Aqueous dispersions of tantalum oxide nanoparticles (NPs) are used as X-ray contrast agents for computed tomography (CT), drug delivery systems, radiosensibilizators, and photocatalysts [1].

In the present work, surfactant-free Ta_2O_5 and Ta_2O_5:Eu NPs were synthesized via a solvothermal method. Stable hydrosols and powder samples were prepared on their basis for a comparative study. The particle size, morphology, and amorphous structure of samples were investigated by transmission electron microscopy and dynamic light scattering. The laser Doppler electrophoresis was used to investigate the pH and temperature dependence of zeta potential of NPs. Obtained results were also discussed within the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory for the first time for tantalum oxide NPs. A turbidimetry study was performed to investigate the coagulation kinetics of Ta_2O_5 NPs in NaCl solutions. The critical coagulation concentration and stability factor were determined experimentally and via DLVO calculations; the obtained results showed a good agreement. The acid-base surface properties of samples were studied by potentiometric titration, and constants of surface acid-base equilibria were determined within 2pK-modeling.

In vitro Cytotoxicity (MTT-test) and *In vivo* Acute Toxicity studies were performed for the Ta_2O_5 hydrosols. The usage of Ta_2O_5 NPs for *In vivo* CT imaging of the rat gastrointestinal tract was shown. The CT values of the rat stomach increased 9 times [1].

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Using near infrared spectroscopy for wood analysis

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Near infrared (NIR) spectra of wood and wood products contain information regarding their chemical composition and molecular structure. Both influence physical properties and performance, however, at present, this information is under-utilized in research and industry. Partial least squares and principal component regression methods to establish the relationship between lingin/cellulose content and NIR data were used. All wood samples (particle size 80 mesh) were oven dried (105 ± 2°C) for 12 hours prior to NIR analysis. After that, the samples were placed in glass cuvettes made of slide and cover glass. Reflection spectra were recorded using a PerkinElmer Lambda 950 FT-NIR spectrometer (Waltham, MA, USA). Each spectrum covered the range from 1000 to 2500 nm (4000 to 10000 cm^{-1}) with a spectral resolution of 4 cm^{-1}. Each spectrum is the average of 32 scans. In the spectral region between 1445 and 1450 nm and near 2134 nm, there are bands associated with the content of lignin and extractives. The region from 1470 to 1490 nm is mainly related to cellulose and hemicelluloses. The bands at 2267 nm are associated with lignin, and at 2270 nm the bands can be assigned to cellulose components. Between 1800 and 1900 nm a greater difference in peak absorption intensity between wood species could be tested. This region is associated with all components of the cell wall, while the bands between 1916 and 1942 nm are associated with OH from water [1]. The NIR spectra of all types of wood were similar (Fig. 1a). Analysis of the content of the main components of wood was carried out on the basis of the transformed spectra (Savitsky-Golay transformation) (Fig. 1b).

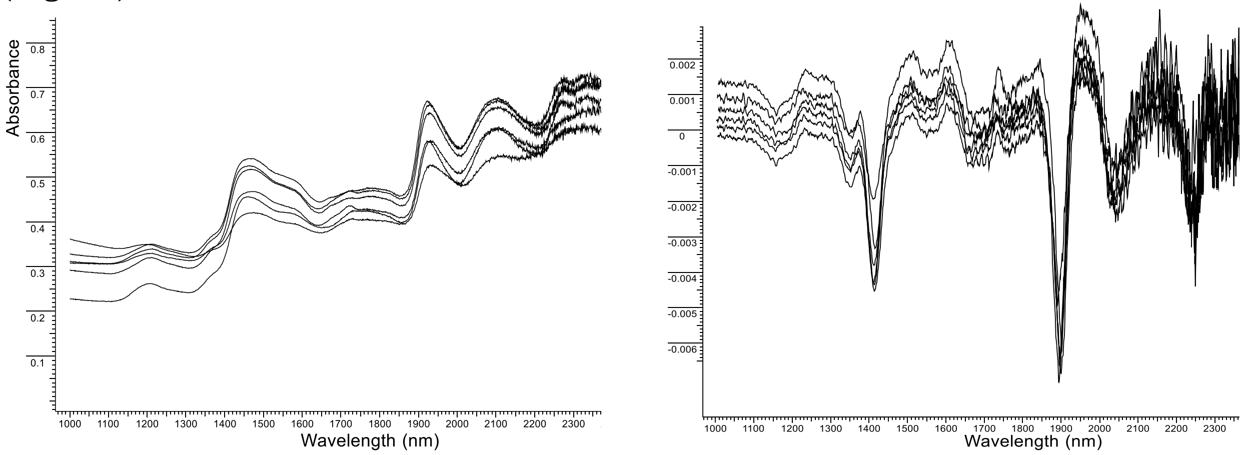

Fig. 1. Near-infrared spectra (a) and second derivative near-infrared spectra (b) for wood samples: pine, spruce, larch, birch, oak, aspen.

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Carbon nanotubes network for lithium metal anodes

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With the rapid development of electric vehicles and large-scale energy storage systems over the past decades, the conventional graphite anodes for lithium ion batteries cannot meet the demand since the limited capacity (372 mAh g^{-1}). At the same time, lithium metal anodes possess an ultra high theoretical specific capacity (3860 mAh g^{-1}) and the lowest negative standard electrochemical potential (−3.045 V). However, lithium metal batteries cannot be applied before their safety and cyclability issues can be well solved. In contradistinction to graphite anodes, which form a lithium intercalated compound, lithium metal anodes store energy by plating/stripping of lithium across the lithium/electrolyte interface. This situation results in the growth of lithium dendrites, which causes low reversible capacity, poor cycling stability and serious safety problems [1].

According to the Sand's time model, low local effective current density and fast anion mobility will delay dendrite nucleation. In this case, 3D matrices or current collectors have attracted many attentions. Carbon materials with high specific surface area and high electrical conductivity such as hollow carbon nanospheres, carbon fibers, carbon nanotubes and reduced graphene oxide, can effectively regulate Li plating/stripping [1, 2]. 3D matrices have ability to decrease the effective current density for Li metal plating/stripping. As the result, a decrease in the lithium dendrites growth rate was achieved in a lot of research works [1-4].

In our study, carbon nanotubes (CNT) were synthesized by CVD method on a Co/MgO catalyst. Aqueous suspension of carbon nanotubes (0.4%) and NaCMC binder (0.6%) was thoroughly dispersed with an ultrasonic homogenizer. The copper foil as a hypothetical current collector was coated with the resulting suspension by a doctor blade method.

The received layer possess a uniform structure with a thickness of about 20 μm and resistance of 1.2 Ω. These parameters are sufficient for further research of carbon nanotubes as a precursor of an effective carbon network for modifying the surface of the current collector of lithium metal batteries.

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Synthesis of 1,24-oxadiazoles containing an acridinyl fragment

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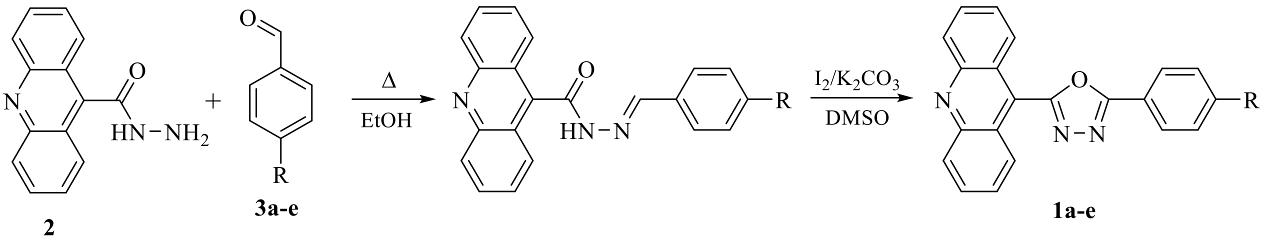
1,3,4-Oxadiazoles and their derivatives have a wide spectrum of biological activity [1]. Strongly pronounced spectral-luminescent properties make it possible to obtain on their basis fluorescent and phosphorescent luminophores [2], organic semiconductors and other materials for modern optoelectronics [3]. Thus, 1,3,4-oxadiazoles containing an acridine fragment are undoubtedly of interest as substances with potentially high biological activity. The development of methods for obtaining them is a promising goal.

Oxadiazoles **1a-e** were obtained by condensation of acridine-9-carbohydrazide **2** with the corresponding aromatic aldehydes **3a-e**, followed by oxidation with the I_2/K_2CO_3/DMSO system.



R = H (a), Me (b), OMe (c), NO_2 (d), Cl (e)

Compounds **1a-e** were isolated in the individual form by recrystallization. They are characterized by fluorescence, IR, UV, ^{1}H and ^{13}C NMR spectra as well as by elemental analysis data. The resulting 1,3,4-oxadiazoles **1a-e** luminesce with a high quantum yield in polar and nonpolar solvents (λ^{fl}max = 476–484 nm, φ = 0.38–0.91).

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Crystal structure and photocatalytic properties of new Dion – Jacobson titanoniobates

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Dion – Jacobson phases belong to the layered perovskite class of complex oxide compounds with the general formula A'[$A_{n-1}B_nO_{3n+1}$]. The number *n* defines the quantity of stacking octahedral perovskite-like layers separated by A' cation. Since perovskite crystal structure is flexible, many elements can be embedded in the structure: A' = (Li^+, Na^+, K^+, Rb^+, Cs^+, H^+, Ag^+, NH_4^+, $CuCl^+$, $FeCl^+$), A = ($Ca^{2+,}$ Sr^{2+}, Ba^{2+}, Bi^{3+}, Na^+, Ln^{3+}) and B = (Nb^{5+}, Ta^{5+}, Ti^{4+}, Mn^{4+}). Dion – Jacobson phases exhibit a wide range of practically useful properties, such as: high dielectric constant, high Curie temperatures, hybrid improper ferroelectricity and ionic conductivity. Recently, however, the main efforts of researchers are focused on photocatalytic properties of Dion – Jacobson phases in decomposition reactions of water and organic pollutants. It was found that the band structure of these semiconducting materials consists of B*nd* orbitals in the conduction band and O*2p* orbitals in the valence band. Therefore, one can tune the bang gap (and, hence, the wavelength of absorbed light) by configuring atoms in B position of the perovskite structure. It was found that Nb^{5+} cation can be unboundedly isomorphically substituted by Ta^{5+} and Ti^{4+} while maintaining electroneutrality. In general, substitution by Ta^{5+} leads to increasing of band gap energy, while substitution by Ti^{4+} leads to decreasing of band gap. Dion – Jacobson phases $RbNd_2Ti_2NbO_{10}$ and $RbPr_2Ti_2NbO_{10}$ were synthesized by solid-phase reactions between the corresponding oxides or nitrates. Protonated forms of compounds $HPr_2Ti_2NbO_{10}$ and $HNd_2Ti_2NbO_{10}$ were obtained by leaching the Rb-phase in 6M HCl solution. The crystal structures of the previously unknown Dion – Jacobson phases $RbNd_2Ti_2NbO_{10}$ and $RbPr_2Ti_2NbO_{10}$ were refined by the Rietveld method for the first time. The crystal structures of the ion exchange products were not refined due to their poor crystallinity. Tetragonal P4/mmm $RbLa_2Ti_2NbO_{10}$ structure was used as initial model for refinement. The outermost octahedrons in the structure are distorted. In both cases, the Nb1/Ti2 atoms occupying *2g* position are out of the equatorial plane of the octahedron, while the Ti1 octahedron is almost symmetrical. Diffuse reflectance spectroscopy was used to determine the band gap energies of the materials. The band gaps were calculated from the optical absorption spectra by the Tauc method. Band gap energies for all synthesized compounds are greater than 3 eV, which means that they cannot be used as photocatalysts under visible light, but rather only under UV irradiation. Photocatalytic activity of obtained materials was studied in a methylene blue dye decomposition reaction under UV-light. Rubidium-containing Dion – Jacobson phases showed the highest degree of conversion; therefore, these samples were chosen for kinetic studies of dye decomposition. The maximum degree of conversion was observed for $RbNd_2Ti_2NbO_{10}$. The total methylene blue conversion (photocatalytic decomposition) within 6 hours is about 61%.

Study of the various RAFT agents effect on the controlled radical polymerization of methacrylic acid

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One of the most significant problems of modern medicine is the high number of people with cancer group of diseases. The high relevance of this issue determines a wide range of studies aimed at the solution to this problem. Currently used anti-cancer drugs are equally toxic to both tumor and normal tissues. The usage of polymer systems containing anti-cancer drugs could become the appropriate response to this issue. When delivered to the body along with antigens, such systems enhance the immune response.

It was found that the polymeric carriers used for injection, which are not degradable in the body, should have a molecular weight value of not more than 40 kDa in order to avoid their sedimentation in the reticuloendothelial system. To obtain required polymer matrix, it is necessary to select the optimal polymerization conditions. The main component that determines the molecular weight of the synthesized polymer is a reversible addition-fragmentation chain transfer (RAFT) agent. Thus, the aim of this work is to find the best conditions for the controlled radical polymerization of methacrylic acid by selecting the optimal RAFT agent.

In the course of the research, a number of methacrylic acid polymers were obtained. Dodecyl mercaptan (DDM) and 4-cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoic acid (CDSPA) at concentrations of 0.01–0.1 mol/L were used as RAFT agents. 2,2′-azobis(isobutyronitrile) was used as an initiator, and dimethylformamide as a solvent.

The polymerization was carried out in thermostatically controlled, pre-degassed ampoules at a temperature of 70°C for 8 hours. The polymers were purified by threefold reprecipitation with chloroform from ethanol solution. Analysis of molecular weight characteristics was carried out by gel permeation chromatography in tetrahydrofuran at 40°C on a high performance liquid chromatograph LC-20 AD Prominence (Shimadzu).

For the obtained samples, conversions were calculated, and the dependences of molecular weight characteristics on the concentrations of the introduced RAFT agents were studied. Using CDSPA, polymers with lower polydispersity index were synthesized compared to polymers obtained in the presence of DDM. The revealed dependencies showed a higher efficiency of CDSPA in the obtained polymers molecular weight control.

Preparation of nanostructured gallium sulfide by PECVD

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In recent decades, great interest has been riveting on study of the ionic conductivity of chalcogenides and materials on their base both from scientific and academic points of view due to their potential practical applications. Because of the high polarizability of chalcogen - sulfur, selenium or tellurium - the chalcogenide materials are more conductive than their oxide counterparts [1,2]. In addition, alkaline (mainly lithium) chalcogenide glasses are being actively studied as potential candidates for the development of an electrolytic base for solid-state batteries. In this work the Ga-S materials have been synthesized by direct interaction of gallium and sulfur vapors in non-equilibrium plasma discharge. Argon of high purity was also used as a career gas for precursors transport to the plasma zone and as a plasma feed gas. The process was carried out at the low pressure (0.1 Torr) in inductively coupled RF (40 MHz) plasma. Optical emission spectroscopy (OES) was used to identify the exited species and to assume the possible mechanisms of plasma-chemical reactions. The stoichiometry, structure and morphology of the surface of the materials obtained was also studied by deferent analytical techniques dependently on the conditions of the plasma process. The obtained materials were studied by various analytical techniques. The schematic diagram of PECVD installation is illustrated in figure 1.

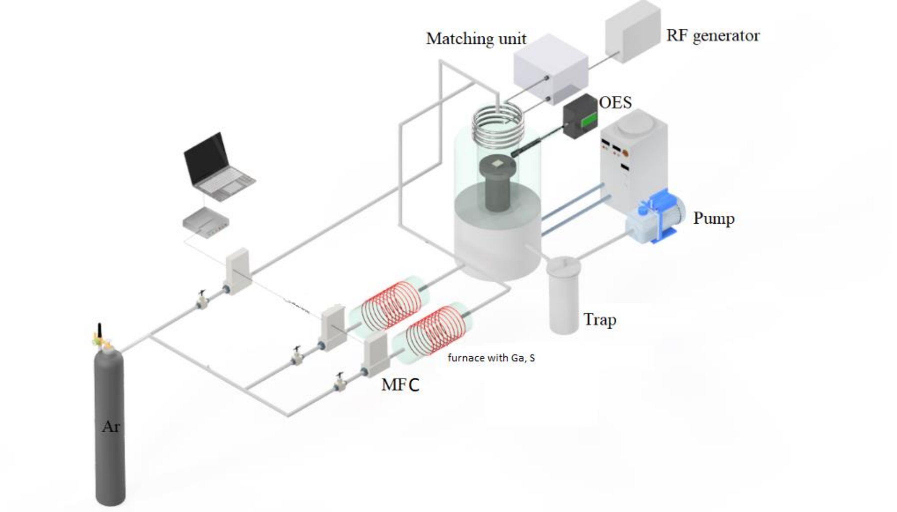

Fig. 1. Scheme of the experimental setup

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Effect of H_2O-EtOH and H_2O-DMSO solvents on the γ-cyclodextrin solvation state

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Increasing the solubility, regulation of the rate and degree of drug release from various carriers are topical tasks of modern pharmaceuticals. This problem can be solved by including drugs in the "host-guest" type of complex with cyclodextrins. The molecular structure of cyclodextrins can be described as a truncated cone, in the cavity of which molecules of other substances can be placed, and with the help of hydrophobic interactions and other bonds, the so-called “inclusion compounds” are formed. The original properties of the included substances change in the process of such complexation, while the cyclodextrin itself also serves as a protector of the “guest” molecules. The scientific selection of the solvent composition can enhance the solubilizing ability of cyclodextrins by changing the solvation of the reagents.

Thus, in this work, we studied the effect of solvents H_2O-EtOH and H_2O-DMSO on the solvation of γ-cyclodextrin (γ-CD). The distribution coefficients of γ-CD in water and its mixtures with EtOH and DMSO were determined by the interfacial distribution method of a substance between two immiscible phases (water or a mixed solvent and n-hexane). Changes in the Gibbs energy of γ-CD transfer from water to mixed solvents are calculated. The data obtained are presented in the table 1.

Table 1. Distribution coefficients and change in the Gibbs energy of γ-cyclodextrin during its transfer from H_2O to H_2O-EtOH and H_2O-DMSO solutions, T=298.15 K

X_2, mol. fr.	0.0	0.05	0.10	0.15	0.2
K_1	0.08 ± 0.02	-	-	-	-
H_2O-DMSO					
K_2	-	0.16 ± 0.13	0.13 ± 0.06	0.12 ± 0.07	-
$\Delta_{tr}G^0$(γ-CD), kJ/mol	0	1.64	1.11	0.96	-
H_2O-EtOH					
K_3	-	0.13 ± 0.06	0.23 ± 0.07	-	0.37 ± 0.14
$\Delta_{tr}G^0$(γ-CD), kJ/mol	0	1.04	2.48	-	3.62

The distribution coefficient of γ-CD in mixed solvents is higher than in water. Changes in the Gibbs energy during the transfer of γ-CD from water to its mixture with dimethylsulfoxide and ethanol demonstrate a weakening of the macrocycle solvation.

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Synthesis and structure of α-$CaMg_2(SO_4)_3$ phosphate-analogues

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Phosphates belonging to the structural type of the kosnarite mineral $KZr_2(PO_4)_3$, which is isostructural to the synthetic $NaZr_2(PO_4)_3$ (**NZP**), and a large class of solid-state superionic conductors NASICON ($Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$), represent a series of isomorphic compounds based on the modified structure $Fe_2(SO_4)_3$. The substitution of sodium and iron atoms in the known phosphate $Na_3Fe_2(PO_4)_3$ with the NZP structure by elements in the oxidation state +3 allows the existence of yet unstudied phosphates $RR'_2(PO_4)_3$ (R' = Fe, Al, Cr, Ga, Sc). In the synthesis of phosphates with R = Bi, Sb, La, Ce, Pr, Nd and R' = Fe, Cr, it was assumed that they would be structural analogues of NZP-phases. The purpose of this work is the synthesis and study of the crystal structure of $RCr_2(PO_4)_3$ compounds. According to X-ray diffraction data, all samples of the composition $RCr_2(PO_4)_3$ crystallize in the new structural type α-$CaMg_2(SO_4)_3$ for phosphates. The data of electron probe microanalysis showed the homogeneity of the composition of their grains and the correspondence between the expected (predicted) and actual compositions, taking into account the error of the method (table 1).

