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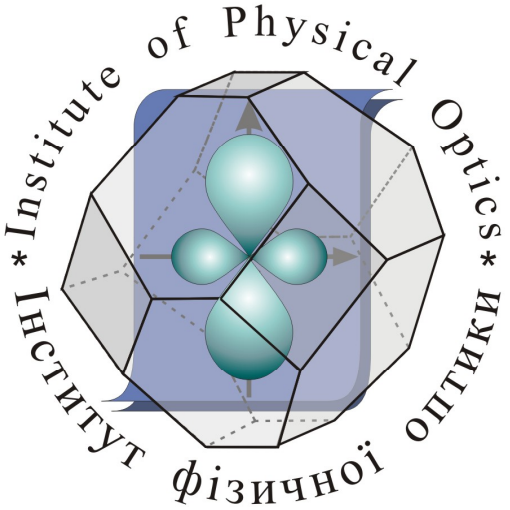

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INVITED LECTURES

Distribution of relaxation times in $0.4Na_{0.5}Bi_{0.5}TiO_3$-$(0.6-x)SrTiO_3$-$xPbTiO_3$ solid solutions

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$Na_{0.5}Bi_{0.5}TiO_3$ (NBT), $SrTiO_3$ (ST) are one of the most popular ferroelectric materials. These materials are often found in various complex relaxors or normal ferroelectrics. One of the most widely studied compounds are NBT with barium titanate, lead titanate or strontium titanate. The reason why many secondary materials are brought along with NBT is to investigate the peculiarities of phase transitions that occur in pure sodium bismuth titanate as well as to find ceramics which would be attractive for practical applications.

Dielectric properties of 0.4NBT-(0.6-x)ST-xPT system varies quite drastically when value of x increases. At certain values this system can be normal ferroelectric, relaxor and also may contain features of dipolar glases.

The purpose of this report is to present distributions of relaxation times and compare them with earlier investigations on other relaxor ferroelectrics and dipolar glasses.

Dielectric and dilatometric studies of phase transitions and kinetics in $(Gua)_4SO_4Cl_2$ crystal

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The crystal of $(Gua)_4SO_4Cl_2$ is a room temperature ferroelectric one and undergoes successive phase transitions [1,2]. The dielectric studies showed diffused dielectric anomaly in the range of phase transitions at faster heating. Slow heating (0.01 K/min) gives evidences for two successive phase transitions III-II at T_2 = 354 K and II-I at T_1 = 357.5 K. Pyroelectric studies evidenced ferroelectric properties of phase III and II. Disappearance of polarization is diffused at first heating run. The sample kept for 400 min in phase II undergoes direct sharp transition II-I during heating. Dilatometric studies at slow heating run confirmed two successive phase transitions and one transition on cooling. The dielectric, pyroelectric, dilatometric and optical studies allowed to conclude that the phase transition III-II at T_2 is characterized by slow kinetics. The studies of permittivity and dimensions changes of the samples which were kept at constant temperature inside of phase II during 400 min gave some detailed information about kinetics of III-II phase transition. The changes of permittivity and dimensions in function of time one can describe with Avrami model. The characterics of kinetics observed in dielectric and dilatometric studies are roughly in agreement.

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Strontium-barium niobate: a lead free multifunctional material

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Solid solutions of the strontium-barium niobate $Sr_xBa_{1-x}Nb_2O_6$ where $0 < x < 1$ (SBN) are environmental friendly (lead free) polar materials of oxygen octahedral family. Their potential applications are based on very attractive pyroelectric, electromechanical, electro-optic, photorefractive, and nonlinear optical and dielectric properties. Strontium-barium niobate is distinguished by its open tungsten bronze structure, i.e. the compound contains five AB_2O_6 formula units per tetragonal unit cell in which six *A* sites are occupied by five divalent metal atoms A. As a result the empty sites give rise to quenched electric random fields even in the stoichiometric compound. Consequently, by changing the ratio between strontium and barium components one may tune the system from ferroelectric ($x < 0.5$) to a generic relaxor ($x > 0.6$) behavior while maintaining the structure unchanged [1].

Using the Czochralski method four single crystalline compounds with nominal $x = 0.40$, 0.50, 0.61 and 0.75, designated hereafter as SBN40, SBN50, SBN61, and SBN75 have been grown. The crystals grown along the [001] tetragonal direction were up to 22 mm in diameter and 40 mm in length with characteristic 24 faces, free from striations and other extended defects. Density of etch pits was found to be of the order of $10^2 - 10^3$ cm^{-2}.

