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# Condensed Matter and Interphases

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## Аннотации на английском языке

Research article

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Kinetic regularities of electrochemical oxidation of the methionine anion on platinated platinum

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### Abstract

The purpose of this study was the determination of the kinetic regularities of the methionine electrooxidation process on the Pt(Pt) electrode in an aqueous-alkaline medium.

The main kinetic regularities of the methionine anion electrooxidation process were determined using by the methods of cyclic voltammetry, coulometry, and electrochemical impedance spectroscopy. The concentration of methionine in the alkaline solution before and after anodic oxidation was determined spectrophotometrically using spectrophotometer UNICO 2800. The measurements were carried out at room temperature both in an argon atmosphere and in an aerated aqueous solution. The results of voltammetric measurements were adjusted for the limiting oxygen recovery current and the charging current of the double electric layer.

The range of potentials of the electrochemical activity of the methionine anion on the Pt(Pt) electrode, the number of electrons involved in the anode process, and its kinetic scheme were determined. The main product of the electrooxidation of methionine in an alkaline medium on Pt(Pt) was the methionine sulfoxide anion. It was shown that the electrooxidation of the methionine anion on Pt (Pt) was carried out from the adsorbed state and was irreversible.

Keywords: Amino acid, Methionine, Platinum, Voltammetry, Electrooxidation, Anodic process

Research article

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Entropy features of the PeTa effect during phase transformations of water

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## Abstract

The article discusses a hypothesis put forward by V. A. Tatarchenko and M. E. Perelman. According to it, the first order phase transition during vapour condensation or melt crystallisation (PeTa effect) is accompanied by the appearance of nonthermal radiation of the media. The generally accepted point of view is that the latent heat of phase transformation can only be released in the form of heat. When the authors of the hypothesis tried to prove the existence of the effect of nonthermal radiation and considered the facts confirming it, they did not take into account the peculiarities of the initial and final states of the medium (i.e. their entropy). To clarify the physics of the process of liquid crystallisation and to consider the possibility of nonthermal radiation, we studied the peculiarities of water crystallisation and the formation of ice. This is the process the authors referred to in order to prove their hypothesis. It was shown that in various experiments, it is necessary to consider both the state (structure) of the initial water samples and the formed ice, which can consist of various crystalline modifications with chaotic packing. These features of initial and final states, i.e. the entropy of water and ice samples in real experiments and under observed natural phenomena, make it more difficult to assess the characteristics of a possible radiation. The entropy of the initial and final states was determined by the procedure of the system preparation and the peculiarities of the phase transition dynamics. Its values depend on macroscopic parameters, as well as on the microstructure of the media, the determination of which is a very challenging task in each specific case. In addition, in many cases, we have to deal with metastable media, for which it is necessary to take into account the influence of fluctuations on the process of the phase transition. Therefore, the concepts of equilibrium thermodynamics are not applicable to them. However, these are the media where non-heat radiations may occur in accordance with the laws of self-organisation in nonlinear weakly nonequilibrium objects. This work shows a method for preparing low-entropy medium with its subsequent phase transformation into ice. To do so we conducted an experiment which involved freezing concentrated alcohol in order to obtain deeply supercooled water. It appears that to find the characteristics of the PeTa radiation it is necessary to take into account the entropy constraints for each specific case, which will allow assessing the spectrum of possible non-heated radiations and their characteristics.

Keywords: Phase transition, Non-heat radiation, Supercooled water, Entropy

Research article

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Cylindrical model of electrochromic colouration of hydrated vanadium pentoxide thin films with point contacts

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### Abstract

This article analyses experiments on the kinetics of the internal electrochromism of thin (micron) films of hydrated vanadium pentoxide xerogel with point contacts. It describes a cylindrical model of electrochromic colouration, which was used to evaluate the concentration of the colour centres in the initial film and after additional hydrogenation of this film by plasma-immersion ion implantation.

When we compared the calculated values of the concentration of colour centres with the equilibrium concentration of protons in the xerogel, we saw that the mobility of the protons migrating from the depth of the film to the cathode region, which are involved in the electrochemical reaction, was not a determinant of the electrochromism kinetics.

The rate of electrochromic colouration could be increased by the formation of layered film structures based on hydrated vanadium pentoxide, which have increased overall electron conductivity and, as a consequence, low faradaic resistance of the electrochromic cathodic reaction.