Table 1. Results of electron probe microanalysis of $RCr_2(PO_4)_3$ compounds.

Substance	Expected composition	Actual Composition
$LaCr_2(PO_4)_3$	$La_{1.00}Cr_{2.00}P_{3.00}O_{12}$	$La_{1.02(3)}Cr_{2.02(1)}P_{3.00(2)}O_{12}$
$CeCr_2(PO_4)_3$	$Ce_{1.00}Cr_{2.00}P_{3.00}O_{12}$	$Ce_{1.02(3)}Cr_{2.02(2)}P_{3.00(1)}O_{12}$
$PrCr_2(PO_4)_3$	$Pr_{1.00}Cr_{2.00}P_{3.00}O_{12}$	$Pr_{1.02(3)}Cr_{2.02(2)}P_{3.00(2)}O_{12}$
$NdCr_2(PO_4)_3$	$Nd_{1.00}Cr_{2.00}P_{3.00}O_{12}$	$Nd_{1.02(3)}Cr_{2.02(3)}P_{3.00(1)}O_{12}$

$BiFe_2(PO_4)_3$ single crystals were also obtained; preliminarily synthesized polycrystalline phosphate was used as a batch. Single crystals were obtained by lowering the temperature of the $BiFe_2(PO_4)_3$ melt from 1080 to 950°C at a rate of 2.7 deg/h. The sample was then cooled to room temperature for 24 h. Comparison of the crystal structures of $BiFe_2(PO_4)_3$ and isoformular phosphate $NaZr_2(PO_4)_3$ reveals their topological relationship. Although between sp. gr. $R3c$ and $P6_3/m$ do not have a direct group–subgroup relationship, the similarity is obvious in relation to chain linking via PO_4 tetrahedra. The difference between the two structures lies in the nature and placement of the columns. $BiFe_2(PO_4)_3$ contains chains of two types: infinite columns of BiO_6 octahedra connected to each other by edges and columns of Fe_2O_9 dimers. In $NaZr_2(PO_4)_3$, only one type of column with one NaO_6 and two ZrO_6 octahedra is implemented. The IR-spectra are typical of complex anhydrous phosphates and, according to factor group analysis, represent a complex superposition of a large number of vibrations. The number of distinguishable maxima in the regions of stretching (1245–900 cm^{-1}) and deformation (675–400 cm^{-1}) vibrations reaches 12–13, which is lower than theoretically predicted.

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RAFT copolymerization of N-vinylpyrrolidone and fluoroacrylates with various structures

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One of the most convenient methods of controlled radical polymerization, which shows high efficiency in creating materials with desired properties, is living radical polymerization with reversible chain transfer (RAFT polymerization). Its advantages are the tolerance of the compounds used to functional monomers, wide possibilities in obtaining macromolecules of complex architecture, rather mild conditions for their synthesis [1]. Interest in the study of fluorinated polymers is due to their ability to significantly improve the properties of coatings used in modern products. Fluorine-containing polymers have high chemical resistance, low surface energy, friction coefficient and refractive index. N-vinylpyrrolidone (NVP) is a stable, hydrophilic compound that shows good biocompatibility [2]. Based on these properties, NVP is excellent for use as a second block of copolymers. This type of copolymer includes the positive properties of both fluoropolymers (low surface energy) and N-vinylpyrrolidone polymers (non-toxicity).

One of the main applications of such copolymers can be the creation of low surface energy (hydrophobic) coatings with a slippery surface that prevents fouling. Fluorine-containing thin polymer films are promising materials for the manufacture of biosensors, artificial endoprostheses, mitral valves, and other implants, for which the adhesion of thrombogenic components is unacceptable [3].

It can be expected that the resulting copolymers will exhibit amphiphilicity and improved self-assembly ability due to the presence of hydrophobic and hydrophilic units. The aim of this work is to study the features of the RAFT copolymerization of 1,1,1,3,3,3-hexafluoroisopropylacrylate (HFIPA) and NVP; 2,2,3,3,4,4,5,5-octafluoropentyl acrylate (OPPA) and NVP. In addition to copolymerization in the presence of a low molecular weight reversible chain transfer agent (dibenzyl trithiocarbonate), copolymerization in the presence of high molecular weight RAFT agents based on PHFIPA and POFPA was studied. Other important tasks are obtaining curves for the composition of copolymers, calculating the relative activities of monomers, and studying surface pressure isotherms.

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Synthesis and evaluation of carbon nitride-based catalysts for hydrogen evolution reaction

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Increasing energy consumption and depletion of fossil fuels reserves rise the demand for new alternative renewable energy sources. Solar energy is of paramount importance as a free alternative energy source with a great practical prospect. One of the approaches for solar energy accumulation is production of hydrogen — the known prospective energy carrier and fuel. Today, special attention is paid to the production of hydrogen by water splitting under visible light in the presence of catalysts. Graphitic carbon nitride-based materials are of great interest as such catalysts.

In this work, we investigated the influence of synthetic conditions (type of precursors, heat treatment mode, the amount of Ni, Co, Fe-based cocatalysts) on the properties of g-C_3N_4-based catalysts. The optimized procedure for the synthesis of g-C_3N_4 catalyst has been developed. The factors influencing the properties of g-C_3N_4-based catalysts has been studied. The most promising results were achieved for the samples with Co-based cocatalyst.

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Chemical Properties of Ruthenium Functional Materials of Thick Film Resistors

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Ruthenium-based functional materials have proven to be the best conductive phases for the production of thick film resistors. Their advantage, in comparison with other thermal power plants, in addition to electrical properties, is due to good thermal and chemical stability.

However, the latter property requires additional study, since the products of interaction with the participation of ruthenium conductive phases were discovered in commercial TFRs by a number of developers of these microelectronic products [1, 2]. We studied the chemical properties of ruthenium functional materials (RuO_2, $Pb_2Ru_2O_6$, $Bi_2Ru_2O_7$, RuO_2–Nb_2O_5, $CaRuO_3$, $SrRuO_3$, $BaRuO_3$) with respect to common and promising modifiers of the electrical properties of thick film resistors (CuO, NiO, Bi_2O_3, Al_2O_3, TiO_2, Nb_2O_5, WO_3, $(NH_4)_{0.2}H_{0.2}Me_{0.1}W_{0.9}O_3$ and $K_{4x}Me_xW_{1-x}O_6$, where M is Ni or Co) and glasses used as constant binders, systems: SiO_2–B_2O_3, PbO–SiO_2 , PbO–SiO_2–B_2O_3, PbO–SiO_2–B_2O_3–Al_2O_3, as well as more complex composition in this work. It is shown that ruthenium functional materials during heat treatment of resistive pastes can enter into chemical interaction with both modifiers and constant binders according to the following schemes:

$$Pb_2Ru_2O_6 + 2WO_3 \rightarrow 2RuO_2 + 2PbWO_4;$$
$$Pb_2Ru_2O_6 + 2NiWO_4 \rightarrow 2RuO_2 + 2PbWO_4 + 2NiO;$$
$$Pb_2Ru_2O_6 + 2PbO\cdot SiO_2 \rightarrow \text{no interaction};$$
$$2RuO_2 + 2(2PbO\cdot SiO_2) \rightarrow Pb_2Ru_2O_6 + 2(PbO\cdot SiO_2);$$
$$Pb_2Ru_2O_6 + 2(PbO\cdot 2SiO_2) \rightarrow 2RuO_2 + 4(PbO\cdot SiO_2).$$

This interaction proceeds according to the mechanism of acid-base interaction, when components with pronounced properties of a base and an acid are present in the resistive paste. The obtained patterns are well described by the scale of acid-base properties based on Milliken's orbital electronegativity (Table 1) [3].

Table 1. Milliken's orbital electronegativity (χ_M) some compounds

Compo-und	$Pb_2Ru_2O_6$	WO_3	RuO_2	$PbWO_4$	$NiWO_4$	NiO	$2PbO\cdot SiO_2$	$PbO\cdot SiO_2$	$PbO\cdot 2SiO_2$
χ_M, Ev	6,31	6,72	6,51	6,44	6,48	6,00	6,16	6,32	6,43

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Indole derivatives as promising hydrogen carriers. Thermodynamic analysis of hydrogenation-dehydrogenation reactions

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The idea of storing hydrogen in a chemically bound form by addition it to unsaturated molecules, such as aromatic hydrocarbons or unsaturated heterocycles, looks promising. This is due to the fact that the compounds used for hydrogen accumulation do not differ much in their physical and chemical properties from traditional fuels. Thus, the entire existing fuel infrastructure can be used for their storage and transportation. Compounds capable of storing hydrogen are called liquid organic hydrogen carriers (LOHC).

The addition of hydrogen to LOHC (hydrogenation) is a catalytic process, as is the reverse reaction of dehydrogenation. In this case, dehydrogenation is an endothermic process and requires significant energy. One of the methods of reducing the enthalpy of the dehydrogenation reaction is to replace the carbon atom in the cyclohexane ring with a nitrogen atom. Indole derivatives in this case are of particular interest as LOHC. It is obvious that in order to evaluate the effectiveness of these compounds, it is necessary to carry out a thermodynamic analysis of the hydrogenation-dehydrogenation reactions involving all intermediate compounds. While reliable thermodynamic data are available for initial and final structures, it is absent for partially hydrogenated products.

In this study, indole and its derivatives are considered as promising liquid organic hydrogen carriers. The aim of the work was to search for systems of reversible accumulation and release of hydrogen and to study their thermodynamic and thermochemical properties. For each system, a series of experiments was carried out to study the equilibrium of the hydrogenation-dehydrogenation reaction. Extensive thermochemical studies of these compounds have been carried out, including vapor pressure measurements and combustion calorimetry. The obtained data are compared with the results of a theoretical study of the same reactions by quantum chemical methods. In addition, our work demonstrates the effectiveness of each system in terms of the concept of hydrogen storage.

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Calculation of the parameters of vacancy formation and self-diffusion in a single-component crystal

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An analytical method for calculating the parameters of electroneutral vacancy formation and self-diffusion of atoms in a single-component crystal is proposed. The method is based on the four-parameter pairwise Mie–Lennard-Jones interatomic interaction potential. The method allows calculation of all activation process parameters, that is, Gibbs energy, enthalpy, entropy, and volume, for both the vacancy formation process and the self-diffusion process. The method is applicable at any pressure (P) and temperature (T). The temperature dependences of the activation process parameters for gold have been calculated from T = 10 K to 1330 K along two isobars, P = 0 and 24 GPa. It has been shown that, at low temperatures, due to quantum regularities, activation parameters strongly depend on temperature, and the entropy of activation processes (s_i, where i = v – for the vacancy formation, i = d – for self-diffusion) in this region has a negative value. The dependencies $s_i(P, T)$ are shown in Fig. 1. In the high-temperature region, the probability of vacancy formation and the self-diffusion coefficient pass into classical Arrhenius dependences, with a weakly temperature-dependent enthalpy and a positive value of the activation process entropy. Good agreement has been obtained with estimated activation parameters for gold in the literature. It has been shown that at T = 0 K the activation process parameters reach their minima: the Gibbs energy, enthalpy, and volume of the activation process all become zero, and the minimum of the activation process entropy lies in the negative region.

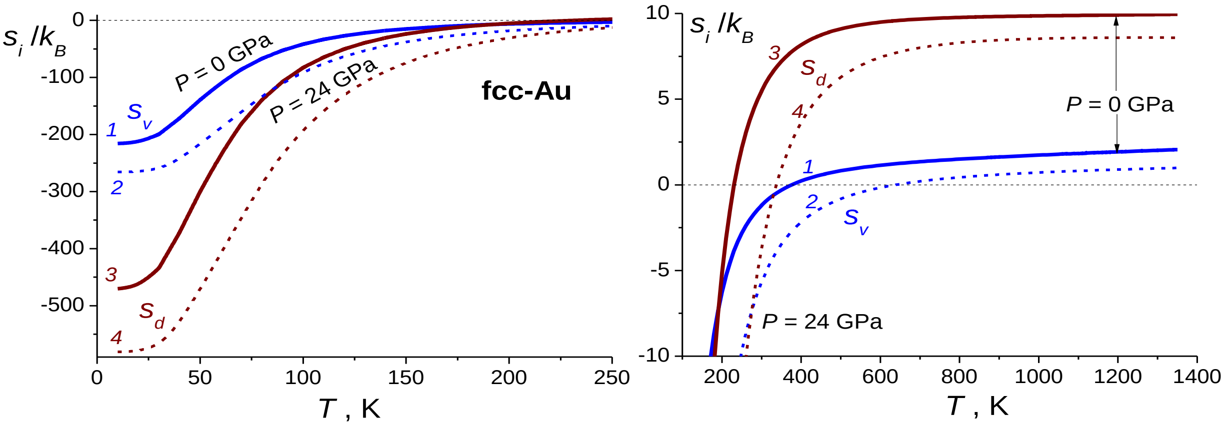

Fig. 1. Temperature dependences of the activation process entropy for gold. Curves *1* and *2* – calculation of entropy for vacancy formation, curves *3* and *4* – calculation of entropy for self-diffusion. Solid curves *1* and *3* – isobars P = 0; dashed curves *2* and *4* – isobars P = 24 GPa. The left graph shows the dependences of $s_i(T) < 0$ in the low temperature region, the right graph shows for the high temperature region.

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Quantification of cellulose lignin and hemicellulose in plant materials by IR spectroscopy

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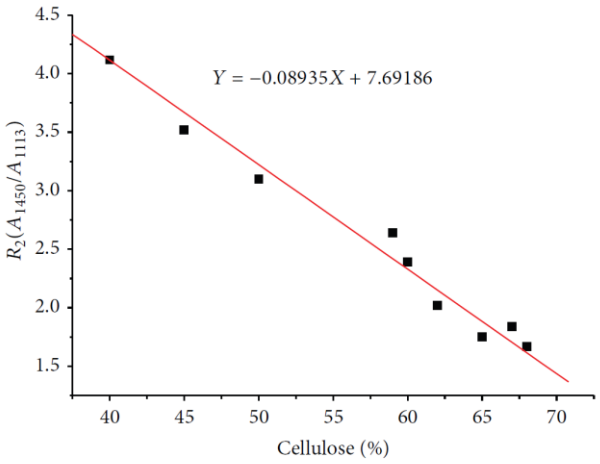
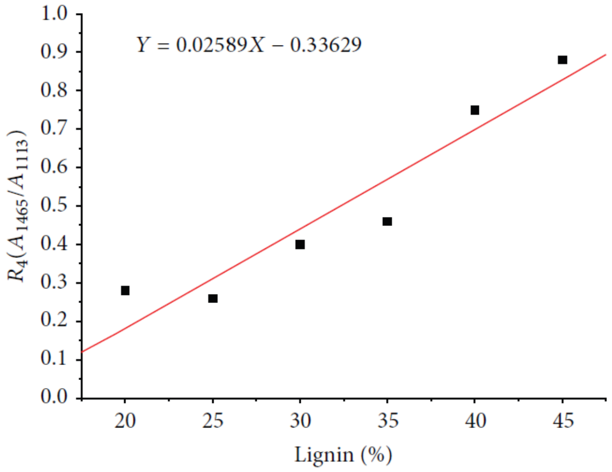
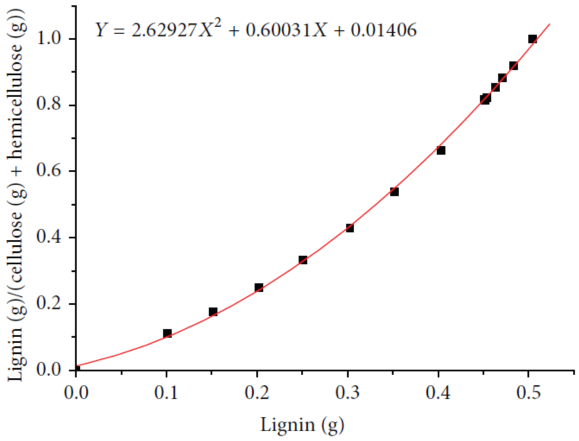
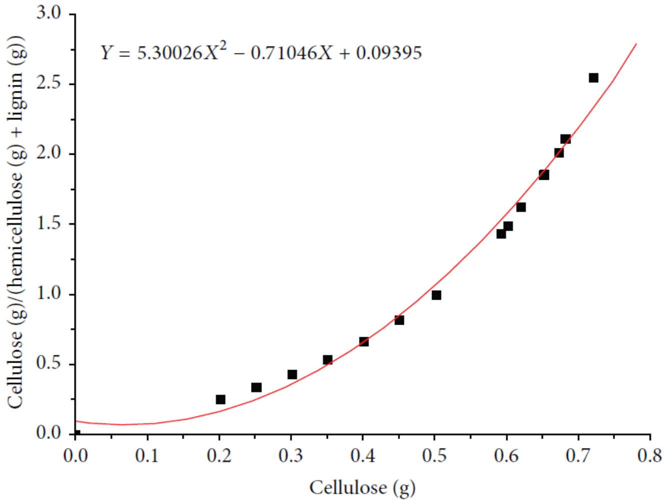
A method has been developed and tested for determining the content of cellulose lignin and hemicellulose in plant materials using FT-IR spectroscopy. The determination procedure is based on the use of ternary mixtures consisting of cellulose, hemicellulose and lignin in various proportions. For the determination of lignin, the analytical band at 1510 cm^{-1} (the area integrated between 1535 and 1495 cm^{-1}) was chosen, for cellulose, the band at 1450 cm^{-1} (the area integrated between 1530 and 1397 cm^{-1}). The absorption band at 1113 cm^{-1} (the area integrated between 1142 cm–1 and 1092 cm–1) was chosen to normalize the analytical bands. Indirect correlations were used to determine hemicellulose.









The calculated values in wood samples of pine, larch, aspen, poplar, birch, oak and willow fluctuate in the ranges of 40–55% cellulose, 15–25% hemicellulose, and 20–25% lignin, which corresponds to the literature data [1].

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Stability of the structural fragments in layered transition metal dichalcogenides substituted with 3,4d-transition metals

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Solid solutions based on layered transition dichalcogenides TCh_2 (T – 3,4d-transition metal, Ch = S, Se, Te) are promising materials for use as a cathode in lithium batteries. For example, the kinetics of electrode processes in $Li_yV_xTi_{1-x}Se_2$ drastically differ from those in Li_yTiSe_2 and Li_yVSe_2, despite the same crystallographic positions of Li atoms in all the mentioned compounds. At the same time the morphology of the single crystals of the TCh_2-based solid solutions appear to be inhomogeneous and can be responsible for this difference. To study the morphology of the single crystals we used such X-ray photoelectron spectroscopy (XPS) methods as Scanning PhotoElectron Microscopy (SPEM), resonant XPS (ResPES) and angle resolved XPS (ARPES). For these purposes we used ESCA Microscopy and BACH beamlines at the Elettra synchrotron facility (Trieste, Italy) and ANTARES beamline at the SOLEIL synchrotron facility (Paris, France). To determine the stability limits of the substitution phases we used the electromotive force (EMF) method. Using SPEM we found [1] that the single crystals of $Cr_xTi_{1-x}Se_2$ and $Cr_xTi_{1-x}S_2$ contain mesoscopic structural fragments (SFs), which chemical bonding depends on the type of chalcogen atoms. The $CrSe_2$-based SFs are being formed in the $Cr_xTi_{1-x}Se_2$ system at $x \geq 0.75$, but only $Cr_xTi_{1-x+y}S_2$ SFs are formed in the $Cr_xTi_{1-x}S_2$ system with different concentration *y* of superstoichiometric Ti. The SFs in the $TiSe_{2-x}S_x$ system [2] are of the different type and can be considered as S-Ti-Se Janus layers alternating with $TiCh_2$ (Ch = S, Se) layers. Other systems under study demonstrating the formation of stable SFs of different types are the $V_xTi_{1-x}Se_2$, $Nb_xV_{1-x}Se_2$ and $Zr_xTi_{1-x}Se_2$ ones. All the structural fragments are electrostatically bonded with each other since the charge transfer between them is clearly visible on the ResPES spectra.