Investigations of the linear dielectric susceptibility measured within $10^0 \le f \le 10^5$ Hz along the polar *c*-axis of the obtained single crystals revealed a gradual crossover from ferroelectric (SBN40) to generic relaxor (SBN75) behavior. Complementary, temperature dependences of the lattice parameters confirm existence of structural phase transitions.

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New multiferroics based on $Sr_xEu_{1-x}TiO_3$ nanowires and nanotubes

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Using Landau-Ginzburg-Devonshire phenomenological theory with parameters extracted from the first principle calculations and experimental data, we calculated the radii and temperature dependence of phase diagrams in $Sr_xEu_{1-x}TiO_3$ nanowires and nanotubes, that include the paraelectric, ferroelectric, paramagnetic, ferromagnetic and antiferromagnetic phases. Nanosized $Sr_xEu_{1-x}TiO_3$ wires and tubes are the new multiferroics while bulk $EuTiO_3$ is antiferromagnetic at temperatures less than 5.5 K and paraelectric at all other temperatures.

Ferroelectric spontaneous polarization of about ~(0.1–0.5)C/m^2 is induced by the intrinsic surface stress present under the curved surface of the nanowire. Since the stress is inversely proportional to the nanoparticle radius, the spontaneous polarization exists for the radii less than (2–5) nm, for acceptable values of the surface stress coefficient ~ (10–30) N/m and temperatures lower than 300-400 K (see [1] for the case of pure $EuTiO_3$ nanowire).

Due to the strong magnetoelectric coupling, the spontaneous polarization in turn induces the ferromagnetic phase in $Sr_xEu_{1-x}TiO_3$ nanowires and nanotubes. Thus we predicted that prolate $Sr_xEu_{1-x}TiO_3$ nanoparticles becomes ferroelectric-ferromagnetic, i.e. multiferroic, which can be important for their potential applications. For application nanowires and nanotubes can win the competition with $EuTiO_3$ thin films, which become ferromagnetic only at $T < 4.24$ K.

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Optical monitoring of ferroelecric phase transitions in selected crystals and thin films in visible and ultraviolet spectral range

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In the present study, the dispersion dielectric function $\varepsilon_{1,2}(E)$ in the photon energy range of electronic excitations for lead germanate, $Pb_5Ge_3O_{11}$, strontium-barium niobate, $Sr_xBa_{1-x}Nb_2O_6$, single crystals at different values of the ratio x in the range of 0.40 – 0.75 and epitaxially grown thin films of $PbTiO_3$ on $SrTiO_3$ substrates have been measured. The temperature dependent spectral ellipsometry method using the synchrotron radiation in the spectral range 1.5 – 10 eV was applied. Range of temperatures used covered phase transition points of the materials studied. These results are supplemented also by the nonlinear optical and piezooptical studies of the crystals. Experimental dispersion of pseudodielectric functions for the crystals are discussed in comparison with analogous values obtained from the first principles calculations on the basis of the density functional theory.

Lead germanate, $Pb_5Ge_3O_{11}$, is a known crystal undergoing second order ferroelectric phase transition at 177°C and symmetry is changed from hexagonal to trigonal one at the cooling run. Single crystals of lead germanate and solid solutions on their basis have attracted considerable interest because of their reversible optical activity, application in pyroelectric detectors and lasing materials.

Strontium-barium niobate, $Sr_xBa_{1-x}Nb_2O_6$, is a well-known ferroelectric crystal considered as one of the very attractive material for practical applications. In particular, much attention is paid to its optical properties: electro-optic, photorefractive, and acousto-optic.

The ferroelectric materials with perovskite structures, such as $PbTiO_3$, are of the considerable interest for applications in electronics such as non-volatile memories, IR sensors and actuation devices due to their piezoelectric and dielectric properties.

Photorefractive properties of modified $Sn_2P_2S_6$ crystals

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Photorefractive effect, i.e. light-induced variation of the refractive index, is studied due to its many potential applications in the schemes of dynamic interferometry, image processing, wavefront corrections etc., and takes place in many ferroelectric crystals. From the other side, because this effect is connected with space-charge formation due to diffusion (or other) processes and is determined by electron traps in the crystals, its investigations provide information about the defect states.