Keywords: Electrochromism, Hydrated vanadium pentoxide, Plasma-immersion ion implantation, Ion current kinetics

Research article

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High-temperature spectrophotometry of indium chloride vapours as a method of study of the In - Se system

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### Abstract

The goals of this work are as follows: (a) searching for a method of study of the In – Se system taking into account the specified problems and difficulties, (b) choosing a way for the instrumental implementation of this method, and (c) obtaining experimental evidence that this method and its implementation are promising.

The choice of the In – Se system is related to the fact that indium selenides, layered structures and semiconductor phases with stoichiometric vacancies, are promising from the point of view of materials science. This choice is also related to the use of binary precursors for the synthesis of heterostructures based on CIS compounds.

We studied the possibility of applying the auxiliary component method using the equilibrium with the participation of indium chloride vapours which were made to contact the condensed phases of the In – Se system. Equilibrium was achieved using high-temperature spectrophotometry of the vapour phase. The experiment had two stages. During the first stage we determined the absorption characteristics of the InCl<sub>3</sub> vapour. During the second stage we studied the heterogeneous equilibrium of the unsaturated indium chloride vapour with several phases of the In – Se system. Over the course of the study, we determined the molar attenuation coefficients of the InCl<sub>3</sub> vapour and plotted the temperature dependences of the value  $K_s^*$ .

It was found that the phase composition of the alloys significantly influences the position of the corresponding lines on the  $K_p^*-T$  diagram, which proves the possibility of using the suggested auxiliary component method in its specific instrumental (spectrophotometric) implementation in order to study the In – Se system. We also showed the additional possibilities of using this method for plotting T-X diagrams of binary systems in such high-temperature areas where the binary solid phase is in equilibrium with the melt. This application of the method is related to the solubility of a vapour of an auxiliary component (chlorine in the form of indium chlorides) in the melts of binary phases (indium selenides).

**Keywords:** High-temperature spectrophotometry, In – Se system, Phase diagram, Heterogeneous equilibria, Indium chlorides

Research article

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Nonlinear optical properties of single-walled carbon nanotubes/water dispersed media exposed to laser radiation with nano- and femtosecond pulse durations

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## Abstract

The constant increase in the power of laser systems and the growth of potential fields for the application of lasers make the problem of protecting sensitive elements of electro-optical systems and visual organs from high-intensity radiation an urgent issue. Modern systems are capable of generating laser radiation in a wide range of wavelengths, durations, and pulse repetition rates. High-quality protection requires the use of a universal limiter capable of attenuating laser radiation, not causing colour distortion, and having a high transmission value when exposed to low-power radiation. For this, dispersed media based on carbon nanotubes with unique physicochemical properties can be used. Such media have constant values of their absorption coefficient and refractive index when exposed to low-intensity laser radiation and change their properties only when the threshold value is reached.

The aim of this work was the study of the nonlinear optical properties of an aqueous dispersion of single-walled carbon nanotubes exposed to nano- and femtosecond radiation. For the characterization of the studied medium, Z-scan and fixed sample location experiments were used. The optical parameters were calculated using a threshold model based on the radiation transfer equation.

As a result of the experiments, it was shown that the aqueous dispersion of single-walled carbon nanotubes is capable of limiting radiation with wavelengths from the visible and near-IR ranges: nano- (532, 1064 nm) and femtosecond (810 nm). A description of nonlinear optical

effects was proposed for when a medium is exposed to radiation with a nanosecond duration due to reverse saturable absorption and twophoton absorption. When the sample exposed for a femtosecond duration the main limiting effect is spatial self-phase modulation. The calculated optical parameters can be used to describe the behaviour of dispersions of carbon nanotubes when exposed to radiation with different intensities. The demonstrated effects allow us to conclude that it is promising to use the investigated media as limiters of high-intensity laser radiation in optical systems to protect light-sensitive elements.