The contribution of the surface tension of interfaces between SFs to the thermodynamic free energy can be much higher in 2D materials than in ordinary 3D materials. This discrepancy can lead to a redistribution of the components, which will compensate for this spatial inhomogeneity of free energy. We believe that the formation of turbostratic disordered structural fragments is expected to be a widely observed phenomenon in low-dimensional materials.

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Photocatalytic properties of phosphates $MgHPO_4{\cdot}3H_2O$, $MgKPO_4{\cdot}6H_2O$ and $MgNH_4PO_4{\cdot}6H_2O$ as additives to mortars and concretes

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The development of photocatalytic additives to concretes that promote the oxidation of various volatile pollutants (including aromatic hydrocarbons) is an urgent material science problem in building technologies [1, 2]. In this vein, phosphate additives are promising objects for research due to their good solubility in the base material, the possibility of obtaining them without high-temperature firing, and varying particle sizes (as a result, surface area) [3]. Double magnesium phosphates ($MgHPO_4{\cdot}3H_2O$, $MgKPO_4{\cdot}6H_2O$, $MgNH_4PO_4{\cdot}6H_2O$) with the structure of Newberite and Struvite(-K) minerals were synthesized in the form of a powder by co-precipitation at room temperature. The phase purity of the product, the surface morphology and chemical composition homogeneity were determined by X-ray phase analysis (XPA) and scanning electron microscopy (SEM). Using the method of static vacuum volumetry, the specific surface area of the studied powders was determined: 7,35 m^2/g for $MgHO_4{\cdot}3H_2O$ and 17,082 m^2/g for $MgKPO_4{\cdot}6H_2O$. The band gap and absorption energy were determined by the method of optical diffuse reflection spectroscopy of polycrystalline samples. For magnesium phosphate $MgHPO_4{\cdot}3H_2O$ the absorption energy was 3,10 eV, for magnesium-potassium phosphate $MgKPO_4{\cdot}6H_2O$ it was 3,13 eV, for magnesium-ammonium phosphate $MgNH_4PO_4{\cdot}6H_2O$ it was 4,17 eV, which corresponds to absorption in the region of 400, 396, 297 nm, respectively. The obtained results on the photocatalytic decomposition of toluene indicate the catalytic activity of the obtained polycrystalline phosphates. During a two-hour experiment using visible light and UV irradiation, the aromatic hydrocarbon concentration decreased by 12.2% and 1.9% for magnesium phosphate $MgHPO_4{\cdot}3H_2O$, by 9.8% and 9.1% for magnesium-potassium phosphate $MgKPO_4{\cdot}6H_2O$, by 3.2% and 4.7% for magnesium-ammonium phosphate $MgNH_4PO_4{\cdot}6H_2O$, respectively.

The research was carried out with the financial support of the Ministry of Science and Higher Education of the Russian Federation (the basic part of the State Assignment, project 0729-2020-0053) and using the equipment of the New Materials and Resource-Saving Technologies Central Collective Use Center (Lobachevsky University).

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Study of formation limits, phase and hydrolytic stability of aluminum-phosphate glass matrices for immobilization of lanthanide and minor-actinide fractions of radioactive wastes in comparison with phosphate ceramic compositions.

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The problem of safe handling of nuclear waste is one of the most important tasks of materials science, classical chemistry, physics and radiochemistry. The most progressive, from the point of view of environmental safety and the concept of non-proliferation of radioactive waste, is the idea of binding waste into inert, stable matrix materials. Such matrices are subject to high requirements for physical and chemical stability, high capacity for radioactive waste, thermal conductivity, mechanical strength, etc. [1].

Now, for high-level radioactive waste of a wide elemental composition, it has not been possible to create a **single** matrix that meets all of the above requirements. The actual world concept is the fractionation and subsequent consolidation of groups of cations with similar chemical properties in the form of separate inorganic matrices, including ceramic, glass and glass-ceramic ones [2, 3].

In this work, studies were carried out to determine the limiting fraction of the inclusion of various lanthanides (1-15 mass.%) in the composition of the base aluminophosphate glass used in the current technology of radioactive waste management (imitation of the lanthanide and minor actinide fractions). Also, depending on the specific content of lanthanides (Nd, Eu, Gd, Y, La, Ce, Pr, Nd, Sm - jointly and separately), the phase composition, thermal stability, microstructure, hydrolytic stability of the resulting glass compositions in static and dynamic conditions in distilled, mineral water, acid/alkali solutions. The results obtained were compared with literature data and similar characteristics for phosphate ceramic matrices (with the structures of kosnarite, langbeinite, garnet, pollucite, monazite, xenotime) with a similar specific content of lanthanides, studied within the framework of this scientific project by our research team.

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New bismuth-based catalyst for photocatalytic decolorization of RB19 dye from polluted water

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The textile industry is one of the industries with the highest water consumption, producing a huge amount of wastewater that can be toxic, carcinogenic, mutagenic, or teratogenic [1]. Among several wastewater conventional treatment options (sorption [2], electrocoagulation [3], microbial degradation [4]), heterogeneous photocatalysis can be a method for a high level of dye removal from textile industrial wastewater.

In that purpose, the photocatalyst based on bismuth, concretely bismuth tartrate (BiTar) for decolorization RB19 from water was synthesized. The BiTar was prepared by sol-gel process from bismuth (III) nitrate pentahydrate, ethylene glycol and 2,3-dihydroxybutanedioic acid. XRD, FTIR, SEM and EDX analyses were used to determine the properties and structure of the BiTar. The BiTar had a smooth surface, without pores (SEM), which was confirmed by BET analysis where the specific surface area was not large and amounted 23.7 m^2 g^{-1}. The structure and composition of BiTar was confirmed using XRD, FTIR and EDX analyses. The decolorization process of the RB19 was the most efficient at the optimal conditions: photocatalyst dose of 0.50 g dm^{-3}, stirring speed of 250 rpm, pH of 2.0 and with light intensity of 1750 μW cm^{-2}. Complete decolorization of 50.0 mg dm^{-3} RB19 under optimal conditions was performed within 6 minutes. The decolorization of RB19 follows the Langmuir-Hinshelwood kinetic model well. BiTar has shown high photocatalytic potential for application in purification of textile industrial wastewater contaminated with RB19 dye.

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Development of scientific foundations for the technology of obtaining chemoresistive materials for the «electronic nose» based on complex nanostructured oxide matrices

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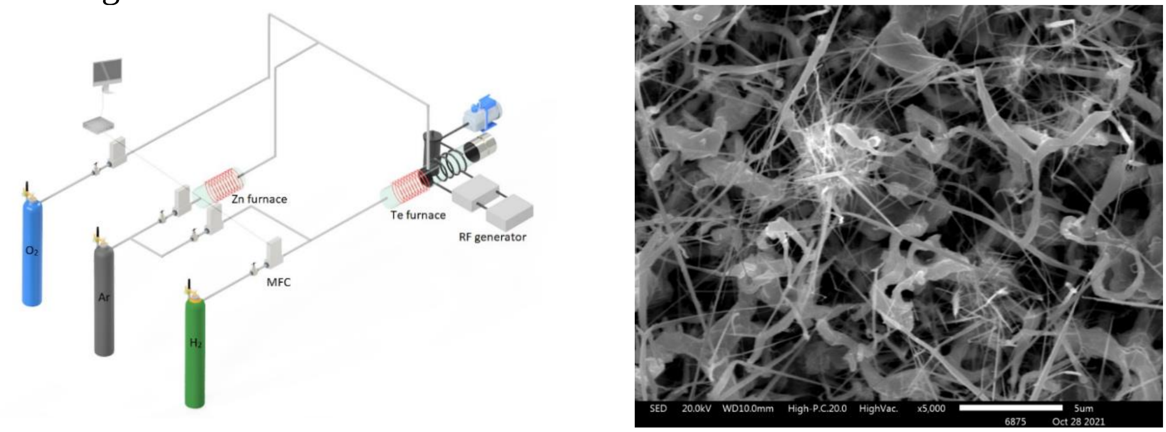
Nowadays the multifunctional nanostructured complex oxide materials are highly demanded e.g. as multiporous nanosystems for creation of a new generation of highly sensitive chemo resistors for «e-nose» [1]. The properties of these nanostructured materials are mainly defined by the preparation technique. Traditional methods of synthesis possess a number of disadvantages, including insufficient purity, a large number of defects in the structure, the absence of the ability to vary the composition over a wide range, *etc*. [2]. The aim of this work is to develop a novel plasma-based approach to synthesis of these type nanostructured materials [3]. We utilized a modified plasma-enhanced chemical vapor deposition method (PECVD), when the high-purity elements were the starting materials. Zn and Te were delivered by a carrier gas to the reaction zone, where they interacted with oxygen. RF non-equilibrium plasma discharge at low pressure (0.01 Torr) was used for the initiation of the precursors oxidation. OES (optical Emission Spectroscopy) allowed us to find out the reactive species formed in the plasma discharge. The ZnO-TeO_2 were studied by various analytical techniques. The schematic diagram of PECVD installation is illustrated in Figure 1a. The SEM image of the obtained sample is shown in Figure 1b.



a b

Fig. 1. Universal PECVD setup and SEM image of the nanostructured material

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Surface modification of fiber materials with composites based on amorphized calcium phosphates and phosphomolybdic acid

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Calcium phosphates in amorphous form have enhanced adsorption-structural characteristics, which allows them to be used as carriers for active compounds [1]. Previously, it was shown that amorphized hydroxyapatite (HA, $Ca_{10}(PO_4)_6(OH)_2$) and tricalcium phosphate (TCP, $Ca_3(PO_4)_2$) adsorb phosphomolybdic acid (PMA, $H_3PMo_{12}O_{40}\cdot 14H_2O$) from aqueous systems without changes in their phase composition. It is known that the introduction of vanadium atoms into the PMA structure leads to an increase in their oxidizing properties [2]. In this regard, it is of interest to create calcium phosphate adsorption centers with vanadium-containing PMA on the surface of fiber materials (cotton cellulose fabric, polypropylene nonwoven fabric).

Modification of the surface of fiber materials was carried out by the immersion method using a 2–4% calcium phosphate suspension ($Ca_{10}(PO_4)_6(OH)_2$ / $Ca_3(PO_4)_2$) and a 0.1–1% solution of vanadium-containing PMA ($H_3PMo_{12}O_{40}\cdot 14H_2O$ / $(VO)_3P_4O_{13}$). The data of thermal, X-ray phase analysis and IR spectroscopy indicate the appearance of calcium phosphate adsorption centers on the surface of the fibers as a result of such treatment.

The presence of vanadium-containing PMA contributes to the partial oxidation of cellulose and a decrease in its heat resistance. In the case of polypropylene fiber, the temperature at which polymer degradation begins does not depend on the method of modification.

Surface treatment of fiber materials with composites based on calcium phosphates and vanadium-containing PMA is accompanied by structural transformations in polymers and an increase in their moisture-binding capacity by 1.5–5.2 times (maximum for a polypropylene fabric). The obtained cellulose and polypropylene fiber materials contain up to 2–6% of modifying additives and can be proposed as model systems for binding active biological structures.

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Influence of a compatibilizer on the crystallization regularity of a highly filled composite based on aluminum hydroxide and polyethylene mixture

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The problems of the environment and human health arising from the combustion of polymers lead to the search for new environmentally friendly flame retardants. Metal hydroxides such as $Al(OH)_3$ and $Mg(OH)_2$ are alternative materials that are safer and can be used instead of halogen additives. The purpose of this study was to evaluate the effect of a compatibilizer on the crystallization regularity of a highly filled composite based on an environmentally friendly flame retardant ($Al(OH)_3$) and a mixture of polyethylenes.

Industrial samples of high-density polyethylene (HDPE), low-density polyethylene (LDPE), aluminum hydroxide, compatibilizer DuPont^{TM} Fusabond ® P353 Polimer Modifier were used as the object of research. Composite materials based on a mixture of HDPE/LDPE in a ratio of 50/50, with a fixed concentration (50 wt %) of $Al(OH)_3$ and 1, 3, 5 wt % of the compatibilizer were obtained by mixing the components on laboratory rollers. Dilatometric studies were carried out on the IIRT-1 device converted to a dilatometer during stepwise cooling in the temperature range from 180°C to room temperature (load 5.3 kg).

When studying the influence of the compatibilizer concentration on the density and temperature of the onset of crystallization, which characterizes the first-order phase transition, it was found that with an increase in the amount of the compatibilizer, the temperature of the onset of crystallization does not undergo any changes and corresponds to 105°C. At the same time, the density values of the composites at room temperature are almost equal. By crossing the upper and lower branches of the dilatometric curves, the approximate values of the glass transition temperature of the samples under study were found. The glass transition temperature of the initial LDPE / HDPE + 50 wt % $Al(OH)_3$ and composites based on it containing 1, 3, 5 wt % compatibilizer, respectively, are -35, -56, -56, -78°C. It has been established that the value of the free specific volume of melts of compatibilized composites is higher than that of the initial mixture of HDPE / LDPE + 50 wt % $Al(OH)_3$. After crystallization, the values of the free specific volume of the compatibilized composites approach each other, and at a temperature corresponding to room temperature, they practically become equal. The convergence of the values of the free specific volume of the modified composites at room temperature can be explained by the fact that the compatibilizer, in the given concentration range, to some extent contributes to the uniform growth of crystalline formations.

Application of bismuth oxo citrate for photocatalytic decolorization of textile dye RO16

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Effluents from the textile industry are a significant concern for the environment, because dyes are often non-degradable compounds and can be toxic, carcinogenic, mutagenic or teratogenic [1]. During the last decades, photocatalysis has been widely used as a "green" technique in the decomposition of various organic pollutants [2].

In this study, the synthesis of the photocatalyst bismuth oxo citrate and its application for the decolorization of the textile dye Reactive Orange 16 (RO16) was performed. The photocatalyst was synthesized by the precipitation process from an acidic solution of bismuth nitrate to which citric acid was added and subsequent thermal treatment at 200 ºC. The obtained material was characterized by SEM-EDX, FTIR, XRD and BET analyses. SEM images showed that the photocatalyst consists of slightly sintered polyhedral particles of different shapes and sizes. The specific surface area of photocatalyst was about 9 $m^2\ g^{-1}$. The chemical structure of bismuth oxo citrate photocatalyst was determined by EDX, FTIR and XRD analyses. The results showed that the photocatalyst are in form of $BiOC_6H_7O_7 \cdot H_2O$. The photocatalytic performance of bismuth oxo citrate was determined by decolorization of textile dye RO16, which was used as a pollutant model. Complete decolorization of the dye with a concentration of 25.0 mg dm^{-3} was achieved in less than 6.0 minutes at native pH and with photocatalyst dose of 500.0 mg dm^{-3}, which shows that bismuth oxo citrate can be successfully used as a photocatalyst.

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Computer simulation of chemical systems promising for materials science, catalysis, and medicine: non-covalent interactions and reactivity

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Computer simulation of chemical systems is one of the most dynamically developing areas of modern materials science and related natural science disciplines. This kind of research serves as a starting point for the creation of innovative smart materials applicable in catalysis and medicine.

This report is devoted to the presentation and brief discussion of the results of my scientific research over the past 10 years in the field of theoretical study of various non-covalent interactions in organic/inorganic/organometallic chemical compounds and their reactivity. This report is based on more than 230 articles in high-ranking international scientific journals, including *Nat. Commun., J. Am. Chem. Soc., Angew. Chem. Int. Ed., Chem. Commun., Chem. Eur. J., Chem. Asian J., ACS Catal., RSC Catal. Sci. Tech., Crystal. Growth Des., CrystEngComm, Inorg. Chem., J. Org. Chem., Organometallics, Org. Biomol. Chem., Phys. Chem. Chem. Phys., Dalton Trans., J. Phys. Chem. Lett., J. Comput. Chem.* and others – for details and some recent publications see [1–5] and my Scopus ID: 50262902200.

The results obtained in the course of my research contribute to the understanding of the nature of compounds and materials that have a wide range of applications in biology and medicine (in particular, in the neutron capture therapy of oncological diseases), which are promising catalysts for the most important organic cross-coupling reactions (in particular, the Suzuki and Sonogashira reactions), as well as having valuable redox, magnetic and optical properties, promising for the manufacture of LEDs and photocells for solar power plants.

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Isothermal calorimetric study of the cement hydration process with the modifiers

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Today modern additives-modifiers are used in all production technologies. They contribute to the emergence and development of new technologies, such as the production of high-strength, self-compacting concrete, etc. Moreover, chemical additives can significantly reduce the cost per unit of production, improve the quality and efficiency of a large range of reinforced concrete structures, and extend the service life of both structures and buildings, and structures in general. The introduction of additives into the concrete mix in small amounts, usually tenths of a percent by weight of cement, allows you to control the properties of concrete, physical and chemical hardening processes, the morphology of neoplasms and its performance characteristics. Previously [1] the effect of introducing superplasticizer into the concrete mix was studied which allows modifying the concrete construction and technological indicators. This work presents the results of studying the behavior of modified cement compositions. Portland cement grade CEM I 42.5B was used as a binder with the mineralogical composition of its clinker, %: C_3S – 62; C_2S – 14; C_3A – 6,5; C_4AF – 12. The additive "Polyplast PK type S" is produced by Poliplast LLC in the form of a transparent aqueous solution with a density of at least 1.05 g / cm^3 at 20 C and a pH of at least 4 according to TU 5745-098-58042865-2016 with change No1, 2 [2]. Registration of heat release during hydration of cement with and without additives was carried out using a TAM III microcalorimeter of TA Instruments in isothermal mode. Samples were prepared on the basis of cement paste with W/C=0.35. An analysis of the data obtained when determining the hydration process of a binder system based on cement and a regulator showed that the additive in the studied composition promotes greater heat release with a more pronounced exo-effect and an increase in the induction period of hydration. This effect can be presumably explained by the fact that type S PC contributes to some heating of the cement composition, allowing earlier C_2S reaction, with acceleration of the mixture hardening process. Thus, further study of the hydration process of cement with additives opens up prospects for the development of composition design, structure adjustment and prediction of the properties of effective road, hydraulic and other types of concrete.

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New variants of T-x diagram with three allotropes of one component

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In [1] there are 4 variants of T-x diagram with 3 allotropes of the component A: 1) the only peritectic transformation; 2) closed loop of 2-phase region with 2 low-temperature allotropes: 3) peritectic and evtectoid, divided by the eutectic; 4) metatectic and peritectoid, divided by the eutectic. Two additional variants are offered here: 5) metatectic and evtectoid, divided by the eutectic (Fig. 1,a); 4) peritectic and peritectoid, divided by the eutectic (Fig. 1,c). They were elaborated by means of flow diagrams (phase reaction scheme) [2]. Hypothetical variants of phase diagrams allow to optimize the assembling of 3D computer models for the real systems [3-6].

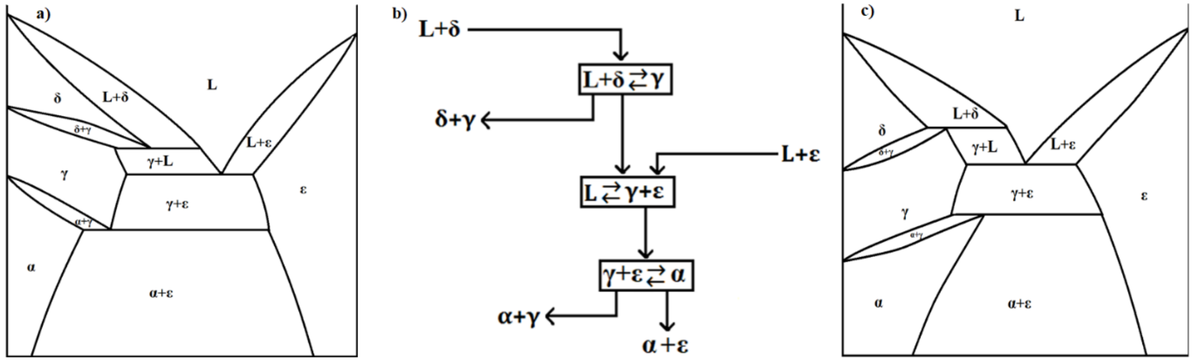

Fig. 1. T-x diagram with metatectic and eutectoid transformation (a) and flow diagram (b) for the variant with peritectic and peritectoid transformation (c)

In view of the widely spread use of computerized calculations of phase diagrams, there was an attempt to introduce a strict definition of Scheil reaction scheme (flow diagram) for the ternary systems [7]. As it was suggested that it be adopted for the production of computer-plotted flow diagrams, it’s better to start with the T-x diagrams of binary systems (like Fig. 1,b).