The $Sn_2P_2S_6$ crystals are promising photorefractive materials for red and near infra-red spectral range with high amplitude parameters and fast enough response time, which possess perspectives of applications [1]. In the previous works [2-4] it was shown that an enhancement of these properties can be achieved by variation of the crystal growth technology and by goaled doping by various elements (Te, Sb, Bi, Ge, Se, Ag…).

In this communication the experimental data on the photorefractive parameters of the $Sn_2P_2S_6$ crystals, modified by goaled doping and post-growth treatment are presented. The basic photorefractive parameters are measured using conventional holographic technique, and the two-wave mixing gain Γ and the response time τ were determined. It was found that goaled doping can substantially modify the gain coefficients, and the time constants. Different dopants (Te, Bi) can also change the spectral range of the sensitivity in near infrared. Besides, the variation of the photorefractive parameters by the post-growth treatment (annealing in the various atmosphere) is also studied. Basing on the results of the dielectric and photorefractive measurements, the microscopic parameters responsible for photorefractive effect in these doped crystals are estimated.

Some photorefractive schemes realized on the base of the $Sn_2P_2S_6$:Te(Sb,Bi) crystals and their potential applications of are also discussed.

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Phase diagram of $Ba_2Nd_{(1-x)}Pr_{(x)}FeNb_4O_{15}$ solid solution

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Relaxors are very interesting materials but most of the time they are restricted to perovskite materials and thus their flexibility is limited. Here we present our results of dielectric and ultrasonic investigation of novel lead-free $Ba_2Pr_xNd_{1-x}FeNb_4O_{15}$ solid solutions with a more open (compared with perovskites) tetragonal tungsten bronze (TTB) structure. The TTB structure is based on interconnected octahedra, leaving three different channels of threefold, fourfold and fivefold pseudo-symmetry. Numerous cations can be hosted within these channels, thus enabling a wide range of new interesting compositions, which could possess ferroelectric, relaxor or even multiferroic properties [1]. Pure $Ba_2PrFeNb_4O_{15}$ shows relaxor response at low temperatures, while $Ba_2NdFeNb_4O_{15}$ is ferroelectric. On scanning the whole solid solution (x = 0, 0.2, 0.4, 0.5, 0.6, 0.8 and 1), we demonstrate here a continuous crossover between these end member behaviors with a coexistence of ferroelectricity and relaxor in the intermediate range. This allows for the coexistence of long range and short range orders and thus opens up the range of relaxor materials.

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Light propagation in photoinduced dynamic structures using ferroelectric crystals

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By the combination of an applied electric field and a properly spatially structured illumination, photoconducting ferroelectric crystals can be used to realize dynamically reconfigurable local refractive index structures. The latter can take the form of waveguides where light is confined in one or two dimensions, arrays of waveguides, or other more complex structures. We discuss the formation mechanism of the photoinduced structures as well as the peculiar light propagation properties in specific structures that bear analogies with discrete physical systems.

The size effect in ferroelectrics embedded into the porous glasses matrices

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Ferroelectric materials are used as infrared detectors, piezoelectric sensors and transducers, components of photonic and optoelectronic circuits and non-volatile memory. Miniaturization of such devices raises questions about the impact of particle size on their physical properties and phase transitions. For these reasons the study of the size effects on ferroelectric particles is very interesting problem and is the subject of investigations in many research and development centers. One method of obtaining nanometer-sized ferroelectrics is their incorporation in various types of porous matrices.

We present the results of experimental investigations of physical properties of several of different types ferroelectrics embedded in porous glass matrix with different average pore sizes. The impact of stresses arising between matrix and nanocrystals, size effect associated with the polarization of the surface layer, and dielectric relaxation resulting from the interaction between the glasses matrix and embedded nanocrystals are discussed.

The most interesting result of our investigations is non-monotonic dependence of the phase transition temperature on the average pores size in KDP crystals embedded into the porous glasses (Fig. 1.). This type of dependence has been provided by the phenomenological theories [1], [2], [3], [4], but so far it was lacking experimental confirmation.

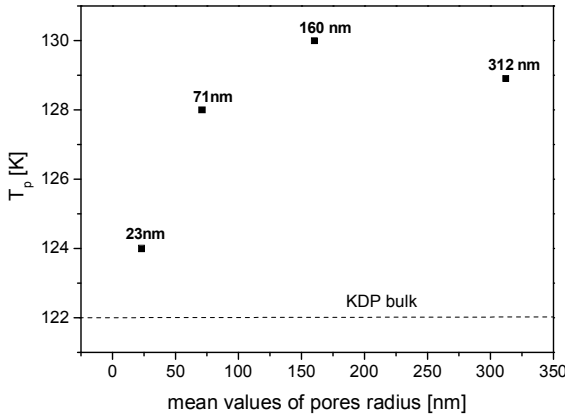

Fig.1. The phase transition temperature of KDP embedded into the porous glasses as a function of the mean value of pores radius.