**Keywords:** Laser radiation Limiters, Nano- and femtosecond radiation, Carbon nanotubes, Reverse saturable absorption, Spatial self-phase modulation, Z-scan, Radiation transfer equation

Research article

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Formation of a quasi-equilibrium domain structure of crystals of the TGS group near  $T_c$ 

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### Ahstract

In the temperature range  $\Delta T \approx 321$  K  $\div 322$  K, the kinetics of the nonequilibrium domain structure of triglycine sulphate crystals, both pure and with specially introduced defects, has been studied by means of piezoresponse force microscopy technique. The temporal change in the domain structure as a set of regions with a scalar order parameter of P(t,t) = +1 and -1 for oppositely polarized domains was analysed by the behaviour of the space-time correlation function  $C(t,t) = \cdot P(t,t)P(0,t)$ . At different distances from the Curie point  $T_c$ , the characteristic length  $L_c$ , as a scale measure of the average domain size, increases with time according to the power law  $L_c(t) \sim (t-t_0)^3$ . A decrease of the exponent a with distance from  $T_c$  can be a consequence of the transition of the domain structure of TGS crystals from a non-conservative state to a conservative one.

**Keywords:** Piezoresponse atomic force microscopy, Triglycine sulfate, space-time correlation function, Characteristic length, Time dependences, Power law

Research article

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Electrodialysis of a sodium sulphate solution with experimental bentonite-modified bipolar membranes

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## Abstract

The aim of this work is to study the characteristics of the electrodialysis of a sodium sulphate solution with experimental bipolar membranes based on the MA-41 anion exchange membrane and a liquid sulphonated cation-exchanger modified with bentonite clays. The conversion of sodium sulphate was conducted by electrodialysis with bipolar membranes obtained by applying a liquid sulphonated cation-exchanger containing particles of bentonite clay to the MA-41 anion-exchange membrane.

To increase the performance of membranes in terms of hydrogen and hydroxyl ions, we carried out organomodifications of bentonite with alkyldimethylbenzylammonium chloride and stearic acid at various concentrations. The bipolar membrane with the addition of bentonite modified with alkyldimethylbenzylammonium chloride (2 wt%) showed a higher performance in terms of H\*-ions. The bipolar membrane with bentonite modified with stearic acid (3 wt%) added to its cation-exchange layer is the most effective in terms of obtaining a flux of OH\*-ions. It was shown that a combination of alkyldimethylbenzylammonium chloride (2 wt%) and stearic acid (3 wt%) used to modify bentonite can increase the performance of the bipolar membrane during the conversion of sodium sulphate, both in terms of the acid and alkali.

Keywords: electrodialysis, bipolar membrane, modification, bentonite, organobentonite, sodium sulphate, acid, alkali

Research article

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Statistical approach to the process of tunnel ionisation of impurity centres near the heterointerface

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## **Abstract**

To date, the processes of tunnel ionisation of impurities near the interface between two different semiconductors have been comprehensively studied. The most important parameters of the contact electron states of impurities have been determined. However, the calculated expressions for these parameters have been of local nature, as applied to individual impurities. Meanwhile, it is easy to understand that a number of processes, such as the flow of charge carriers and their diffusion through a heterojunction, are clearly statistical in nature. The same applies to the processes of tunnel ionisation of shallow and/or deep impurities near the interface. A statistical approach to the calculation of the parameters of tunnel ionisation of impurities broadens the opportunities for obtaining fundamental information regarding surface electron states.

The aim of this work was to use a statistical approach to study the effect of the heterointerface on the energy spectrum of shallow and deep centres. For this purpose, the expansion of the reflected quasi-classical wave function within the complete system of spherical harmonics and the subsequent extraction of the zero harmonic amplitude (s-component) was used to estimate the minimum distance from the impurity to the heterobarrier and to specify the limitations of the applicability of the results obtained in other works. The article analyses the conditions of the quasi-classical approximation which are used to estimate the order of the value for the minimum height of the potential barrier (pit).

This work (with due consideration given to the minimum distance estimate) presents averaged formulas obtained for the energy shift of the ground state and the lifetime of the quasi-stationary state depending on the distance from the heterobarrier. Some qualitatively new considerations can also be found in the article. The distribution of impurity centres near the heterobarrier is assumed to be uniform. The article discusses the

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role of electron transitions in causing the buffer field effect for both shallow and deep centres. The focus of the article is on the estimates of various physical parameters characterising electron transitions near the heterobarrier.

Keywords: Heterobarrier, Tunnelling, Shallow and deep centres, Energy shift of the ground state, Lifetime

Research article

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Anodic behaviour of manganese germanide Mn. Ge, in a sodium sulphate aqueous solution

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### Abstract

Germanides are an interesting class of two-component systems which consist of metal and germanium. They are similar in their structure with silicides but have the specific properties. The target of the investigation was finding the main anodic electrochemical behaviour mechanisms for magnesium germanide  $Mn_cGe_x$  in an  $Na_xSO_4$  aqueous solution.