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Thermodynamical analysis of synthesis glasses based on germanium and gallium tellurides using chemical transport reactions

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Glasses based on germanium and gallium tellurides have a high transparency in the near and mid-IR ranges. Due to their properties, these glasses find application in IR-fiber optics and thermal imaging sensors.

The thermodynamically determined equilibrium compositions of thevapor phase in the studied systems are shown in Fig. 1a and 2a. The content of tellurium in the vapor phase is presented as the total amount of its intramolecular allotropes, taking into account the number of atoms included in them.

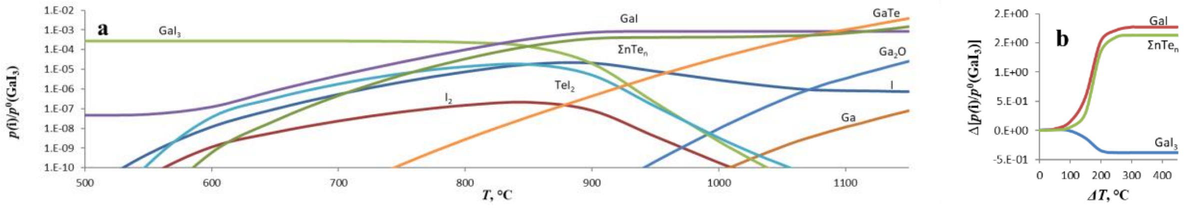
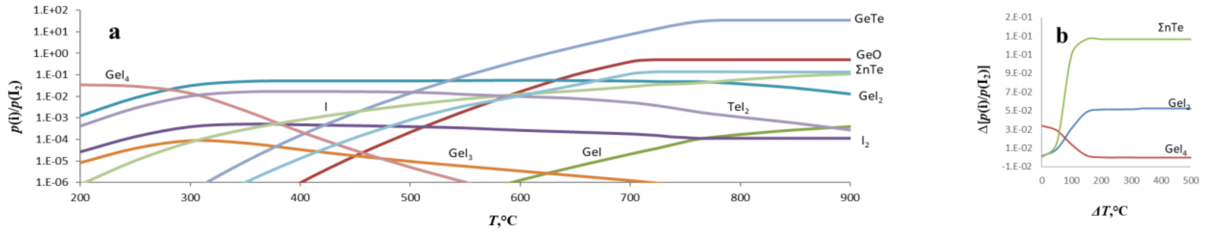


Fig. 1. Thermodynamically determined equilibrium composition of the vapor phase in the GaI_3-Ga_2Te_3-Ga_2O_3 system (a); dependence of the amount of the transferred component of the vapor phase on the T(750 °C)–$T(x)$ temperature difference (b).

Fig. 2. Thermodynamically determined equilibrium composition of the vapor phase in the GeI_4-GeTe-GeO_2 system (a); dependence of the amount of the transferred component of the vapor phase on the T(700 °C)–$T(x)$temperature difference (b).

According to the results obtained in this work, loading gallium(III) telluride into a reactor by the chemical transport using gallium(III) iodide as a transporting agent in combination with loading germanium through GeTe is an effective approach for producing Ga-Ge-Te and Ga-Ge-Te-I glasses with low oxygen impurity content. This is due to the high values of the separation coefficient of oxygen-containing impurities in chemical transport.



The reported study was funded by the Russian Science Foundation (project № 21-73-10104).

Analysis of molecular weight characteristics of collagen during enzymatic hydrolysis using different enzymes

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There is a high demand for tissue engineering products, the main task of which is to create cell matrices (scaffolds) with the subsequent formation of complex cellular compositions similar to tissue or organ for further transplantation to the patient to replace damaged or lost ones. Scaffolds are created using natural and synthetic polymers, such as collagen, etc. with the use of proteolytic enzymes.

The purpose of this work is to analyze and compare the molecular weight characteristics of fish collagen (FC) during hydrolysis in the presence of pancreatin and trypsin enzymes.

The enzymes used in the work were pancreatin and trypsin. During enzymatic hydrolysis, a 1% solution of FC was used [1]. 1M NaOH was added to the solution of high molecular weight FC to achieve a neutral medium and brought to a certain volume with distilled water. Hydrolysis in the presence of enzymes was carried out at the enzyme-substrate ratio collagen : enzyme = 10 : 1, adding an enzyme to the resulting mixture. Samples (1 ml) were taken from the reaction medium at certain intervals after the addition of the enzyme. To interrupt hydrolysis, a 4 % AcOH solution was poured into the samples. Molecular-mass characteristics of samples of FC hydrolysate were determined by the GPH method.

Thus, enzymatic hydrolysis of fish collagen was carried out under conditions close to those during the formation of scaffolds by different enzymes – pancreatin, trypsin. Analysis of the molecular weight characteristics of collagen hydrolysates by gel-penetrating chromatography during three days of the process showed that the destruction of the protein occurs with the formation of two low-molecular fractions, so the high efficiency of pancreatin and trypsin leads to the fact that there is no high-molecular fraction in the solution immediately after the first minute. However, there is a slight difference in the characteristics of hydrolysis products and their ratio, which is due to the nature of the catalytic centers of enzymes. The data obtained are of interest for the development of collagen-based matrices in the presence of enzymes of different nature.

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IR-transparent Y_2O_3-MgO (YMO) composite ceramics

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Recently, significant progress has been achieved in the manufacture and study of the properties of nanocomposite materials based on magnesia and rare earth oxides, such as yttrium oxide (Y_2O_3-MgO, YMO). The combination of the high optical, mechanical and thermal properties of the composites determines the prospects for their use as infrared windows, luminescent, and laser materials, as well as parts requiring plasma resistance in the semiconductor processing industry.

The fundamental requirement for ensuring high light transmission of the YMO composite in the near and mid-IR spectral region is the formation of a pore-free structure while maintaining the submicron grain size of yttrium and magnesium oxides. These characteristics require careful selection of the initial powders synthesis conditions and applying an appropriate method for the ceramics consolidation without significant grain growth.

In this work the Y_2O_3-MgO nanopowders were synthesized by the method of self-propagating high-temperature synthesis (SHS) using metal nitrates as an oxidizer and glycine as a fuel. The powders have a composite nature and correspond to the target materials in the crystal structure. The morphology of the powders is characterized by the presence of loose agglomerates with a porous structure, which is a consequence of intense gas formation during SHS.

Consolidation of YMO ceramics was performed by Hot pressing (HP) and Spark-plasma sintering (SPS). Average grain size of the SPS-derived MgO-Y2O3 ceramics is about 150 nm up to temperatures of 1200°C, after which it increases rapidly. The minimum porosity is observed for samples sintered at a temperature of 1150-1200 °C. The transmission of the ceramics after SPS does not exceed 60% due to significant contamination with carbon-contained impurities. Additional annealing in air at a temperature of 1100°C leads to an increase in IR transmission to 80.9% at a wavelength of 5 μm for samples obtained at a temperature of 1150°C.

The optimal temperature for hot pressing of MgO-Y2O3 ceramics is 1400°C, which is higher compared to SPS. At that, HP leading to the production of samples with the transmission of 83.6% at a wavelength of 5 μm.

Thus, the chosen methods allow the sintering of ceramics with a density of more than 99% while maintaining an average grain size of 100-150 nm. The transmission of these samples in the infrared range corresponds to the best published results.

The study was funded by the Russian Science Foundation (research project No. 19-73-10127).

Thermodynamic and Quantum Chemical Study of Bi_2O_3 - B_2O_3 - BaO Glasses for Optical Applications

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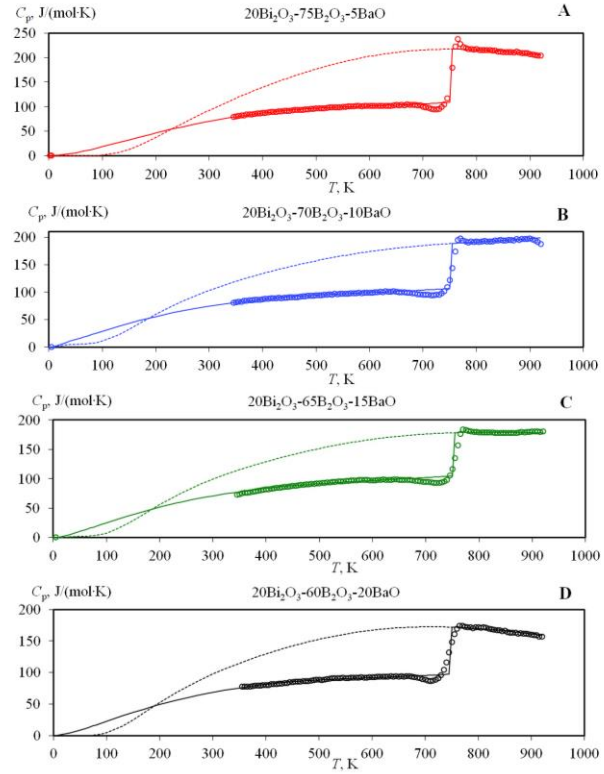
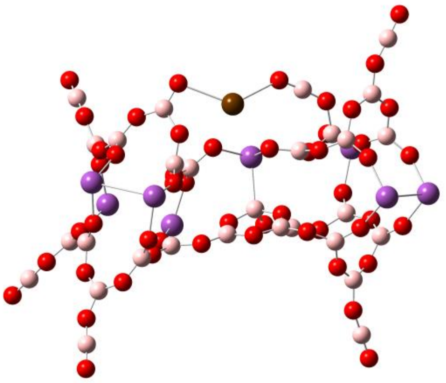
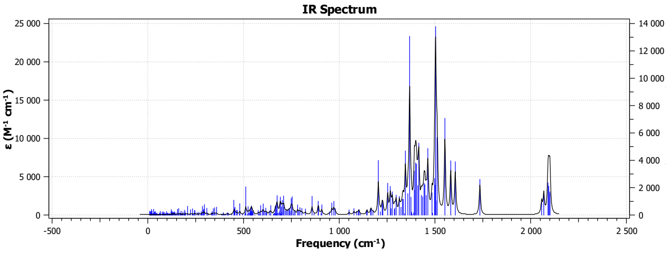
The study of the structure, spectral and thermodynamic properties of the glass-forming phase Bi_2O_3 - B_2O_3 – BaO, compatible in optical, thermophysical and chemical properties with the crystalline phase of yttrium aluminum garnet, is an urgent task for creating glass-ceramics for optical use.

In work by the method of dynamic calorimetry on the device DSC 404 F1 Pegasus heat capacity of glass, supercooled melt and glass transition characteristics were studied. Using the DFT/uB3LYP/Lanl2DZ method, the geometry of structural fragments was established and the spectroscopic characteristics of glasses of the composition $0.20Bi_2O_3$ - xBaO - $(0.80\text{-}x)B_2O_3$, containing x = 5, 10, 15 and 20 mol % BaO.







The results of quantum-chemical calculations, which made it possible to establish the structure of bismuth-barium borate glass and calculate the spectrum of collective vibrations, are necessary to establish its relationship with the low-temperature part of the heat capacity.

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Radiation studies of mineral-like ceramics - materials for the consolidation of radioactive waste components

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Mineral-like compounds are being studied as possible matrices for the consolidation of radioactive waste components. Materials based on such compounds must be resistant to various kinds of influences, including radiation.

In this work, ceramics $SrMoO_4$ (scheelite structure) and $PrPO_4$ (monazite structure) were irradiated with Ar (E = 46 MeV), Kr (E = 107 MeV), Xe (E = 160 MeV) heavy ions to fluences in the range $6\times10^{10} - 2\times10^{12}$ cm^{-2}. The ceramics were sintered by spark plasma sintering (SPS) using the “DR. SINTER model SPS-625 Spark Plasma Sintering System” (SPS SYNTEX INC. Ltd., Japan). Phase compositions of ceramics before and after irradiation were studied by X-ray diffraction (XRD) on a Shimadzu LabX XRD-6000 powder diffractometer. Radiation testing of the samples was carried out on the IC-100 cyclotron of the Laboratory of Nuclear Reactions of the Joint Institute for Nuclear Research, Dubna.

According to XRD data, for samples of $SrMoO_4$ ceramics, a highly crystalline state was observed even after irradiation with Xe ions with a fluence of 2×10^{12} cm^{-2} (a decrease in the intensity of diffraction maxima associated with partial amorphization of the structure occurred by ~ 40%), which indicates a high radiation resistance of the compound. The $PrPO_4$ phosphate sample was resistant to the action of an ion with a relatively low energy (Ar); upon irradiation with Xe ions at the maximum fluence, a significant decrease in the intensity of diffraction maxima and their broadening are observed, which indirectly indicates the formation of an amorphous layer on the ceramic surface. At the same time, complete amorphization was not achieved.

Thus, the investigated ceramics are evaluated as radiation-resistant under the conditions under study, capable of withstanding irradiation with high-fluence ion fluxes without undergoing complete amorphization. The SPS method makes it possible to obtain high-density ceramics, the proposed matrices for RW components, in a short time, which is promising from an environmental point of view.

The authors are grateful to the staff of the Laboratory of Nuclear Reactions of the Joint Institute for Nuclear Research, Dubna: Skuratov A.V. and Kirilkin N.S.

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Structure and properties of high-entropy superconducting oxide R-123

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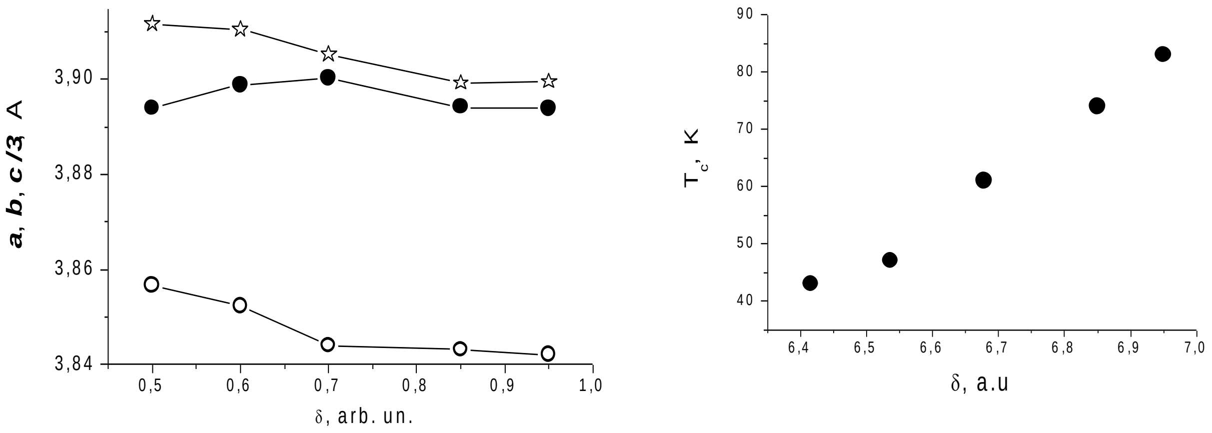
High-entropy oxides where more than four substitutions on cation site coexist are relatively new word in crystal chemistry. For $YBa_2Cu_3O_{6+\delta}$ superconducting oxides, the substitution of yttrium by rare-earth elements is possible and leads to an increase of critical current and chemical stability [1, 2]. We study crystal structure and magnetic properties of the single-phase $Y_{0.2}Nd_{0.2}Eu_{0.2}Sm_{0.2}Ho_{0.2}Ba_2Cu_3O_{6+\delta}$ (R-123) compound with different oxygen content (Fig. 1). Critical current was estimated by Bean method. The temperature of superconducting phase transition coincides with results for pure Y-123 compounds.



b)

a)

Fig 1 – Unit cell parameters ***a*** (open circles), ***b*** (filled circles) and ***c/3*** (starlets) (a) and critical temperature T_c (b) as function of oxygen content δ in $Y_{0.2}Nd_{0.2}Eu_{0.2}Sm_{0.2}Ho_{0.2}Ba_2Cu_3O_{6+\delta}$.

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Synthesis and investigation of thermal properties of sodium-chromium and sodium-iron arsenate-phosphates

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Mineral-like compounds with a garnet structure are notable for their chemical resistance, ability to withstand high temperatures and radiation. The stability of the garnet structure with respect to cation substitutions creates the prerequisites for the wide use of materials based on them in the electronics, in the abrasive and construction industries, in the field of radioactive waste management.

The size of the PO_4 tetrahedra does not allow orthophosphates to fix the garnet structure. This type of structure is realized in compounds with larger tetrahedral anions, for example, in arsenates $Na_3M_2(AsO_4)_3$ (M = Cr, Fe) [1]. We can hope to obtain mixed phosphates with the garnet structure, taking into account that the average value of the radius of the "formal" anion formed by the combination of PO_4 and AsO_4 anions is equal to the radius of the anion SiO_4: $r[(As_{0.5}P_{0.5})O_4] = r(SiO_4)$.

The purpose of this work is the synthesis of arsenate-phosphates with the expected garnet structure in the systems: $Na_3Cr_2(AsO_4)_x(PO_4)_{3-x}$ and $Na_3Fe_2(AsO_4)_x(PO_4)_{3-x}$.

Samples of limited solid solutions with the garnet structure $Na_3Cr_2(AsO_4)_x(PO_4)_{3-x}$ and $Na_3Fe_2(AsO_4)_x(PO_4)_{3-x}$ were obtained by co-precipitation of metal salts, arsenic acid and ammonium hydrophosphate from an aqueous solution followed by heat treatment. The samples were dried under 90−150°C and subjected to isothermal heat treatment until synthesis was complete at 600−900°C.

According to XRD data (Shimadzu LabX XRD-6000 X-ray diffractometer) and combined DTA−TG analysis (Shimadzu DTG-60H thermal analyzer), the received solid solutions exhibit dimorphism: low-temperature modifications with garnet structure are obtained at 800°C, and high-temperature rhombohedral modifications − at 900°C.

The use of variable-temperature X-ray diffraction (on the same diffractometer, using an Anton Paar TTK 450 temperature control chamber) allowed us to determine the thermal expansion parameters of the synthesized materials in the range from −130 to 200°C. As the temperature is varied, the samples of solid solutions expand isotropically and are classified as materials with low thermal expansion. Their thermal expansion does not cause shear deformations and minimizes the possibility of cracking.

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Phosphors based on aluminium-gallium garnets of rare earth elements for LED lighting sources.

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An industrial synthesis technology has been developed and the luminescent parameters of LED phosphors based on aluminium-gallium garnets of rare earth elements activated by cerium, such as $Ln_3(Al,Ga)_5O_{12}$- Ce^{3+}, where Ln: Y, Gd, Lu, have been studied.

Phosphors are designed for photoluminescent conversion of blue radiation (440-460nm) of nitride heterostructures into the luminescence of phosphors from green to yellow-orange, which makes it possible to obtain a total white glow from cold to warm shades at the output in ready LED lighting sources [1].

The indicated compositions of garnet phosphors were obtained by the method of solid-phase melt synthesis using nanosized initial components . Synthesis is carried out in a reducing atmosphere at a temperature t 1300-1500°C for 3-5 hours.