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Graphene on ferroelectric substrate: physical properties and applications

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Graphene-on-ferroelectric system has several unique features. Among them are: the possibility to obtain the high ~ 10^{12} cm^{-2} concentrations for the moderate (of 1V order) gate voltages, and the existence of hysteresis (or antihysteresis) in the dependence of the resistance of graphene channel on the gate voltage. The use of ferroelectric substrates for graphene had enabled the construction of the robust elements of non-volatile memory of new generation. These elements works for more than 10^5 switches and preserve information for more than 1000 s. Such systems can be characterized theoretically by the ultrafast rate of switching (~ 10-100 fs).

A quantitative model is proposed to explain the anti-hysteresis behavior in graphene on $Pb(Zr_xTi_{1-x})O_3$ ferroelectric substrate resistance on gate voltage sweep [1]. The model takes into consideration a screening of electric field in the substrate by electrons, captured by the states, connected with graphene-ferroelectric interface, and it explains experimental data obtained previously. The estimations being made can be useful in fabrication of non-volatile memory of new generation, based on the bi-stable system, where logical "0" corresponds one value of graphene's resistance, and "1" – the other.

It was also demonstrated theoretically, that the effective, fast and small modulators of the middle- and near-IR radiation for different optoelectronic applications can be constructed on the base of graphene on the $Pb(Zr_xTi_{1-x})O_3$ ferroelectric substrate [2]. The depth of modulation for 5 layer graphene for the range of gate voltages, where thin PZT epitaxial film behaves as high-κ dielectric, can be of 10% order.

A model for hysteresis behavior in reflectivity *R* of the system "graphene - $Pb(Zr_xTi_{1-x})O_3$ (PZT) ferroelectric substrate – gate" with gate voltage variation including electrons trapping on graphene-PZT interface states was analyzed in [3]. It was demonstrated, that this hysteresis in *R* can be observed experimentally for the telecommunication range radiation $\lambda = 1.55$ μm at low gate voltages, and can be used for a creation of a fast bi-stable system for the new non-volatile memory devices with on-chip optical interconnection.

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Phase transitions in H-bonded molecular networks

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The properties of cooperativity, selectivity and directionality make the H-bonds extremely useful assembling element of ordered supramolecular structures (OSS). Modeling of phase transitions between OSS is a difficult problem due to (i) large size of molecules and long intermolecular distances, (ii) complicated interaction mechanisms of large molecules, (iii) subtle balance between short-range and long-range interactions, etc. Nevertheless, certain statistical models used to describe ordering schemes in liquid crystals, polymers, proteins or colloid particles might be successfully transferred for description of OSS ordering. These models are more complicated versions of the 2- or q>2-state models. In these models the molecules are represented by rather simple geometrical shapes and orientations on a lattice and governed by defined interaction rules. Simulations of these models allow to predict the phase diagrams and growth dynamics of different OSS.

Here we present several examples of such models and results of their simulation by Monte Carlo method. In particular, we discuss (i) 3-state model for ordering of triangular molecules into honeycomb and some other phases on Au(111); (ii) 4-state model explaining ordering of elongated molecules of antraquinone in a pin-wheel honeycomb structure on Cu(111) and (iii) “random tiling model” representing the example of a glass structure in H-bonded molecular systems.

Electric properties and relaxation phenomena in $Li_2Ge_7O_{15}$ single crystal

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We report the results of investigations of electric properties and relaxation processes occurring in AC and DC electric field in pure and doped with Cr, Mn $Li_2Ge_7O_{15}$ crystals [1-3]. Measurements of temperature- frequency dependencies of dielectric permittivity ε and conductivity σ are supplemented by EPR spectroscopy of Cr, Mn impurity ions.

It has been shown, that above 500 K conductivity of $Li_2Ge_7O_{15}$ measured in AC field becomes strongly anisotropic and sufficiently depends on small amount of Cr, Mn dopants. The experimental data show that σ is highest along the structural channels in which regular Li ions are located. Accounting the EPR data on microstructure of Cr, Mn centers, it has been concluded that conductivity is determined by motion of interstitial Li ions (A_{Li}). Temperature growth of $\sigma(T)$ above 500 K is attributed to thermal activation of A_{Li} mobility.