Electrochemical behaviour of manganese germanide obtained by Czochralski method was investigated by polarization curves and electrochemical impedance spectroscopy methods and accomplished by microscopy data. Individual manganese and germanium were investigated in the same way for comparison. It was established that in the anodic oxidation process germanium is the potential-determining component. The passivation process associated with the formation of surface oxide films was accomplished by the current density oscillations appearing due to the bad adhesion of oxide film to the surface of the sample, its imperfection and discontinuity. The nature of oxide film formed in the polarization process was partially established. The dependence of the anodic behaviour of the sample on the sulphate concentration was established: in the diluted solutions the passivation occurs at more positive potentials than in the concentrated. This phenomenon can be explained by the different mechanisms of anodic oxidation in the solutions of different concentrations.

Keywords: Manganese, Germanium, Manganese germanide, Oxide films, Anodic oxidation, Impedance spectroscopy

Research article

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# Complexation processes in "PbCl $_2$ -N $_2$ H $_4$ CS" aqueous solutions during deposition of lead sulphide films V. N. Semenov $^1$ , V. V. Volkov $^2$ , N. V. Pereslytskikh $^1$

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## Abstract

In this study, we proposed a new approach to assessing the processes of complexation in aqueous solutions using the example of the interaction of lead chloride with thiourea. The goal of this study was the investigation of processes of complexation in "PbCl $_2$ -N $_2$ H $_4$ CS" aqueous solutions and determination of the regions of dominance of thiourea coordination compounds, which are precursors during the deposition of lead sulphide films

Based on the diagrams and cross section lines of equal fractions constructed in three-dimensional space, the regions of dominance of all complex forms existing in the studied solution were found. Such a graphic image is the most informative, since it allows selection of the concentration ranges of the predominance of certain coordination compounds, especially thiourea complexes, which are precursors during the deposition of lead sulphide films. It was shown that an increase in the concentration of  $N_2H_4CS$  led to an increase in the total fraction of thiourea complexes: for a twofold excess of  $N_2H_4CS$  its fraction was 0.25, for a threefold excess it was 0.35, for a fourfold excess it was 0.5, for a fivefold excess it was 0.7

Keywords: Distribution diagrams, Complexation, Thiourea, Lead chloride, Coordination compounds

Research article

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Synthesis, structure, and photo-Fenton activity of PrFeO<sub>2</sub>-TiO, mesoporous nanocomposites

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## Abstract

Porous nanocomposites based on  $PrFeO_3$ - $TiO_2$  were synthesized using the glycine-nitrate combustion method with different values of mass content of  $TiO_2$  (0–7.5 %) and subsequent heat treatment in air. The results of X-ray phase analysis and Raman spectroscopy confirmed the presence of ultradispersed  $TiO_2$ , structurally close to that of anatase. The morphology, specific surface area, and porous structure of the obtained powders were characterized by scanning electron microscopy and adsorption-structural analysis, the results of which showed that the samples had a foam-like mesoporous structure. The specific surface area and the average pore size were in the ranges of 7.6-17.8 m²/g and 7.2-15.2 nm, respectively, and varied depending on the  $TiO_2$  content. The optical properties of the nanocomposites were studied by UV-visible diffuse reflection spectroscopy, the energy of the band gap was calculated as 2.11-2.26 eV. The photocatalytic activity of  $PrFeO_3$ - $TiO_2$  nanocomposites was investigated in the process of photo-Fenton-like degradation of methyl violet under the action of visible light. It was shown that the maximum reaction rate constant was 0.095 min<sup>-1</sup>, which is ten times higher than the value for the known orthoferrite-based analogs. The obtained photocatalysts were also characterized by their high cyclic stability. Based on the studies carried out, the obtained porous  $PrFeO_3$ - $TiO_2$  nanocomposites can be considered to be a promising basis for photocatalysts applied in advanced oxidative processes of aqueous media purification from organic pollutants.

Keywords: Solution-combustion synthesis; Praseodymium orthoferrite; Titanium Oxide; Nanocomposites; Photocatalysts; Fenton-like reactions

## Research article

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Pd-Pb nanoscale films as surface modifiers of Pd,Cu alloy membranes used for hydrogen ultrapurification

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## **Abstract**

The purpose of the article is to reveal the role of the thickness of the layer of the lead-palladium alloy deposited on a copper-palladium membrane in the processes of cathodic injection and the anodic extraction of atomic hydrogen.