One of the main requirements for LED lighting devices is a wide range of color temperatures from 2600 to 6000K depending on the specific application. To solve the problem of controlling the emission spectrum of phosphors, the possibility of using various degrees of substitution of lanthanide ions in the basis of phosphors for a number of homovalent solid solutions of $Y_3Al_5O_{12}$ – $Gd_3Al_5O_{12}$ – $Lu_3Al_5O_{12}$ is shown. Obtaining a warmer shade of glow due to the shift of the spectrum to the long-wavelength region, from 530 to 580 nm, is achieved by introducing into the composition along with yttrium, additionally gadolinium garnet. The introducing of a lutetium ion, $Lu_3Al_5O_{12}$, into the composition of a solid solution makes it possible to obtain a shift of the maximum in the spectrum to the short-wavelength region up to 515 nm.

The possibility of a similar homovalent scheme is also realized for the anionic component of the phosphor and instead of a 6-fold coordinated Al^{3+} ion, a gallium ion, Ga^{3+}, can be introduced into the sublattice, which leads to a shift in the emission of the main activator Ce^{3+} to the short-wavelength region.

According to the results of the study of a number of phosphors based on solid solutions $(Y,Gd.Lu)_3(Al,Ga)_5O_{12}$-Ce it was found that the variation of the ratio Y/Gd/Lu/Ce in the cationic– and Al/Ga- in the anionic component of the compositions allows controlling the main spectral-luminescent-color parameters of phosphors. The obtained compositions of LED phosphors with a spectral maximum position of 515-580 nm and with a range of color temperatures T,K 2700-5900 are offered for use in lighting devices for various purposes.

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Influence of the composition and surface structure of poly(titanium oxide)-containing organic-inorganic copolymers modified with fluoracrylate latexes on material properties

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The development of materials with a switchable mode of surface wetting, when its transition from hydrophobic to hydrophilic state takes place, is currently of particular socio-economic importance in connection with the possibility of expanding environmentally friendly ways of protecting the environment from the negative technogenic impact on it. The usage of light irradiation (including solar) seems to be the most promising and environmentally friendly impact for this task. One of the most common light-sensitive materials are composites containing anatase polymorphic TiO_2. The one-electron transition $Ti^{4+} + e^- \rightarrow Ti^{3+}$ occurs when TiO_2 is exposed to light with $\lambda < 400$ nm. This process results in the reversible breaking of the Ti-O bond and the formation of electron-hole pairs, which are the cause of surface hydrophilization. The wetting angle of the oxide surface decreases from $72° \pm 1°$ to $(0 \pm 1)°$, the water droplet completely spreads over the material, removing the contaminants in its wake. However, the polarity of the unirradiated TiO_2 surface is too high to realize the maximum switching of wetting modes from "lotus effect" to superhydrophilicity. The problem of reducing the polarity of TiO_2 while maintaining its photosensitivity can be solved by using optically transparent organic-inorganic copolymers containing nanostructured poly(titanium oxide). In this regard the hydrophobization of the surface of films of binary organic-inorganic copolymers based on $Ti(OPr^i)_4$ and hydroxyethyl methacrylate by inclusion of butyl methacrylate, 2-ethylhexyl acrylate, octafluoropentyl acrylate, vinyl butyl ether or by modifying their surface with fluoracrylate latexes was performed in this resarch work. Optical transparency of terpolymers regardless of the composition is ~90% in the visible region of the spectrum. The introduction of more hydrophobic monomer units into copolymers leads to the decrease of PTO content on the surface layer of films, the increase of surface roughness and contact angle of wetting by water from 77° up to 93° in comparison with copolymers of binary composition. The surface treatment of terpolymers with fluoroacrylate latexes containing poly(1,1,5 - trihydroperfluoroacrylate) or copolymers(1,1,5 - trihydroperfluoroacrylate-styrene) increases their hydrophobicity to 105° and does not affect their optical transparency. A reversible photochromic one-electron transition of $Ti^{4+} + e^- \rightarrow Ti^{3+}$ occurs in the PTO chains upon UV-irradiation of the terpolymers. The greatest depth of change in light transmission - by ~ 60% for 180 min of UV-irradiation - is observed in terpolymers with butyl methacrylate and octafluoropentyl acrylate units. All materials exhibit a switchable hydrophobic-hydrophilic surface mode in which their water-wetting angle reversibly decreases to 10° in several cycles of use.

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Synthesis of nitrophenoxy-substituted magnesium zinc and aluminum phthalocyanines complexes and investigation of their spectral-luminescent properties

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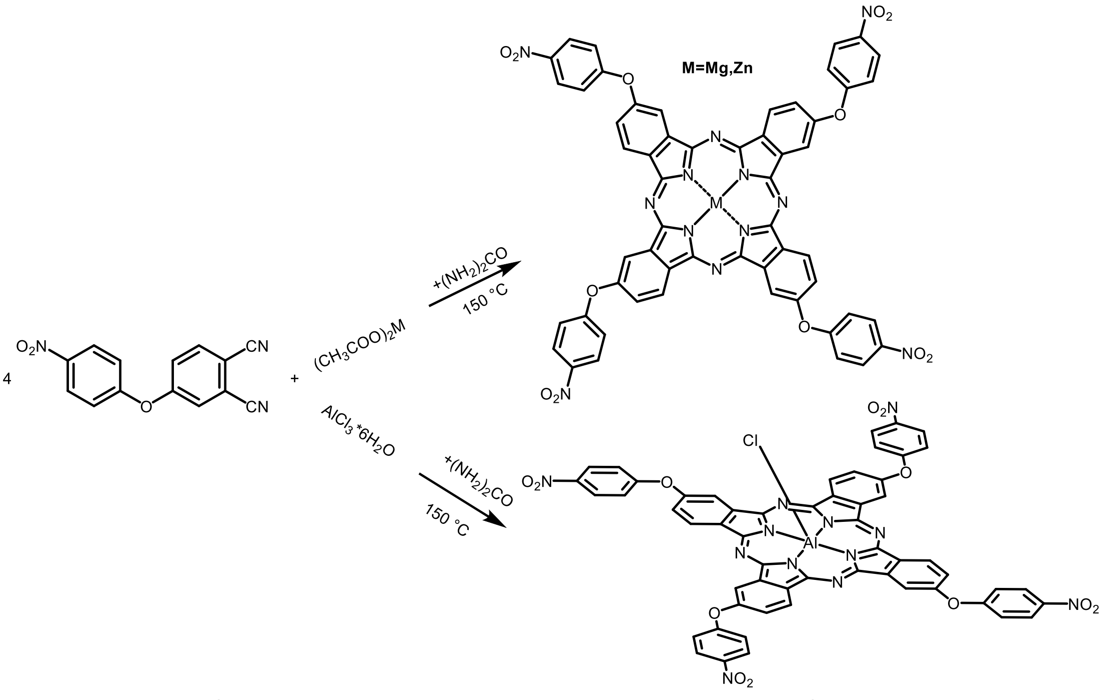
Phthalocyanines are a class of macrocyclic synthetic compounds, relatives of porphyrins, their 18-π electron structure determines their special physical and chemical properties. Intensive absorption in the visible area, gives them wide usage as dyes and pigments. Aggregation is an important factor in studying the properties of phthalocyanines, as complexes have a high tendency to form aggregated molecules.

This work describes the synthesis method (Scheme 1) of metal complexes of nitrophenoxy-substituted phthalocyanines. For these compounds, the electronic absorption spectra, the values of fluorescence quantum yields, Stokes shifts, and fluorescence lifetimes were studied.



Scheme 1. Synthesis of tetra-4-(4-nitrophenoxy) phthalocyaninates of zinc and magnesium

The synthesis was carried out by the method of template fusion of phthalonitrile with metal acetates in a molar ratio of 4: 1, in the presence of carbamide. Fusion took place at 150°C and lasted for 20 minutes. The reaction mixture then was purified by Soxhlet extraction with chloroform. The structure of the compounds was confirmed by using ^{1}H NMR and IR spectroscopy, MALDI-TOF mass spectrometry and electron spectroscopy.

Electronic absorption spectra were recorded in dimethyl sulfoxide and acetone.

The work was supported by the Russian Science Foundation, grant № 17-73-20017.

Phosphate ceramics containing rare-earth metals

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Studies of $NaZr_2(PO_4)_3$ (NZP) based ceramics have perspectives in materials science due to a number of unique properties of this group of substances. High resistance to the action of extreme environmental factors, ionic conductivity, catalytic activity and other properties typical of NZP-phosphates can be complemented by magnetic and optical activity with the introduction of rare-earth metal ions into their structure. Within the present investigation we have studied phase formation and thermal expansion of NZP complex phosphates containing rare-earth and IVB group elements of the compositions $Na_{1-x}R_{0.33x}D_2(PO_4)_3$ (R – Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Er, Yb; D – Ti, Zr). Synthesis of phosphates was realized by sol-gel method (including the Pechini technique), the final temperatures of annealing were 650-800°C. According to powder X-ray diffraction (Shimadzu XRD-6000) and IR-spectroscopy data (Shimadzu FTIR-8400S), it was found that the studied compounds belong to the structural type $NaZr_2(PO_4)_3$ (NZP). Analysis of X-ray patterns of complex phosphates of titanium and rare-earth elements in accordance with the laws of extinction of the obtained set of reflexes showed that the studied solid solutions with a high concentration of Na^+ were characterized by $R\bar{3}c$ space group. Titanium phosphates with high content of rare-earth ions crystallized in $R\bar{3}$ space group, and phosphates of zirconium and lanthanides were indicated in $P\bar{3}c$ space group.

To estimate thermal expansion and NZP structure deformation upon heating, the phosphates $Na_{0.5}R_{0.167}Ti_2(PO_4)_3$ (R – Y, La; $x = 0.5$) were studied by X-ray diffraction in the temperature range from 25 to 200°C. Due to the negative α_a value (Table 1), yttrium-containing phosphate can be attributed to the mean expanding substances. Phosphate with larger La^{3+} cations in the cavities is characterized by a greater value α_{av}.

Table 1. Thermal expansion coefficients of $Na_{0.5}R_{0.167}Ti_2(PO_4)_3$ phosphate in the temperature range from 25 to 200 °C

Coefficient	$Na_{0.5}Y_{0.167}Ti_2(PO_4)_3$	$Na_{0.5}La_{0.167}Ti_2(PO_4)_3$
$\alpha_a \cdot 10^6$, °C^{-1}	-4.5	4.1
$\alpha_c \cdot 10^6$, °C^{-1}	24.0	20.6
$\lvert\alpha_a - \alpha_c\rvert \cdot 10^6$, °C^{-1}	28.5	16.6
$\alpha_{av} 10^6$, °C^{-1}	5.0	9.6

High-temperature mass spectrometric study of the Al_2O_3-ZrO_2 and SiO_2-ZrO_2 systems

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The reported study is a part of the research project on the development of improved glass-ceramic luminophores retaining stability at high temperatures. The samples for investigation were prepared by solid-state synthesis from pure oxides and identified by X-ray microanalysis using TESCAN VEGA 3 LMH SEM equipped with the Advanced Aztec Energy system. The thermodynamic properties were explored using MS-1301 mass spectrometer designed for high-temperature Knudsen effusion studies. The samples were vaporized from tungsten effusion cells. In the vapor phase over the samples of the SiO_2-ZrO_2 system SiO, O, WO_2, WO_3, and small amount of SiO2 molecular species were identified in the temperature range 1900-1950 K. Vaporization of the sample containing 96 mol % SiO_2 at the temperature 1912 K resulted in gradual removal of silicon oxide from the sample and allowed to determine partial pressures over the system in the whole range of compositions (32 points). The SiO_2 activity was nearly proportional to silicon oxide concentration demonstrating small negative deviations from the ideal behavior. In the vapor phase over the Al_2O_3-ZrO_2 system at T = 2340-2490 K Al, AlO, and Al_2O species were identified. The partial pressures of components determined during vaporization at T = 2500 K of three samples (87, 77, and 55 mol % Al_2O_3) accompanied by gradual change of the samples composition provided the data on the Al_2O_3 activity (75 points), which showed strong negative deviations from ideality.

The obtained activity data were used for modeling of the thermodynamic properties of the Al_2O_3-SiO_2-ZrO_2 system on the basis of the generalized lattice theory of associated solutions (GLTAS). Optimized concentration dependences of Al_2O_3, SiO_2, and ZrO_2 activities and the excess Gibbs energy, Fig. 1, were obtained.

The reported study was supported by RFBR: grant No 20-53-05013.

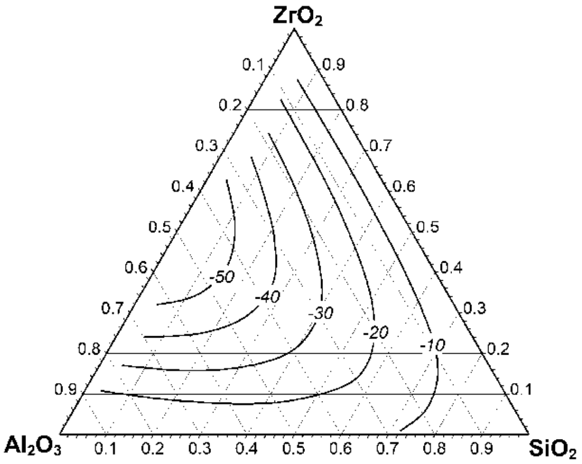

Fig.1. Excess Gibbs energy in the Al_2-SiO_2-ZrO_2 system at the temperature 2500 K calculated using GLTAS approach from the data for two limiting binary systems.

Catalytic systems based on copper (I) and (II) in polystyrene coupling reactions in the presence of acyclic nitrons

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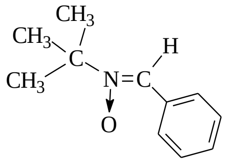
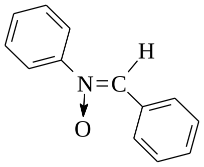
Radical Trap-Assisted Atom Transfer Radical Coupling (RTA-ATRC) technology is the method for obtaining polymer materials with complex architecture [1, 2]. However, this method of coupling has a number of disadvantages associated with the need to use metal-containing catalysts that are unstable in air. Progress in the development of the RTA-ATRC methodology can be associated with using much more stable coupling catalysts and its environmentally-friendly reducing agents. The technology called Activator Generation by Electron Transfer (AGET). In this work, on the example of bromine-containing polystyrene (PS) synthesized using the Atom Transfer Radical Polymerization (ATRP) technology, we studied coupling reactions using two technologies at a temperature of 80°C in the presence of mononitrons of various structures: C-phenyl-N-tert.butylnitrone (PBN), C,N-diphenylnitrone (DFN). Molecular weight (MW) characteristics of modified PS in table 1. CuBr/Cu was used as a catalyst in the RTA-ATRC process, and $CuBr_2$ for AGET RTA-ATRC, glucose (Glu) and ascorbic acid (AA) were used as activators. It has been established the most efficient coupling process with the preservation of PDI, leading to the production of macromolecules with a double MW in comparison with the initial polymer, proceeds with the participation of PBN (χ_p=0.95) using the RTA-ATRC technology; the presence of AA, and for DFN in all cases of combination (χ_p=0.92-0.94). In both cases, the presence of a labile nitroxide group in the middle of the PS chain allows subsequent modification of the macromolecule to form block copolymers. However, the AGET technology, when choosing optimal conditions and recovery system, is much more effective then ATRC methods, more environmentally friendly and easier to implement.

Table 1. Molecular weight characteristics of modified polystyrene

Spin traps	Method	Catalytic system	M_p	χ_p	M_n	PDI
	ATRP	CuBr	4710	-	4080	1.30
	RTA-ATRC	CuBr/Cu	8980	0.95	6180	1.28
	AGET	$CuBr_2$/ AA	8830	0.93	8640	1.29
	AGET	$CuBr_2$/ Glu	4720	0.0	4100	1.24
	RTA-ATRC	CuBr/Cu	6440	0.53	5000	1.28
	AGET	$CuBr_2$/ AA	8860	0.94	5700	1.36
	AGET	$CuBr_2$/ Glu	8690	0.92	5780	1.36

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The formation of compounds with β-pyrochlore structure type in the oxides system A_2O-V_2O_5-$2TeO_2$ (A = Rb, Cs)

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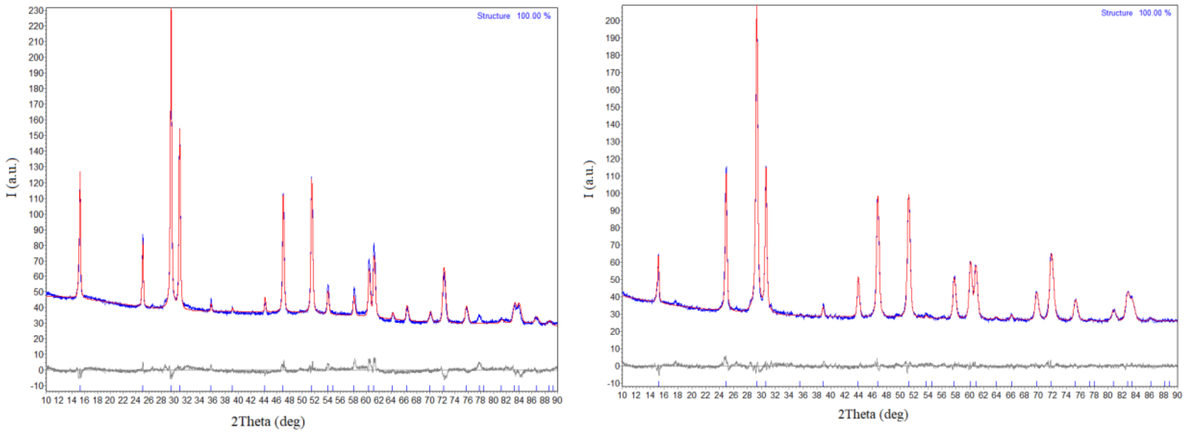
Compounds belonging to the β-pyrochlore structure type AB_2O_6 are very promising for study, because of exhibiting a large number of useful physical properties, including the ability to photocatalytic oxidation of organic compounds and water splitting [1]. In this work, we have studied the formation areas of β-pyrochlore phases in A_2O-V_2O_5-$2TeO_2$ (A = Rb, Cs). We have found the β-pyrochlores with classical cubic symmetry (Fd-3m) with compositions: $RbV_{0.75}Te_{1.25}O_{5.6}$ and $CsV_{0.75}Te_{1.25}O_{5.6}$. The elemental composition was confirmed by X-ray microanalysis, which also showed a reduced oxygen content relative to the stoichiometric one. It can be explained by the structural defects due to the presence of polyvalent elements Te and V. In previous works, we found that β-pyrochlore unit cell usually contains four Te^{4+} atoms, while all the rest is Te^{6+} [2 ,3]. Based on this, the chemical formula of the compounds can be written as $A^{+}V_{0.75}{}^{5+}Te_{0.5}{}^{4+}Te_{0.75}{}^{6+}O_{5.6}$ (A = Rb, Cs). The crystal structures of the obtained compounds were refined by the Rietveld method; the cell parameters for $RbV_{0.75}Te_{1.25}O_{5.6}$ and $CsV_{0.75}Te_{1.25}O_{5.6}$ are 10.0412(27) Å and 10.0912(23) Å, respectively. The unit cell for smaller Rb^{+} possesses a decreased size that for larger Cs^{+}.



a b

Fig. 1. X-ray diffraction pattern of $RbV_{0.75}Te_{1.25}O_{5.6}$ (a) and $CsV_{0.75}Te_{1.25}O_{5.6}$ (b)

This work was supported by the Ministry of Education and Science of the Russian Federation (0729-2020-0053) on the equipment of the Collective Usage Center "New Materials and Resource-saving Technologies" (Lobachevsky State University of Nizhnii Novgorod).

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The Nature of Chemical Transformations in the Process of Tellurite-Molybdate Glasses Synthesis

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Usually tellurite glasses are prepared through melting of binary oxides mixture and melt quenching followed. This technique, as applied to tellurite-molybdate glass preparation, provides glasses with low optical transparency in visual and near IR spectral ranges due to partial reduction of Mo^{+6} atoms into Mo^{+5} oxidation state. The Mo^{+5} concentration in glasses increases with the rise in MoO_3 content in the initial charge and with the increase in temperature and duration of homogenizing fusion. The use of oxidation agents in the solid charge and oxidative gaseous environment around the melt are expected to be capable to hinder Mo^{+6} reduction.