The objects of the study were  $\sim 4~\mu m$  thick copper-palladium film electrodes obtained by magnetron sputtering of a target with a composition of 56 at. % Cu and 44 at. % Pd. The studies were carried out by cyclic voltammetry and double step anodic-cathodic chronoamperometry in a deaerated 0.1 M  $\rm H_2SO_4$  aqueous solution. The calculation of the parameters of hydrogen permeability for samples of finite thickness was carried out by mathematical modelling.

Cathodic injection and anodic extraction of atomic hydrogen were used to study the effect of the surface modification of the foil membrane of a Pd-Cu solid solution on the diffusion and kinetic parameters of hydrogen permeability.

It was found that even a small addition of Pd-Pb (a 2 nm thick film) leads to a decrease in the concentration of atomic hydrogen and the diffusion coefficient in the foil. With an increase in the thickness of the coating there is an increase in the diffusion parameters of the hydrogen injection and extraction processes. However, the hydrogen permeability does not reach the level of the unmodified alloy. The main kinetic parameter, the hydrogen extraction rate constant, changes nonlinearly with an increase in the thickness of the coating.

Keywords: Pd-Cu and Pd-Pb solid solutions, Film electrodes, Cathodic injection and anodic extraction of atomic hydrogen, Hydrogen permeability

## Research article

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# $Synthesis\ of\ chitosan\ and\ \emph{N-} vinylimidazole\ graft-copolymers\ and\ the\ properties\ of\ their\ aqueous\ solutions$

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## Abstract

The aim of this work is to synthesise chitosan and *N*-vinylimidazole graft-copolymers of various compositions and to study the properties of their aqueous solutions.

Chitosan and N-vinylimidazole graft-copolymers were obtained by solution polymerisation in the presence of a ceric ammonium nitrate redox initiator. The synthesised graft copolymers were characterised by FTIR to determine their compositions and the grafted side chains of poly-N-vinylimidazole were characterised by gel permeation chromatography to determine their molecular wights and polydispersity indices. It was established that the obtained products are characterised by high values of yield and grafting efficiency and low values of the polydispersity index. It was found that when the content of the N-vinylimidazole links is above 57 wt%, the synthesised graft copolymers are water-soluble. Aqueous solutions of the obtained copolymers were characterised using dynamic light scattering, transmission electron microscopy, and laser Doppler microelectrophoresis. The study showed that macromolecules of graft copolymers in aqueous solutions have stimuli-sensitive properties with respect to the medium reaction and at a concentration above  $10^{-2}$  wt% are characterised by a tendency to self-association forming corecrown aggregates, the geometry of which depends on the molecular masses of the grafted chains. Associates of macromolecules in solutions are characterised by positive values of the electrokinetic potential, the values of which also depend on the medium reaction. Thus, it was found that the ceric ammonium nitrate initiator allows obtaining chitosan and N-vinylimidazole graft-copolymers showing stimuli-sensitive properties in aqueous solutions and prone to self-association at concentrations above  $10^{-2}$  wt%.

**Keywords**: Graft copolymers, Aqueous solutions of polymers, Stimuli sensitivity, chitosan, N-vinylimidazole

## Research article

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## Synthesis and properties of nanosized ZnO/wood composite

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## Abstract

The aim of the study was to synthesise a ZnO/silver birch wood (Bétula péndula) nanocomposite and evaluate its physical and mechanical properties in comparison with an unmodified natural polymer.

Using the sol-gel method, we synthesised almost spherical impurity-free zinc oxide nanoparticles with a predominant particle size of about 20 nm. Amorphous hydrated  $Zn(OH)_2$  was impregnated into the wood material at the gel formation stage. It resulted in the reaction of zinc hydroxide decomposition with the formation of ZnO nanoparticles in the wood as a nanoreactor.

The hydrophobic properties of the surface of ZnO/silver birch wood nanocomposite improved significantly (the contact angle of wetting doubled). Its moisture and water resistance decreased (2-5 times and 30%, respectively). The nanocomposite also showed less swelling in the radial (8-10 times) and tangential (2.6-10 times) directions in comparison with natural wood.

Keywords: Zinc oxide, Sol-gel synthesis, Nanoparticles, Silver birch wood (Bétula péndula), Impregnation, Modification

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Research article

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Hydrothermal assisted conventional sol-gel method for synthesis of bioactive glass 70S30C

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## Abstract

Bioactive glasses (Bioglasses) are widely synthesized by the conventional sol-gel method consisting of two main steps for sol and gel formation. However, the conversion from sol to gel requires a long time (5–7 days). In this study, the hydrothermal system was used to quickly synthesize the bioactive glass by reducing the conversion time from sol to gel. The hydrothermal assisted conventional sol-gel method was applied for synthesis of the bioactive glass  $70SiO_2$ –30CaO (mol%) (noted as 70S3OC). The synthetic glass was investigated by the physical-chemical techniques. The "in vitro" experiments in SBF (Simulated Body Fluid) solution was also performed to evaluate the bioactivity of synthetic material. The obtained results show that the bioactive glass 70S3OC was successfully elaborated by using the hydrothermal assisted conventional sol-gel method. The consuming time was reduced compared to the conventional method. The physical-chemical characterization confirmed that the synthetic glass is amorphous material with mesoporous structure consisting of interconnected particles. The specific surface area, pore volume and average pore diameter of synthetic glass were  $142.8 \text{ m}^2/\text{g}$ ,  $0.52 \text{ cm}^3/\text{g}$ , and 19.1 nm, respectively. Furthermore, synthetic bioactive glass exhibited interesting bioactivity when immersed in simulated body fluid (SBF) solution for 1 days and good biocompatibility when cultured in cellular media.

Keywords: Bioactive glass, Hydrothermal assisted sol-gel, Bioactivity, in vitro, Cell viability

Research article

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Phase formation in the Ag, MoO<sub>4</sub>-Rb, MoO<sub>4</sub>-Hf(MoO<sub>4</sub>), system

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# Abstract

Systematic studies of the subsolidus structure of ternary molybdate systems allow expanding the representation of ternary molybdates. In this paper we studied the solid phase interaction in the  $Ag_2MoO_4-Rb_2MoO_4-Hf(MoO_4)_2$  system for the first time using X-ray phase analysis.

To determine the quasi-binary sections, we use the method of "intersecting cuts". It helped to reveal the formation of new  $Rb_5Ag_{1/3}Hf_{5/3}(MoO_4)_6$  and  $Rb_3AgHf_2(MoO_4)_6$  phases. We also determined their thermal characteristics using differential scanning calorimetry. The ternary molybdate  $Rb_5Ag_{1/3}Hf_{5/3}(MoO_4)_6$  crystallised in the trigonal syngony with the following unit cell parameters: a = 10.7117(1), c = 38.5464(5) Å (space group R3c, Z = 6). The  $Ag_3MoO_4 - Rb_3MoO_4 - Hf(MoO_4)_5$  system is characterised by the existence of ten quasi-binary cross sections.

The experimental data obtained in this work complement the information on phase equilibria in condensed ternary systems containing molybdates of tetravalent elements and two different monovalent elements. This provides opportunities for the combination of the compositions of ternary molybdates due to cationic substitutions, which will allow controlling their properties.

**Keywords:** Phase diagram, Triangulation, Solid-state synthesis, Ternary molybdate, Silver molybdate, Rubidium molybdate, Hafnium molybdate, X-ray diffraction analysis

Research article

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# Optical and magnetic properties of orthoferrite NdFeO<sub>3</sub> nanomaterials synthesized by simple co-precipitation method Pham Thi Hong Duyen<sup>1</sup>, Nguyen Anh Tien<sup>2</sup>

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## Abstract

In this work, orthoferrite NdFeO $_3$  nanomaterials with particle sizes 20-40 nm have been successfully synthesized via a simple co-precipitation method through the hydrolysis of Nd (III) and Fe (III) cations in hot water with 5% NaOH as a precipitating agent. Single-phase NdFeO $_3$  was generated after calcination of the as-prepared powder at 700, 800, and 900 °C for 1 hour. The UV-Vis spectra at room temperature presented strong absorption in the UV-Vis regions (l = 200-400 nm and 400-600 nm) with small band gap energy ( $E_g = 2.2 \div 2.5$  eV). The obtained NdFeO $_3$  nanomaterials exhibited a hard ferromagnetic behavior with high coercivity ( $H_c = 600-1600$  Oe).