Recently we have proposed to apply other kinds of substances instead of binary oxides to compose initial charge. They are: 1) the precipitates isolated from the solutions of the elements compounds; 2) the mixtures of inorganic acids and their salts which are capable to decompose into binary oxides if taken in the individual state; 3) the mixture of complex oxides of elements.

This report presents the results of research on the chemical processes which take place in the courses of charge preparation, of the thermal treatment of the solid batch, and of batch melting that affecting the optical properties of the glass prepared.

The first kind of charge is the finely dispersed mixture containing particles sized from tens down to a few nanometers. This feature reduces the duration of the homogenizing fusion which contributes to decrease in melt contamination with crucible material. The compounds of elements in the high oxidation state (Te^{+6} in telluric acid and N^{+5} in nitrates) applied in the second kind of charge supply the condensed phase with the oxidant at each stage of the process. The circumstance interferes the reduction of Mo^{+6} atoms which are responsible for the decrease in the glass optical transparency in visible and near infrared spectral ranges. The third kind of charge is composed of the ternary and quaternary oxides which possess a lower melting point as compared with that for the corresponding binary oxides. This property provides a possibility of preparation of glasses of better optical quality with the high content of refractory oxide.

Thus the use of the charge composed of the chemically reactive components of oxidative nature allows to obtain tellurite-molybdate glasses of high optical transparency in visible and near IR spectral ranges.

The research was supported by the Ministry of Science and Higher Education of the Russian Federation, project No. 0729-2020-0039, within the framework of the basic part of the state assignment.

Obtaining a thermoresponsive amine-containing polymer grafted onto the silica surface

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Silica gel modified with amine groups is of interest for use as catalytic systems [1] and in separation processes [2]. Study was carried out to obtain a modified silica gel surface with an amine-containing thermoresponsive methacrylic polymer.

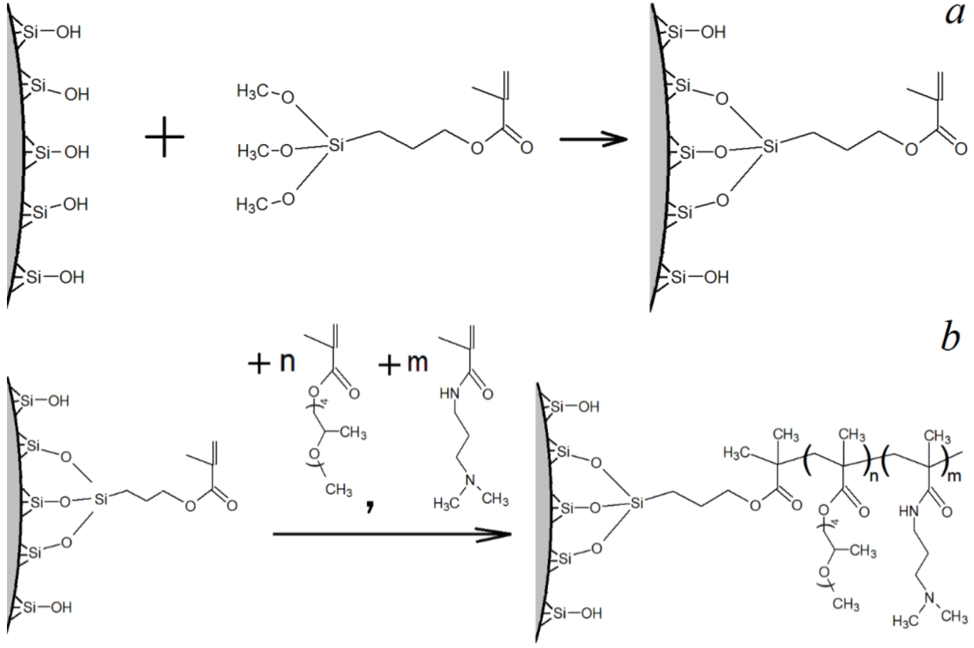

Fig. 1. Scheme for obtaining modified silica

The production of modified silica was carried out in two stages: grafting an “anchor” methacrylic group to the silica gel surface by reacting the silica surface with 3-(trimethoxysilyl)propyl methacrylate (Fig. 1a); solution polymerization of methacrylic monomers in the presence of silica gel with “anchor” groups (Fig. 1b).

The optimal conditions for carrying out both stages of the synthesis were determined, which ensure the introduction of a thermoresponsive amine-containing polymer onto the silica surface. In the course of the study, samples of silica modified with a copolymer of dimethylaminopropyl methacrylamide and methoxyoligoethylene glycol methacrylate were obtained.

The study was carried out within the framework of the state assignment in the sphere of scientific activity (topic No FSWE-2020-0008).

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Thermodynamic properties of indoline based spiropyran

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Spiropyrans are organic compounds with photochromic properties that have recently attracted increased interest. They have one spiro-bond and a pyran heterocycle in their structure. Spiropyrans have been extensively studied lately for their use in specialized settings. They can be applied as high-density optical drives, image processing, optical switches and signals. Due to its possible applications in different technologies, spiropyrans are actively studied nowadays. This work is devoted to thermodynamic study of indoline based spiropyran. The object of study: 1,3,3-trimethyl-8'-methoxy-6'-formyl-spiro [indoline-2,2'-2*H*-chromene]. Methods used in this work are thermal analysis, Knudsen effusion mass-spectrometry and quantum chemistry calculations. Thermal analysis was used to determine the melting point (T_m = 428 K) and decomposition temperature (T_d = 495 K) of spiropyran and to calculate its enthalpy of melting ($\Delta_m H^o$ = 25.5 kJ·mol^{-1}). Mass-spectrometric measurements showed that ions with masses over the mass of the molecule of monomer were not found, indicating monomer molecule is neutral precursor of all ions. It was also confirmed by calculated appearance energies (*AE*) of all main ions (Table 1) and temperature dependencies of ion currents, which show the same slopes.

Table 1. Mass-spectrum and appearance energies of registered ions

m/z	159	320	335
Structure	$[C_{11}H_{13}N]^+$	$[M\text{-}CH_3]^+$	$[M]^+$
I/I_{max}, %	30	16	100
AE, eV	14.2±0.5	14.3±0.5	10.8±0.5

Vapour pressures found by the Knudsen effusion experiment p(409 K) = 0.83 Pa and p(388 K) = 0.11 Pa were used to calibrate the mass-spectrometric data and derive temperature dependency of saturated vapor pressure in the range 350-385 K. The latter in the form ln(p) = f(1/T) was approximated by linear equation:

$$ln(P) = (37.331 \pm 0.552) + (-15.347 \pm 0.203) \cdot 10^3 \cdot T^{-1}$$

The sublimation enthalpy at average experimental temperature $\Delta_s H^o$ (368 K) = 128 kJ·mol^{-1} was recalculated to the standard temperature (298.15 K) with the use of thermodynamic functions obtained in this work. This value was found to be $\Delta_s H^o$(298.15 K) = 132 kJ·mol^{-1}.

This work was supported by the Ministry of science and higher education of the Russian Federation in the framework of Government order (project No. FZZW-2020-0007). The study was carried out using the resources of the Center for shared use of scientific equipment of the ISUCT (with the support of the Ministry of science and higher education of Russian Federation, project No. 075-15-2021-671).

A-site substitution effect near multicritical point for double-perovskite manganites

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The double-perovskite manganites *Ln*$BaMn_2O_6$ attracting much attention due to competing interactions/orders, such as among ferromagnetism (F) and antiferromagnetism (AF) or charge/orbital order (CO/OO) and metallic state [1]. The competition between these interactions/orders in vicinity of the multicritical point at region located near *Ln*=Nd remains unclear.

For the first time solid solutions $Nd_{1-x}Ln_xBaMn_2O_6$, *Ln*= Sm, Pr were obtained by topotactic reaction and attested by X-ray powder diffraction. Magnetization and conductivity measurements were carried out in the range of 4-400 K. The data are interpreted as a diagram of magnetic and conducting states (Fig. 1).

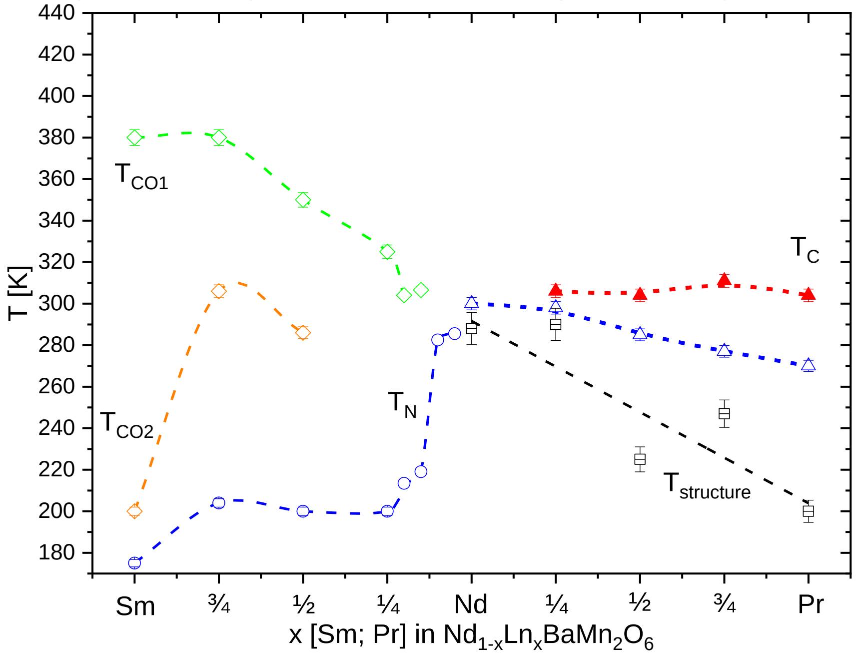

Fig. 1. The diagram of magnetic and conducting states for $Nd_{1-x}Ln_xBaMn_2O_6$, *Ln*= Sm, Pr.

The complex interaction between the magnetic moments of Mn^{3+} and Mn^{4+} ions gives a ferrimagnetic structure rather than a purely AF state. Substitution of Nd with Pr slightly affects the Curie (T_C) and Neel (T_N) temperatures. For $Nd_{1-x}Sm_xBaMn_2O_6$ oxides, CO/OO transitions (T_{CO1}) take place above room temperature in paramagnetic state. Structural defects caused by Sm-doping lead to a strong influence on the T_{CO1} and T_N even for small Sm content 5 at.%.

The work is supported by RFBR, grant No 19-29-12013.

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Research of the effect of temperature conditions on the synthesis of biocompatible graft copolymers of polymethyl methacrylate and fish collagen in the presence of tributylborane

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Collagen is considered as an ideal raw material for regenerative processes and tissue healing, being the most abundant protein in the body of mammals. Due to their ability to bind to available tissues, collagen-based scaffolds have generated huge interest in biomedical implants. The advantages of such scaffolds are biopolymer nature, low immunogenicity, porous structure and permeability of collagen molecules. However, purely collagen scaffolds have insufficient mechanical strength, which leads to limited use in tissue engineering. We have synthesized hybrid copolymers of polymethyl methacrylate (PMMA) and fish collagen, as possible precursors for scaffolds, in the presence of tributylborane, a radical polymerization initiator. To obtain these materials, it was important to preserve the structure of collagen, and organoborane allows polymerization to be carried out in a wide range of temperatures, including room temperature. We have studied the temperature regime for obtaining copolymers at 25-60°C to achieve maximum grafting of a synthetic polymer, while keeping the structure of collagen in the copolymer. Changes in the synthesis temperature did not significantly affect the fraction and molecular weight of the grafted PMMA. The obtained graft copolymers have one glass transition temperature, determined by differential scanning calorimetry, close to the glass transition temperature of PMMA. Micrographs obtained by scanning electron and atomic force microscopy indicate the destruction of the fibrillar structure of collagen in the copolymer at a synthesis temperature above 25°C. A decrease in the concentration of methyl methacrylate (MMA) leads to its complete consumption. The morphology of copolymers depends on the ratio of MMA and collagen. It is known that hydrophobicity impairs cell attachment and division, and also increases the period of scaffold decomposition in the body. Therefore, we analyzed the hydrophilicity of films of PMMA and collagen copolymers. The tests performed showed that all samples of copolymers are wetted by water, the values of the wetting corners are close to the wetting corner of collagen itself.

The work was carried out as part of the implementation of the «PRIORITET-2030» program.

Investigation of the polishing processes of optical elements of CVD-ZnSe doped with Cr^{2+} ions

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Doping of CVD zinc chalcogenides with divalent transition metal ions (Cr^{2+}, Fe^{2+}) using high-temperature gas-static treatment made it possible to obtain bulk samples with high optical characteristics and predicted concentrations of the active component. The use of these materials as optical elements in compact tunable lasers in the 2–5 μm range with high laser breakdown threshold and output power is impossible without their high-quality processing. Thus, the problem associated with the study of the processes of mechanical and chemical-mechanical polishing of optical elements based on CVD-ZnSe doped with Cr^{2+} ions is topical.

Polycrystalline Cr^{2+}:ZnSe samples were obtained by diffusion doping of initially clean plane-parallel CVD-ZnSe wafers. Comparative studies of the processes of mechanical polishing of doped (type 1 samples) and annealed zinc selenide under the same conditions as during alloying (type 2 samples) were carried out. The quality of the obtained surfaces was compared using optical microscopy, as well as by the roughness values, which were controlled using an atomic force microscope and a Micro XAM-800 3D laser profilometer. During the measurements, the parameters of root-mean-square (Rq, Sq) and arithmetic-mean (Ra, Sa) roughness were controlled. It has been established that the degree of alloying affects the roughness of the machined surface under the same machining conditions. For samples of type 1, the following roughness values were obtained: Ra=1.63-4.81nm; Rq=2.04-5.36nm; Sa=1.42-3.24nm; Sq=1.71-4.48nm. The existing scatter does not depend on the processing conditions and is associated with the degree of doping of the samples, which leads to a change in the surface properties of the material and the formation of a textured layer on the surface, which is confirmed by X-ray diffraction experiments. For samples of type 2, the following roughness values were obtained: Ra=0.39-6.51nm; Rq=0.49-8.69nm; Sa=0.61-11.29nm; Sq=0.77-13.7nm. In this case, the spread is more significant, because there are large crystallites on the surface of the samples, and coarsening of the textured layer is observed, which leads to a change in the physical properties of the surface, as evidenced by the change in the removal rate during machining.

The results obtained seem necessary for the further development of a technique for high-quality magnetorheological polishing of optical elements based on CVD-ZnSe doped with Cr^{2+} ions for laser applications.

This work was supported by the Russian Foundation for Basic Research, Grant No. 20-53-00040Bel_a.

Preparation of iron and cadmium sulfides films by spray pyrolysis

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The interest of researchers in the production of films of iron and cadmium sulfides is due to the wide possibilities of their application in solar cells, luminescent devices, and optoelectronics. In [1] the prospects for using Cr_2S_3 and CdS films doped by chromium obtained by spray pyrolysis (SP) as sources of master alloys for obtaining Cr^{2+}:ZnSe laser media were shown for the first time. Thermodynamic calculations is the basic stage in choosing the conditions for obtaining films, which affects their composition and structure. This makes it possible to reasonably determine the process temperature, the composition of the initial precursors, the ratio between them, etc. The purpose of this work was to determine the thermodynamically optimal conditions for the formation and preparation of films of iron and cadmium sulfides doped with iron by spray pyrolysis.

For the thermodynamic analysis of the Fe-Cd-S-H_2O system, the Chemical Thermodynamic Calculator (CTC) software package was used, which combines a computer implementation of the Gibbs method, including calculations of conditionally equilibrium states based on the IVTAN TERMO data bank. The effect of precursors of iron ($FeCl_3$, $FeSO_4$, $Fe(NO_3)_3$), cadmium ($Cd(NO_3)_3$ and $CdCl_2$), and thiourea CSN_2H_4, and the ratio between them on the composition of the solid and gas phases in the temperature range of 473–673 K was studied. The solid phase was calculated in the approximation of individual condensed phases. It has been found that the precipitation is preferably carried out with a twofold excess of thiourea. In this case, the use of ferric chloride should lead to the predominant formation of CdS and FeS_2 at 533–583 K and Fe_3O_4 and $CdCl_2$ at $T < 533$ K and $CdCl_2$, Fe_3O_4, Fe_2O_3 at $T > 583$ K. When $FeSO_4$ is used CdS, FeS_2 and FeS are formed at 473-643 K and Fe_2O_3 is formed with a further increase in temperature. The use of iron (III) nitrate leads to the formation of CdS and FeS_2 at 473-583K and at 603-673 K. In the temperature range from 583 K to 603 K CdO and Fe_2O_3 are formed.

Films of iron and iron-doped cadmium sulfides were deposited by the SP method on quartz substrates. The conditions for their preparation were varied based on the data of thermodynamic calculations. Based on the results of studies of the composition of the films performed using SEM EDX and XRD and Raman spectroscopy, it is shown that the composition of the deposited films is in good agreement with the results of thermodynamic calculations.

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Black PEO coating with enhanced corrosion resistance on Al alloy

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Plasma electrolytic oxidation (PEO), which is also known as micro-arc oxidation (MAO) is a relatively novel technique for producing ceramic coatings on valve metals and their alloys [1]. The characteristics of the resulting coatings strongly depend on the nature of substrates, electric regime, as well as the composition of the electrolyte. Generally, alkaline solutions, which contain mainly aluminate, silicate, and phosphate are usually employed in PEO process. Recently, much attention has been paid to the effect of various additives on the characteristics and properties of PEO coatings. In particular, it has been shown that some additives can be used for preparing PEO coating with uniform decorative colors [2]. This work proposes a new approach to producing uniform black PEO coating on AA2024 aluminum alloy, which consists in the addition of $CoOOH \cdot H_2O$ into an alkaline-silicate electrolyte. Co-additive had no noticeable effect on coating growth kinetics. After 25 min of PEO treatment with and without $CoOOH \cdot H_2O$ addition, typical two-layered coatings with an average thickness of ~17 μm were formed. It is interesting to note that for black PEO coating, Co and Si rich regions surround the voids, separating the inner and outer layers (Fig. 1). Potentiodynamic polarization was employed to study anticorrosion behaviors of PEO coatings in 0.5 wt.% NaCl solution. As shown in Fig. 2, anodic and cathodic currents significantly decreased for coated samples compared to the bare one, indicating that PEO coatings offer good protection of AA2024 alloys again corrosion. Moreover, it can be clearly seen that anodic and cathodic currents are much lower for the black coating, indicating its better anticorrosion performance. The latter may be caused by the formation of Co or Co-Si containing compounds during PEO treatment, which can fill most of through pores, preventing the penetration of aggressive electrolyte to the substrate.

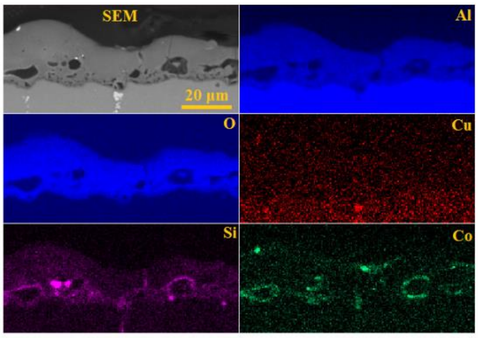

Fig. 1. SEM image and EDS elemental maps of ~17 μm black PEO coating

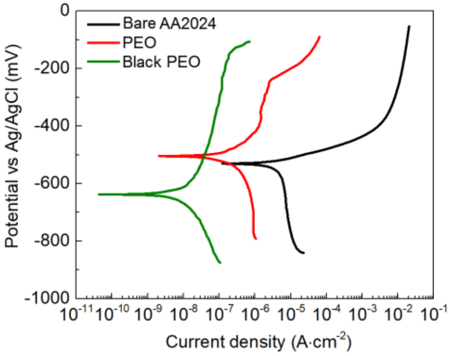

Fig. 2. PDP curves of bare alloy and ~17 μm PEO coatings in 0.5 wt.% NaCl solution

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Isothermal calorimetry as a tool for monitoring the reactivity of substances in solutions and in the solid phase

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Isothermal calorimetry has found widespread application for thermal analysis of chemical reactions in the context of fundamental research as well as process development for a large brunch of industries.