Keywords: NdFeO<sub>3</sub>, Nanomaterial, Co-precipitation, Optical and Magnetic properties

## Research article

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Investigation of the deposition of calcium fluoride nanoparticles on the chips of CaF, single crystals

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### Abstract

The deposition of calcium fluoride nanoparticles on single crystal chips of calcium fluoride was studied.  $CaF_2$  nanoparticles were synthesized by co-precipitation from aqueous nitrate solutions using hydrofluoric acid as a fluorinating agent at a batch system. The prepared samples were examined by atomic force microscopy, scanning electron microscopy, transmission electron microscopy and optical transmission. There is an inhomogeneous coating of the substrate surface with submicron particles of about 100-150 nm in size, which are clusters of nanoparticles of 15-20 nm in size. The initial nanoparticles coherently grow on the surface of the crystal substrate. Heat treatment of the substrate-deposited layer composite at 600 °C leads to the coalescence of submicron particles and the formation of a porous layer of a complex structure.

Keywords: Fluorite, Single crystals, Nanoparticles, Co-precipitation, Mechanism of oriented attachment growth

## Research article

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## New nanocomposites for deep water deoxygenation

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## **Abstract**

New metal-polymer nanocomposites for deep water deoxygenation have been obtained and studied. A macro- and monoporous sulphocation exchanger with a nanometer pore size was used as the polymer matrix, and the metal was nanodispersed copper deposited in the pores of the matrix. A specific feature of the studied nanocomposites is their sodium ionic form, which eliminates the possibility of the formation of soluble copper oxidation products. The established linear dependence of the copper capacity on the number of cycles of ion-exchange saturation - chemical deposition shows that the process of metal deposition into the pores of the matrix does not have significant obstacles during 10 cycles and contributes to the production of high-capacity samples.

The high efficiency and duration of the life cycle of high-capacity copper ion exchanger nanocomposites have been shown. Experimental studies of water deoxygenation in column-type apparatus with a nanocomposite nozzle were confirmed by a theoretical analysis of the process dynamics. Experimental data and theoretical calculations showed the deep level of water deoxygenation had practically unchanged values of pH and electrical conductivity. Residual oxygen can be controlled and does not exceed 3 µg/l (ppb).

The hygienic and economic substantiation of the expediency of using the obtained nanocomposites is provided. The necessity of using modern nanocomposite metal-polymer materials for deep water deoxygenation circulating in technological systems was analysed. When using this innovation, the metal components of the distribution facilities will be protected from corrosion and, therefore, the hygienic requirements for the water quality of centralised drinking water supply systems will be ensured. Deep chemical water deoxygenation using copper ion-exchange polymer nanocomposites in sodium form allows solving the problem of the corrosion resistance of metals, ensuring that water meets hygienic requirements on a large scale.

The competitive advantage of the considered water deoxygenation system in comparison with the known systems is the rejection of the use of precious metals-catalysts (palladium, platinum), pure hydrogen, and complex design solutions. The proposed new nanocomposite installation for water deoxygenation is characterised by its ease of use and can be built into a filter system for water purification.

SWOT analysis of the advantages and disadvantages of the proposed method of water deoxygenation showed that its main advantages are the high oxygen capacity of the nanocomposite, low residual oxygen content (3 ppb ( $\mu$ g/l)) in the water, and ease of operation of the deoxygenator. Calculations of the economic efficiency of the nanocomposite have been carried out. The breakeven point is reached when producing only ~100 l of nanocomposite and a volume of sales ~1,600,000 roubles, above which a profit can be obtained. The payback period for an investment of ~15,000,000 roubles is rather short and will not exceed 2 years.

Keywords: Metal-polymer nanocomposites, Water deoxygenation, Hygiene requirements, Economic efficiency

# Research article

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# Experimental study and mathematical modelling of self-oscillation at the electrode-magnetic fluid interface in an electric field V. S. Chekanov<sup>1</sup>, E. V. Kirillova<sup>2</sup>, A. V. Kovalenko<sup>3</sup>, E. N. Diskaeva<sup>4</sup>

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## Abstrac

The article describes a mathematical model of self-oscillation in the form of a boundary value problem for a nonlinear system of partial differential equations, with a numerical solution. The numerical results were compared to the experimental data to confirm the adequacy of

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the model. The model uses the classical system of differential equations of material balance, Nernst-Planck and Poisson equations without simplifications or fitting parameters. The aim of the article was to study the parameters of concentration self-oscillation in a layer of the dispersed phase particles of magnetic fluid at the interface with an electrode in an electric field. For this purpose, we developed a mathematical model, the consistency of which was confirmed by the corresponding physical mechanism.