This work reviews our experience in use an isothermal calorimetry system TAM III (TA Instruments) in the study of interaction in liquid phase as well as in monitoring of stability of solid compounds in isothermal mode.

Isothermal titration experiments were carried out on a microcalorimeter unit with a 20 mL reaction stainless steel cell and a titration module. A classic titration set up experiment was applied to study the complex formation reactions between complex *d*-metal ions with different ligand's type in mixed solvents [1]. A modification of the titration procedure was applied for the weak "host-guest" complexes of biologically active molecules such as amino acids, peptides, polyphenolic compounds with crown ethers and cyclodextrins [2, 3]. The thermodynamic parameters of complex formations ($\lg K$, $\Delta_r H$, $\Delta_r G$, $T\Delta_r S$) were calculated from isothermal titration calorimetry data by TAM Assistant software of TA Instruments and by "HEAT" program elaborated by Kozlovksy, et al. [4]. The results obtained represent a potential resource for the development of biosimilar technologies and the pharmaceutical industry.

The monitoring of thermal activity in isothermal mode was applied to the study of hydration processes of cements with various additives. Two identical glass ampoules were used for the reaction cell and for the reference cell. During the experiment, the ampoules were hermetically closed.

The elaborated procedure seems to be promising in the study of thermal activity of biological substances in isothermal mode.

The study was carried out with financial support of Ministry of Science and Higher Education of the Russian Federation (project FZZW-2020-0009) using the resources of the Center for Shared Use of Scientific Equipment of the ISUCT (grant № 075-15-2021-671).

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MP-type hexagonal ferrites $BaFe_{12}O_{19}$ and $SrFe_{12}O_{19}$. The Pechini method

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The modern development of technologies presents new requirements to materials, thereby forming new principles and approaches in chemical science and materials science. Increasing relevance is not only modeling and predicting the properties of materials, but also the possibility of varying their characteristics at all stages of production, improving synthesis methods and the possibility of introduction into industry.

Functional materials such as hexagonal ferrite oxides with the magnetoplumbite (MP) structure deserve special attention. They have already found wide application as permanent magnets in various industries, but their unique physical properties have led to the use of these compounds also as phosphors [1], thermal barrier coatings [2], etc. However, the direction that considers compounds with an MP structure as a matrix for the immobilization of radionuclides and the stabilization of toxic metals remains poorly studied [3].

For the $Ba(Sr)Fe_{12}O_{19}$ synthesis, the Pechini method (citrate method; polymer complex method) was chosen, which makes it possible to obtain a product with high homogeneity and dispersion. As a result of optimizing the synthesis conditions, such a ratio of citric acid, ethylene glycol, and metal ions was chosen, as a result of which spontaneous combustion of the mixture occurred with the further formation of a finely dispersed product, and a lower heat treatment temperature was required to obtain a monophase product. The resulting target products, Ba-MP and Sr-MP, were polycrystalline dark brown powders, crystallized in the structural type of magnetoplumbite, sp. gr. $P6_3/mmc$ with cell parameters: $a=5.8960\pm0.0008/5.8884\pm0.0014$ Å and $c=23.2305\pm0.0100/23.1418\pm0.0238$ Å, respectively, which is in good agreement with literature data. The phase composition of the obtained powders was studied by X-ray phase analysis on a Shimadzu LabX XRD-6000 X-ray powder diffractometer using the JCPDS-ICDD PDF-2 Release 2004 crystallographic database, PhasanX2.0, Match!, KRIST software, and original literature.

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Cooperative Jahn-Teller effect in solid solutions of $Nd_{1-x}Sr_xMn_{1-y}Fe_yO_3$ (x = 0; 0.15) (y=0.1)

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Manganites, which have unique electronic properties have been extensively studied in the last decades not only due to fundamental interest but to possible applications of colossal magnetoresistance, magnetocaloric effect [1], ferroelectric properties [2,3], also in the fuel cell research field [4,5]. Doping with divalent atoms (Ca, Sr, Ba) in the A-site leads to the degeneration of eg orbitals of Mn^{3+} ions in manganese-based manganites. These systems are characterized by strong structural and Jahn–Teller distortions. The transport properties, Jahn-Teller distortions and structural transformations depend on the type dopant, and its concentration. Strontium-doped neodymium manganites $Nd_{1-x}Sr_xMnO_3$ are characterized by a strong relation connection between the structure, magnetic and transport properties. $NdFeO_3$ crystallises in the same crystal structure as $NdMnO_3$. The Fe^{3+} ion has the same ionic radius and occupies the same crystallographic position as the Mn^{3+} ion. But the Fe^{3+} ion is not the active Jahn-Teller ion. Doping on both of A and B- sites leads to the formation of substitutive solid solutions and allows us to study the evolution of the Jahn-Teller effect with substitution. All solid solutions of $Nd_{1-x}Sr_xMn_{1-y}Fe_yO_3$ (x = 0; 0.15) (y=0.1) have orthorhombic crystal lattice described by the space group Pbma. Orthorhombic deformation (D) rapidly decreases from D = 3.50% for x(Sr) = 0 to D=1.37 for x(Sr)=0.15 and to D = 0.93% for y(Fe) = 0.1. The Jahn-Teller transition temperature decreases significantly when doped with strontium x = 0.15. Additional substitution of manganese with iron leads to a subsequent decrease in the temperature of the Jahn-Teller transition.

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Plasma-chemical synthesis of thin films of cadmium chalcogenides for the creation of highly efficient tandem solar cells

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Currently, the threat of global warming and a decrease in reserves of traditional energy sources is forcing many countries in the world to increase the pace of production of renewable energy sources, among which solar energy is the most promising. However, in order to achieve grid parity with traditional energy sources, it is necessary to further increase the efficiency of solar cells (SC) and reduce the cost of their production. The deposition of cadmium chalcogenides is carried out from high-purity elements Cd, S, Se and Te, which are fed into the plasma-chemical reactor by thermal evaporation in vacuum, the reaction of interaction of volatile elements is initiated by a plasma discharge, the synthesis of chalcogenide material is carried out under conditions of non-equilibrium plasma of a high-frequency induction (or capacitive) discharge at reduced pressure, and the solid reaction products are deposited on a cooled/heated substrate. The installation diagram is shown in Figure 1 (Fig. 1)

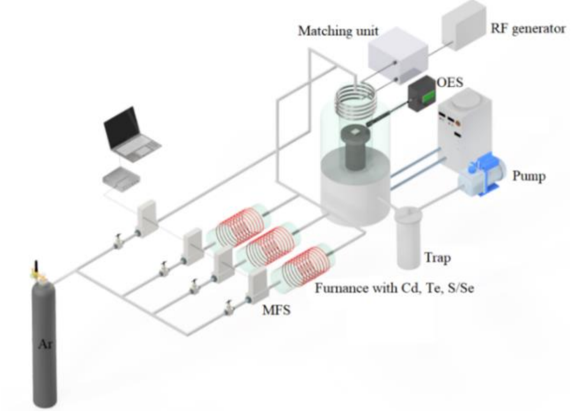

Fig. 1. Scheme of the experimental setup

It should be noted that a-Si materials are very sensitive to high temperatures and exceeding a certain temperature limit will lead to a sharp decrease in the efficiency of such solar cells. For a-Si, this temperature limit lies in the region of 200-250 °C. At the same time, the growth temperature of thin CdTe films in traditional methods exceeds 300–400 °C [1]. Thus, direct deposition of the upper CdTe cascade on a high-efficiency a-Si/c-Si solar cell will lead to deterioration of its performance. Plasma initiation makes it possible to significantly reduce the temperature of the reactor walls, and also makes it possible to achieve 100% conversion of the initial substances due to the removal of kinetic difficulties in the course of plasma-chemical reactions.

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Assembling of the TiO_2-Al_2O_3(SiO_2)-ZrO_2 Phase Diagrams

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Design of the TiO_2-Al_2O_3-SiO_2-ZrO_2 phase diagram 4D computer model related to the fact that it has to face with many contradictions in the initial data of binary and ternary systems [1,2]. For instance, the congruently melting compound Al_2TiO_5 may have two polymorphous modifications (R и R1) [3] and second compound $Al_6Ti_2O_{13}$, incongruently melting, may be formed in a small temperature interval [4]. There are two versions of $ZrSiO_4$ (R3) generation: by peritectic [5] or peritectoid [6] reaction. It has not been fully investigated what is the lower temperature boundary of the incongruently melting $ZrTiO_4$ (R2). Assembling of phase diagrams from surfaces and phase regions [1,2] opens up broad perspectives for designing of T-x-y diagrams 3D models for different versions of initial binary systems. Then the R(R1) polymorphism is taken into account by the reaction V: R□R1+B+L and the kV curve (Figure 1a), and the zircon (R3) formation by the form of its liquidus field (Figure 1b). After additional experiments in dubious fragments of the phase diagram, the 3D model is refined, and in its all volume, including the sub-solidus.

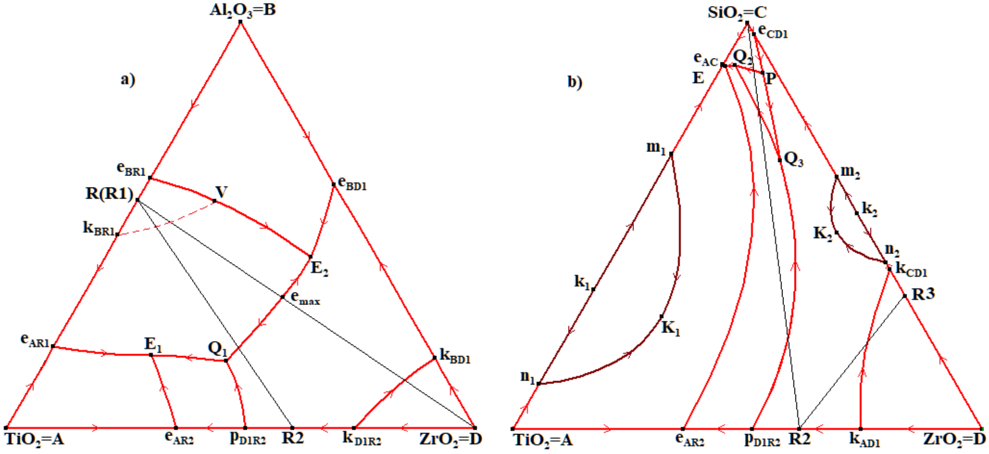

Figure 1. X-Y projections of TiO_2-Al_2O_3-ZrO_2 (a) and TiO_2-SiO_2-ZrO_2 (b) liquidus surfaces with polymorphous modifications (R, R1) of aluminum titanate, zirconium titanate (R2), zircon (R3)

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Исследование антигрибковых свойств сополимера аллилового эфира салициловой кислоты со стиролом

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Как известно, в качестве современных конструкционных материалов большое значение имеют полистирол, полистирол общего назначения, пенополистирол, ударопрочный полистирол и полимер АБС (акрилонитрил-бутадиен-стирол) на основе стирола. Хотя полистирол составляет 6% мировых полимерных материалов в виде пластической массы, он широко используется в различных отраслях промышленности. Одним из наиболее широко используемых направлений применения полистирола является производство упаковочных изделий. При этом важно, чтобы полимерный материал этого типа был устойчив к бактериям и грибам. Включение фрагмента мономера с антимикробными свойствами в макроцепь во время синтеза полимеров или использование антибактериальных полимеров в качестве добавок при создании полимерных композиционных материалов является одним наиболее распространенных методов создания антимикробных полимерных материалов. Целью данного исследования было изучение антигрибковой активности сополимера аллилового эфира салициловой кислоты со стиролом. В качестве тест - культур использовали такие микромицеты, как *Aspergillus niger, A.ochraseus, Penicillium cuclopium, Cladosporium herbarium, Fusarium moniliforme и F.oxysporium.* В присутствии образцов исследуемых полимерных материалов тест-культуры выращивали на питательной среде (отбеленном солодовом соке) в течение 6 месяцев. Установлено что, исследуемый сополимер обладает антигрибковой активностью. Было обнаружено, что ни один из протестированных полимерных материалов не изменился по визуальным или микроскопическим изображениям (рис. 1), что можно оценить как показатель их устойчивости к грибкам.

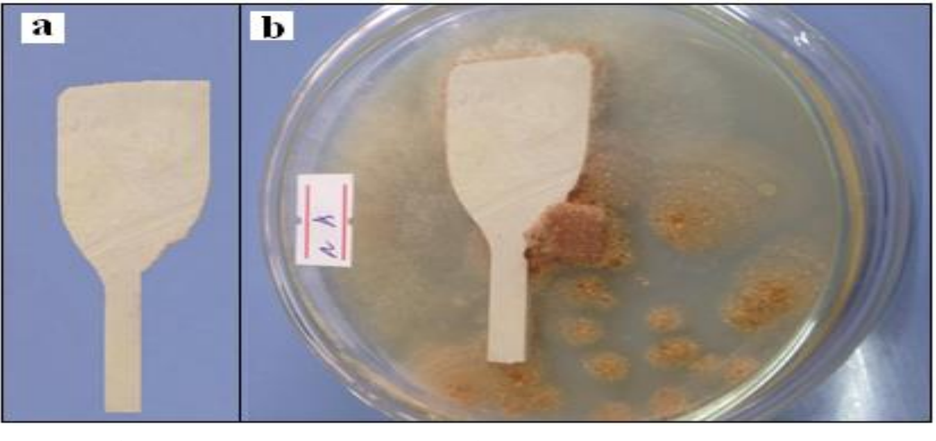

Рис. 1. Биологическая активность сополимера аллилсалицилата со стиролом: а- перед посадкой; б- через 6 месяцев после посадки

Композиты на основе полиэтилена низкой плотности и алюминия

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Приводятся экспериментальные данные по физико-механическим свойствам композитов на основе ПЭНП и алюминия. Сопоставляя данные можно установить, что с увеличением концентрации алюминия от 0.5 до 30%масс. наблюдается закономерное увеличение разрушающего напряжения и модуля упругости на изгиб композитов, а относительное удлинение заметно ухудшается. В то же время, введение алюминия в состав композиции ПЭНП компатибилизатора – сополимера полиэтилена с малеиновым ангидридом (ПЭМА) также сопровождается возрастанием разрушающего напряжения и прочности на изгиб. Различие заключается лишь в том, что значения разрушающего напряжения, прочности на изгиб и относительного удлинения у композитов, содержащих компатибилизатор ПЭМА несколько выше, чем у немодифицированных образцов [1].

Сам факт возрастания разрушающего напряжения у композитов однозначно свидетельствует в пользу того, что алюминий, как наполнитель является усилителем ПЭНП. Известно, что в расплаве полимерной матрицы существуют одновременно гомогенные и гетерогенные центры зародышеобразования. Гомогенные центры образуются в результате взаимной ориентации макроцепей в расплаве, а гетерогенные – в процессе ориентации макроцепей на развитой поверхности частиц наполнителя [1]. Есть основание полагать, что в результате такого ориентационного эффекта прочность адгезионной связи будет усиливаться в присутствии ПЭМА. Иными словами, увеличение полярности полиэтилена в присутствии ПЭМА будет безусловным образом сказываться на увеличении адгезионной связи макроцепи на поверхности частиц алюминия. Образованные в расплаве композита центры зародышеобразования, в процессе охлаждения становятся центрами кристаллизации. Таким образом, если часть алюминия участвуют в создании центра зародышеобразования, то другая ее часть в процессе охлаждения и роста кристаллов вытесняется в межсферолитное пространство (аморфную область), блокируя конформационную подвижность «проходных» цепей.

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Синтез и полимеризация (2-п-амино фенилциклопропил)метилметакрилат

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Известно, что циклопропан содержащие полимеры являются перспективными и относительно безопасными биоцидными, фоточувствительными, прозрачными материалами. Эфиры акрилового ряда относятся к важному классу мономеров, на базе которых получаются полимерные материалы с ценными эксплуатационными свойствами. Однако метакриловые полимеры имеют ряд недостатков: низкая теплостойкость, низкая ударопрочность, низкий предел прочности при растяжении и при изгибе и т.д. Эти недостатки устраняются синтезом различных метакриловых эфиров, имеющих в своем составе различные функциональные фрагменты [1]. Наличие в боковой цепи таких групп может придать макромолекулам бактерицидные и фунгицидные свойства.

Цель настоящей работы заключается в поиске путей синтеза новых циклопропансодержащих метакриловых мономеров, а исследование закономерностей в радикальной полимеризации в изучение некоторых свойств полученного полимера. В работе предложена новая стратегия синтеза функционально замещенного полиметакрилата с боковыми функциональными циклопропановыми фрагментами, которые проявляют их бактерицидные и фунгицидные свойства. Также изучена структура и некоторые свойства полученного полимера.

Синтезированный полимер представляет собой белый порошок, растворимый в ароматических и хлорсодержащих углеводородах, нерастворимый в алифатических углеводородах, в низких спиртах и в диэтиловом эфире. Строение полимеров было доказано ИК- и ПМР спектроскопией. Отметим, что реакционная система остается гомогенной вплоть до высокой конверсии. Образующиеся полимеры хорошо растворяются в хлороформе, ацетоне и не растворяются в низких спиртах.

Использование циклопропансодержащих метакрилатных полимеров обеспечивает получение не только растворимых антибактериальных препаратов, но также биоцидных пленок и покрытий. Таким образом, полимерные материалы с циклопропановыми группами являются многообещающей основой для разработки антибактериальных систем.

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Термодеформационные характеристики нанокомпозитов на основе полипропилена и термозолы бытовых отходов

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Причина столь высокой потребности в композитных полимерных материалов кроется в их высоких качественных показателях и технологичности производственного оборудования. Именно эта особенность композитных материалов позволило их использовать в качестве заменителей цветных и черных металлов, тем самым существенным образом добиться снижения себестоимости изделий, получаемых на их основе. Но, наряду с этим, внимание ученых все больше направляется одновременно на решение и других важных проблем: снижение себестоимости полимерных изделий и экологической напряженности, возникающей в процессе промышленного производства. Так, например, на Балаханском мусороперерабатывающемся предприятии г.Баку в результате термообработки отходов при температуре 1200°C образуется очень большое количество термозолы (ТЗ) [1].

В данной работе нами в качестве полимерной матрицы использовали полипропилен (ПП), который, в меньшей степени восприимчив к различным наполнителям, способствуя тем самым проявлению хрупкости. Большей частью это связано с плохой совместимостью неполярного ПП с полярными наполнителями. Поэтому, считали правильным использовать компатибилизатор на основе сополимера ПП с малеиновым ангидридом (ППМА), который в значительной степени способствует сохранению прочностных свойств композитов. Использование частиц ТЗ по сути дела открывает новые возможности для изучения их влияния на структурные особенности и изменение термодеформационных характеристик, которые оценивались по данным полученным на приборе Канавца. Приводятся термомеханические кривые зависимости деформации от температуры для нанокомпозитов на основе ПП, ППМА и ТЗ. Концентрацию ТЗ варьировали в пределах 5.0-40 %масс. Во всех нанокомпозитах использовали 2.0%масс. ППМА. Показано, что с увеличением концентрации ТЗ полимерные нанокомпозиты в узком температурном интервале из твердого состояния переходят в вязкотекучее.