As a result of numerical experiments, we found the critical value of the potential jump after which self-oscillation began. We also determined the oscillation growth period and other characteristics of the process. We developed software called AutoWave01 with an intuitive user interface and advanced functionality for the study of self-oscillation in a thin layer of magnetic colloid.

Keywords: Magnetic fluid, Interface, Near-electrode layer, Electric field, Self-oscillation, Mathematical model.

Research article

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Semiconductor metal oxide sensor for hydrogen sulphide operating under non-stationary temperature conditions

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### Abstract

The aim of the work was to create a selective gas sensor for hydrogen sulphide. As a result of adding ammonia to the zinc acetate solution, centrifuging the obtained zinc hydroxide and subsequent calcination, a polydisperse zinc oxide powder with a grain size of 5–50 nm was obtained. The material was characterized using X-ray phase analysis and transmission electron microscopy. Subsequently, silver nitrate and terpeniol were added to the zinc oxide nanopowder to form a paste. The gas-sensitive material was obtained by applying the resulting paste on a special dielectric substrate and subsequent calcination, as a result of which the terpeniol burned out, and the silver nitrate turned into an oxide (the mass fraction of the silver was 3%). A non-stationary temperature mode for the operation of the sensor was selected, in which, after rapid heating of the sensor to 450 °C (2 seconds), slow (13 seconds) cooling to 100 °C occurred. Each subsequent heating-cooling cycle with a total period of 15 seconds began immediately after the end of the previous cycle. The use of an unsteady temperature mode in combination with the selection of the composition of the gas-sensitive layer made it possible to obtain a response of 200 for a hydrogen sulphide concentration of 1 ppm. Along with an increase in sensitivity, a significant increase in selectivity was also observed. The cross-sensitivity for the determination of hydrogen sulphide and other reducing gases (CO, NH<sub>3</sub>, H<sub>2</sub>) was more than three orders of magnitude. Thus, this sensor can be used to detect hydrogen sulphide even in the presence of interfering components. The use of highly selective sensors in the tasks of qualitative and quantitative analysis can significantly simplify the calibration in comparison with "electronic nose" devices. Devices based on highly selective sensors do not require the use of mathematical methods for processing multidimensional data arrays.

Keywords: Sensitivity; MOX sensor; Temperature modulation; Qualitative analysis; Quantitative analysis

Research article

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Dps protein localization studies in nanostructured silicon matrix by scanning electron microscopy E. V. Parinova<sup>1</sup>, S. S. Antipov<sup>1,2</sup>, V. Sivakov<sup>3</sup>, I. S. Kakuliia<sup>1</sup>, S. Yu. Trebunskikh<sup>1</sup>, E. A. Belikov<sup>1</sup>, S. Yu. Turishchev<sup>1</sup>

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## Abstract

The present work is related to the microscopic studies of the morphology of the planar and inner part of silicon nanowires arrays before and after immobilization with a natural nanomaterial, Dps protein of bacterial origin.

Silicon nanowires were formed by metal-assisted wet chemical etching. To obtain the recombinant protein, *Escherichia coli* cells were used as excretion strain and purification were carried out using chromatography. The combination of silicon nanowires with protein molecules was carried out by layering at laboratory conditions followed by drying under air. The resulting hybrid material was studied by high-resolution scanning electron microscopy. Studies of the developed surface of the nanowires array were carried out before and after combining with the bioculture. The initial arrays of silicon wires have a sharp boundaries in the planar part and in the depth of the array, transition layers are not observed. The diameter of the silicon nanowires is about 100 nm, the height is over a micrometer, while the distances between the nanowires are several hundred of nanometers. The pores formed in this way are available for filling with protein during the immobilization of protein.

The effectiveness of using the scanning electron microscopy to study the surface morphology of the hybrid material "silicon wires – bacterial protein Dps" has been demonstrated. It is shown that the pores with an extremely developed surface can be combined with a bio-material by deposition deep into cavities. The protein molecules can easily penetrate through whole porous wires matrix array. The obtained results demonstrate the possibility of efficient immobilization of nanoscaled Dps protein molecules into an accessible and controllably developed surface of silicon nanowires.

Keywords: Silicon wires, Developed surface, Ferritin-like Dps protein, Scanning electron microscopy, Combination