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Теоретические аспекты исследования динамически вулканизованных нанокомпозитов

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Целью проводимых исследований являлось исследование термомеханических свойств динамически вулканизованных нанокомпозитов с учетом современных подходов при оценке их структурных особенностей и фазовых переходов. Перед тем, как приступить к исследованию термомеханических свойств нанокомпозитов необходимо было, прежде всего, разобраться с вопросами, связанными с совместимостью смешиваемых полимерных компонентов. В данном случае, в качестве объекта исследования используются несовместимые полимерные смеси на основе РПП и СКН различных марок. В связи с чем, возникала необходимость использования компатибилизатора-совместителя, способного обеспечить смешиваемость компонентов смеси и их технологическую совместимость. С этой целью в качестве компатибилизатора использовали **Exxelor-** привитой сополимер полипропилена с малеиновым ангидридом **(ППМА),** введение которого даже при небольших его концентрациях способствует заметному улучшению свойств композиционных материалов [1]. Экспериментально нами было установлено, что преимущественно этот процесс возможен при концентрации СКН в составе РПП не ниже 40%масс. Особенность динамически вулканизованных композитов заключается в том, что при низких концентрациях перекисных сшивающих агентов межцепная сшивка происходит преимущественно в фазе СКН за счет большого числа двойных связей и соответственно метиленовых групп расположенных в α-положении к винильным группам. При более высоких концентрациях ПД межцепная сшивка протекает не только в дисперсной фазе СКН, но и в жестких доменах РПП по третичным углеродным атомам, что безусловным образом способствует образованию густосетчатой пространственной структуры, предотвращающая возможность переработки сшитого термэластопласта на стандартных оборудованиях. Поэтому, в задачу исследования входило определение той минимальной концентрации ПД, при котором формируется структура динамически вулканизованного композита. В этой структуре сшивка протекает преимущественно по эластомерной фазе. В данном случае следует принять во внимание и сам наполнитель, представляющий собой наноразмерный бентонит. Роль наночастиц бентонита в данном случае заключается в усилении прочности нанокомпозита.

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Физико-механические свойства нанокомпозитов на основе сополимера этилена с гексеном и везувианом

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Приводятся результаты исследования влияния концентрации природного минерала – везувиана на основные физико-механические свойства нанокомпозитов на основе сополимера этилена с гексеном (СЭГ). В качестве структурообразователя использовали двуокись титана (TiO_2). Выбор рассматриваемых компонентов смеси основывался в необходимости выявления их селективного влияния на свойства полиолефинов и совместного воздействия на комплекс важнейших характеристик нанокомпозитов. Использование наночастиц в качестве наполнителя открывает возможность более глубже понять те процессы, которые проходят на границе раздела микрофаз. Приводится зависимость разрушающего напряжения, модуля упругости на изгиб, относительного удлинения и ПТР нанокомпозитов от концентрации везувиана. Увеличение концентрации наночастиц везувиана (размер наночастиц – 17 - 110нм) в составе СЭГ до 2.0%масс. сопровождается повышением разрушающего напряжения от 37.4 до 39.3 МПа. Максимальное значение разрушающего напряжения достигается при 5.0%масс. содержании наночастиц везувиана и составляет 41.5 МПа. Дальнейшее повышение концентрации наполнителя свыше 5.0%масс. приводит к закономерному снижению разрушающего напряжения. При этом, модуль упругости при изгибе постоянно увеличивается с повышением концентрации везувиана [1]. Введение в состав СЭГ 2.0%масс. везувиана приводит даже к незначительному повышению относительного удлинения. Иными словами, при минимальной концентрации везувиана в составе СЭГ (2.0%масс.), последний подобно структурообразователю, способствует улучшению одновременно прочности и относительного удлинения нанокомпозита. Структурообразующий эффект выражается в образовании еще в расплаве композита гетерогенных центров зародышеобразования, которые в процессе охлаждения становятся гетерогенными центрами кристаллизации, способствующими формированию мелкосферолитных образований. В этом случае достигается значительное улучшение деформационно-прочностных характеристик композитного материала.

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Закономерности кристаллизации нанокомпозитов на основе малеинизированного полиэтилена низкой плотности и аппретированного талька

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Химическое связывание частиц наполнителя с аппретом и полимерной матрицей в результате микросшивок по золь-гель реакции выдвигала необходимость учета этого фактора при исследовании влияния температурного фактора на закономерность кристаллизации полимерного материала, которое имеет место при их охлаждении. Изучение процесса кристаллизации нанокомпозитов осуществлялось с помощью метода дилатометрии, позволяющий оценить закономерность изменения удельного объема в широком диапазоне температур. В данной работе для улучшения совместимости частиц наполнителя (талька) с полиэтиленом низкой плотности (ПЭНП), в состав последнего был введен 5.6 %масс. малеинового ангидрида с образованием привитого сополимера полиэтилена с малеиновым ангидридом (ПЭМА). Синтез ПЭМА позволял решать две основные проблемы: улучшить совместимость с тальком и получить (сшитый) химически связанный гибрид частиц наполнителя с аппретом и полимерной матрицей. Для получения более полной информации о процессах кристаллизации композитных материалов приводятся дилатометрические кривые зависимости удельного объема от температуры для нанокомпозитов на основе ПЭМА. Показано, что наличие в макроцепи ПЭМА малеинового ангидрида (МА) способствует некоторому возрастанию температуры фазового перехода первого рода от 88 (ПЭНП) до 91^{o}С. Введение аппретированных наночастиц талька в последовательности 1.0; 5.0; 10; 20 и 30%масс. сопровождается заметным изменением температурной зависимости удельного объема. При этом, фазовый переход первого рода изменяется в следующей последовательности: 88^{o}С (исх.ПЭНП), 90^{o}С (исх.ПЭМА), для композитов на основе ПЭМА– 90; 91; 94; 94 и 94^{o}С. В нанокомпозитах ПЭМА до 5.0%масс. содержания талька фазовый переход протекает при 90-91^{o}С, а при более высоких концентрациях наполнителя его значение составляет 94^{o}С. Установлено, что увеличение концентрации талька в составе ПЭМА сопровождается изменением механизма кристаллизации нанокомпозитов от сферического трехмерного типа роста кристаллических (для исх.ПЭМА и нанокомпозитов с 1.0%масс. содержанием талька) и пластинчатого (двумерному) типа роста кристаллов для нанокомпозитов с 5-10%масс. талька, до линейного (одномерного) типа роста кристаллов для нанокомпозитов с 20-30%масс. талька при непрерывном образовании центров кристаллизации. Определены аналитические выражения уравнения Аврами для рассматриваемых нанокомпозитных материалов.

Низкотемпературная рентгеногафия 6-аминогексановой кислоты

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Особую и, несомненно, важную роль в любом живом организме играют аминокислоты. 6-аминогексановая (аминокапроновая) кислота является антифибринолитическим средством, которое используется для профилактики кровотечений при операциях, в том числе на сердце, в ортопедии, а также в области использования при трансплантации печени.

Используя метод низкотемпературной рентгенографии оценили тепловое расширение исследуемого вещества вдоль различных кристаллографических направлений. Определили коэффициент теплового расширения исследуемого соединения, что является количественной характеристикой теплового расширения. Рентгенограммы образца записывали на дифрактометре XRD-6000 Shimadzu (CuK_α-излучение, геометрия съемки на отражение) с шагом 0.02°, в интервале 2θ: 10÷60° при температуре от 150 К до 450 К (шаг 25К). После обработки результатов эксперимента были получены коэффициенты теплового расширения 6-аминогексановой кислоты, представленные в таблице 1.

Таблица 1. Коэффициенты теплового расширения исследуемой 6-аминогексановой кислоты.

Соединение	T, K	$\alpha_a \cdot 10^5$, K^{-1}	$\alpha_b \cdot 10^5$, K^{-1}	$\alpha_c \cdot 10^5$, K^{-1}	$\alpha_\beta \cdot 10^5$, K^{-1}	$\alpha_V \cdot 10^5$, K^{-1}
6-амино-гексановая кислота	300	-3,07	-4,34	10,17	-0,91	3,15

Было обнаружено, что анизотропия теплового расширения возрастает с повышением температуры (рис.1), наибольшие тепловые деформации наблюдаются по оси *c*, что обусловлено наличием низкоэнергетических водородных связей вдоль этого кристаллографического направления, по оси *a* и *b* происходит сжатие структуры.

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Сокристаллизация эзетимиба

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Проведен анализ способности к сокристаллизации лекарственного вещества эзетимиба с цитраконовой кислотой. Целью сокристаллизации является дальнейшее изучение свойств растворимости лекарственного средства в виде сокристалла и исследование результатов анализа по сравнению с веществом в чистом виде. Общая мотивация для исследования фармацевтических сокристаллов в качестве альтернативного подхода при разработке лекарств - это корректировка физико-химических свойств для улучшения общей стабильности и эффективности лекарственной формы, а также улучшении свойств растворимости.

Эзетимиб – вещество, относящееся к классу гиполипидемических препаратов, которые избирательно ингибируют всасывание холестерина и связанных с ним фитостеролов в кишечнике. Это вещество, нерастворимое в воде, обладающее высокой степенью биологической проницаемости, способное существовать в двух полиморфных формах (форма А, форма В). При перетирании эзетимиба в этаноле, вещество переходит в стабильную форму А.

Проведено совместное растирание эзетимиба с цитраконовой кислотой в эквимолярном соотношении в присутствии этанола. Методом порошковой рентгенографии установлена вероятность образования сокристалла эзетимиба с теофиллином, на рентгенограмме произошел сдвиг спектральных линий (Рис. 1). Запись рентгенограмм осуществляли на рентгеновском дифрактометре Shimadzu XRD-6000 (CuK_{α}-излучение, съемка на отражение θ–2θ) в интервале от 5–45°.

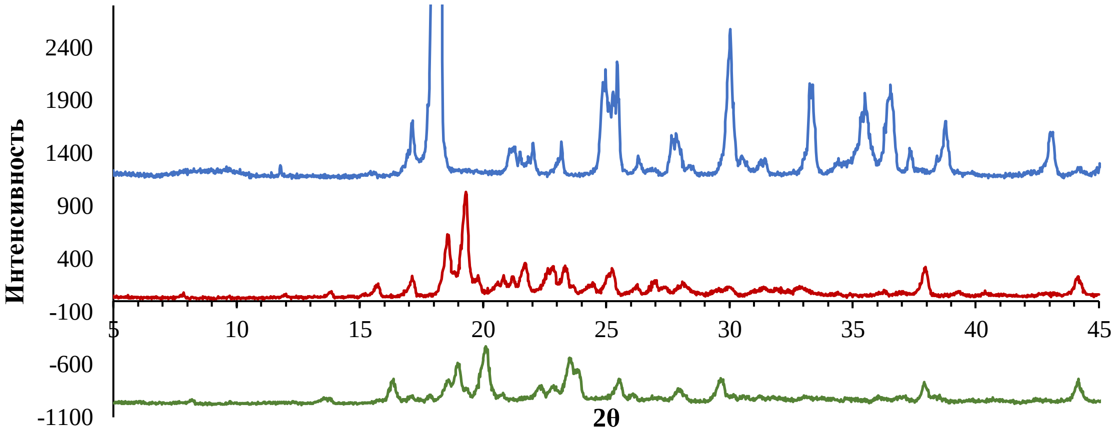

Рис. 1. Рентгенограммы: цитраконовой кислоты (А), эзетимиба в этаноле (Б), сокристалла эзетимиба с цитраконовой кислотой в этаноле (В).

Влияние адсорбированных примесей на эмиссионные свойства углеродных одностенных нанотрубок

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В качестве объекта исследования были выбраны модельные молекулы, аналогичные одностенным углеродным нанотрубкам (ОСУНТ) типа «зигзаг» с различными диаметрами и длиной. Диаметр модели определялся индексами хиральности (n,0), где n=5–9, а протяженность УНТ соответствует числу циклических транс-углеродных цепочек (l_i) (i=3–9) в углеродном каркасе УНТ перпендикулярно ее оси. Все исследованные структуры моделировали ОСУНТ с открытыми концами. Висячие связи при этом насыщались атомами водорода.

В качестве примесных атомов были выбраны атомы водорода и фтора.

Расчеты оптимизированной геометрии молекул, моделирующих УНТ хиральности (n,0) с примесными атомами на графеновой поверхности, и их энергетических параметров были проведены неэмпирическим методом Хартри-Фока в базисе 3-21G с использованием пакета прикладных программ FireFly.

Анализ результатов:

1. Значения энергии адсорбции одного адатома отрицательны, что свидетельствует о протекании взаимодействия молекул водорода (фтора) с двойной С-С связью независимо от количества циклических транс-углеродных цепочек.
2. Величина $E_{ср.}^{ЭМО}$ для модельных молекулах $M_n(l_i)$ для УНТ (n,0) с адсорбированными примесными атомами убывает с увеличением индекса хиральности n, но это уменьшение носит асимптотический характер, то есть работа выхода мало зависит от диаметра нанотрубки.
3. Величина $E_{ср.}^{ЭМО}$ для модельных молекул $M_n(l_i)$ «чистых» УНТ (n,0) так же убывает с увеличением индекса хиральности n.
4. Величина $E_{ср.}^{ЭМО}$ для модельных молекул $M_n(l_i)$ для УНТ (n,0) с адсорбированным атомам водорода больше, чем величина $E_{ср.}^{ЭМО}$ с адсорбированным атомом фтора при всех значениях n.
5. Значение величины $E_{ср.}^{ЭМО}$ для модельных молекул $M_n(l_i)$ «чистых» УНТ (n,0) находятся между значениями величин $E_{ср.}^{ЭМО}$ модельных молекулах $M_n(l_i)$ для УНТ (n,0) с адсорбированными атомами водорода и фтора.

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Перенос протона при образовании комплексов с водой в твердой фазе

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Вода взаимодействует со многими соединениями, образуя комплексы. Возникновение водородной связи в таких системах стимулирует перенос протона между молекулами. Литературные данные о взаимодействии воды с неорганическими и органическими субстратами относятся, главным образом, к жидкой фазе. Вместе с тем, перенос протона существенным образом влияет и на механизм твердофазных превращений (формирование матрицы). Таким образом, основной целью данного исследования было установить образование комплексов с водой в матричных системах и выявить основные особенности их структуры с использованием методов ИК-спектроскопии и квантовой химии.

Выбор объектов осуществлен таким образом, чтобы рассмотреть основные типы систем с переносом протона в твердой фазе и выявить общие закономерности такого переноса. Для этого были исследованы следующие системы, содержащие молекулы воды: 1) Галогениды щелочных металлов (Li, Na, K, Cs); 2) Ароматические соединения, которые играют важную роль в каталитических процессах гидроочистки топлив на поверхности твердофазных катализаторов. 1,2,4-Триазол и его замещенные аналоги, в которых водородная связь образуется с участием подвижного водорода гетероциклической молекулы (Рис.1); 3) Органические аминобораны, в которых могут возникать структурные формы с водородной связью между молекулой воды и BH_3-группой, играющие существенную роль в электрохимических процессах.

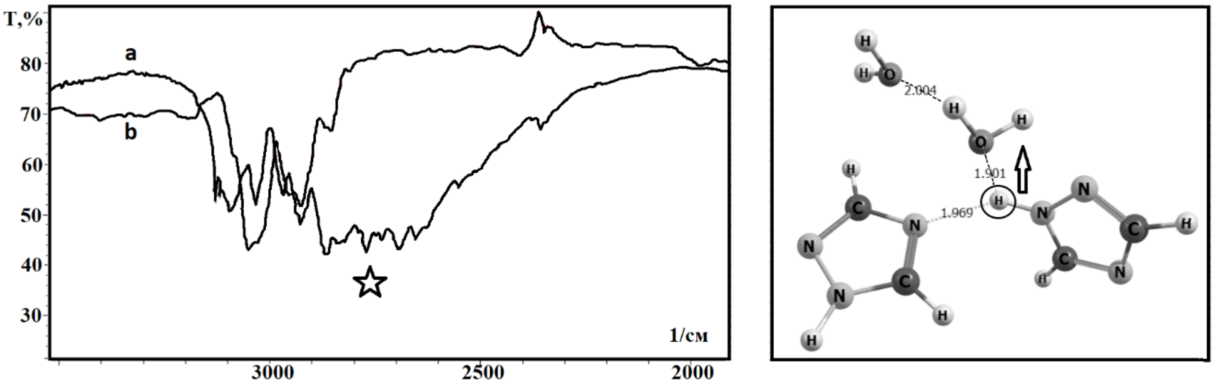

Рис. 1. ИК-спектр триазола (звездочкой отмечена полоса OH валентных колебаний подвижного протона) и оптимизированная геометрия комплекса триазола с водой

Методами ИК-спектроскопии были выявлены факторы, позволяющие установить перенос протона между молекулами воды с формированием гидроксоний-катиона в твердой фазе. В рамках квактово-химических расчетов с использованием теории функционала плотности предложен механизм переноса. протона в исследованных системах.

Контролируемый синтез сополимеров на основе стеарилметакрилата и их применение в качестве присадок к дизельному топливу

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Гомо- и сополимеры стеарилметакрилата (**СМА**) зарекомендовали себя в качестве эффективных присадок для улучшения низкотемпературных свойств дизельного топлива (**ДТ**) [1]. Показано, что полярный сомономер способствует повышению депрессорного эффекта полимерной присадки. Цель данной работы - сравнительный анализ влияния сополимеров СМА с акрилонитрилом (**АН**) различной структуры на низкотемпературные свойства ДТ.

Для синтеза статистических сополимеров поли(СМА-*со*-АН) использована каталитическая система CuBr(I) / трис[(2-пиридил)метил]амин (**ТПМА**) / этил-2-бромизобутират (**ЭБИБ**).

Синтез линейных блок-сополимеров проведен с использованием полиСМА и полиАН, содержащих на конце цепи атом галогена. ПолиСМА-Br и полиАН-Br получены с применением каталитической системы CuBr(I)/ ТПМА / ЭБИБ, диапазон молекулярных масс (**ММ**) составлял 10-85 кДа и 5-25 кДа соответственно. ПолиСМА-I (ММ 5-10 кДа) и полиАН-I (ММ 2-7 кДа) синтезированы в присутствии йодистого цианизопропила в условиях облучения белым светом. Реинициирование полимеризации проводилось с помощью системы CuBr(I)/ ТПМА.

Установлено, что использование CuBr(I) / ТПМА позволяет получать сополимеры полиСМА-*б*-полиАН широкого спектра ММ и составов вне зависимости от природы макроинициатора и концевого галогена.

В результате исследования влияние образцов сополимеров на низкотемпературные характеристики ДТ в концентрациях 200-1600 ppm установлено, что статистические сополимеры поли(СМА-*со*-АН) в плане снижения температуры застывания ДТ оказываются более эффективными, чем блок-сополимеры полиСМА-*б*-полиАН.

Работа выполнена при финансовой поддержке РФФИ (проект № 20-03-00150).

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THE TRAINING OF HIGHLY QUALIFIED PERSONNEL

Enhancing english language teaching at the unn chemistry faculty with ict and edutainment

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The paper raises issues of enhancing the educational process in teaching the English language to meet all the requirements set in terms of the distinct language skills that must be developed in students at the UNN Chemistry Faculty. The project-based method and Vocabulary eBooks [1] have already been integrated into English teaching means of developing both hard skills and soft skills which lead to learning process optimization. Taking into account the knowledge gained and specific know-how from good practice abroad under the Erasmus+ program at the University of Cordoba, Spain, in 2021, the author's attention is focused on the implementation of ICT and edutainment technology into the English language course. An approach that combines traditional content and teaching methods in the context of new ICTs, has led to the development of edutainment teaching technology which is based on the concept of "education + entertainment" [2]. One of the primary goals of edutainment is to ensure that the recipient enjoys the learning process. This technology comprises emotional and motivational aspects, which create highly favorable conditions for the involvement of digital generation into learning. There are many proven benefits of using gamification in the classroom: higher engagement and concentration level; fun learning; lower level of anxiety; intrinsic motivation for learning; thinking outside the box; proactive learning. It is advisable to use various platforms and sites, guided by the principle of novelty and diversity of educational and entertainment technologies. First of all, the portal of Lobachevsky State University of Nizhny Novgorod can be used to stimulate students' written communication in English. It might also be used to engage chemistry students in various foreign language marathons, e.g., a vocabulary booster marathon with respect to students' major. Then, free of charge game-based learning platform vznaniya.ru which can be recommended to work on grammar and vocabulary. Finally, Kahoot! is a game-based learning platform that makes it easy to create distinct types of questions, such as multiple choice, true/false; the platform helps to cover any kind of content (e.g., grammar, vocabulary, reading). This type of teaching and learning creates favorable conditions for intensifying the process of forming foreign language competence. Furthermore, students can consolidate knowledge and develop skills relevant for their professional development.

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