In DC field an exponential decay of σ with time has been detected. Kinetic dependences $\sigma(t)$ are interpreted as the result of compensation of drift by diffuse current. The diffusion coefficient D is estimated in the temperature interval 500÷700 K. The spectra of complex impedance ρ^* are measured and described within equivalent circuit approach that gives evidence for hopping conductance of A_{Li} and space charge accumulation near to blocking Ag and Pt electrodes.

In whole, the results of dielectric, impedance and EPR spectroscopy allow to reveal the microscopic mechanisms of the polarization and charge transfer phenomena in lithium heptagermanate crystal. It has been demonstrated that relaxation phenomena in nominally pure and doped $Li_2Ge_7O_{15}$ crystals are determined by the processes of various nature: - thermally activated re- orientations of the dipole moments of Cr^{3+}-Li^+ pair centers; - migration mobility of interstitial A_{Li} through the channels formed by Ge-O framework of the crystal lattice; - accumulation of A_{Li} charge carriers near to blocking electrodes.

The experimental data evidence that structural matrix of lithium germanates is appropriate to design the crystalline materials with high ionic conductivity. Introducing of heterovalent impurities allows to control electric conductivity of $Li_2Ge_7O_{15}$ in a wide range.

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Lifshitz point and tricriticality on phase diagram of $Sn_2P_2(Se_xS_{1-x})_6$ ferroelectrics

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Recently by a high-resolution ac photopyroelectric technique have been evaluated [1], that for the $Sn_2P_2(Se_xS_{1-x})_6$ mixed crystals with Se doping the ferroelectric transition change from second order character to first order while passing the Lifshitz point ($x_{LP} \approx 0.28$), as well as the splitting of the transition with intermediate incommensurate phase at high Se concentrations was determined. The critical behavior of the ferroelectric transition in terms of the different universality classes and their underlying physical dominant effects (tricriticality, long-range dipole interactions, Lifshitz point) in the very close vicinity of the critical temperature has been discussed. It was found that for Se concentrations around the Lifshitz point, long-range dipole interactions do not play a significant role and that the critical exponents are close to those predicted for the Lifshitz point universality class.

The interaction between soft optic and acoustic phonons was investigated for x = 0.28 mixed crystals by Brillouin-scattering and ultrasonic pulse-echo techniques [2]. The elastic softening of hypersound velocity of transverse-acoustic phonons and for both longitudinal and transverse ultrasound waves which propagate near direction of the modulation wave vector in the incommensurate phase at $x > x_{LP}$ was found at cooling to the Lifshitz point in the paraelectric phase. The strong increase in the ultrasound attenuation has also been observed. Such phenomena are related to the linear interaction of the soft optic and acoustic branches in the region of relatively short-range hypersound waves and to the strongly developed long-range order-parameter fluctuations in the ultrasound frequency range.

For $Sn_2P_2S_6$ ferroelectrics with three-well local potential [3,4] under hydrostatic compression the second order phase transition approaches tricritical point, as expected according to Blume-Emery-Griffiths (BEG) model. Joint consideration of BEG model and ANNNI model allows to draw conclusion about possibility of tricritical point presence on temperature - pressure diagram of $Sn_2P_2S_6$ without incommensurate phase appearing. Investigations of temperature dependences of longitudinal ultrasound velocity at different pressures for $Sn_2P_2S_6$ crystals confirm such conclusion [5].

The dielectric susceptibility and acoustic properties investigations with high temperature resolution were performed for the $Sn_2P_2(Se_xS_{1-x})_6$ crystals with different electric conductivity, that was varied by introducing of tin addition amount at the monocrystals vapor transport growing. Possible role of the partial screening of the dipole - dipole interaction by charge carriers in the studied ferroelectrics-semiconductors is discussed.

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ORAL REPORTS

Ferroelectric flat panel display: a new modern applications of ferroelectric thin films

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Under the influence of external electric field the bound electric charge can be generated at a surface of any dielectric sample. For spontaneously polarized ferroelectric sample, the density of this surface charge can attain magnitude of $\sigma \leq 2P_s$, where P_s is the spontaneous electric polarization; the depolarizing electric field related to this charge density can be high as $10^6 - 10^8$ V/cm. This field is strong enough to produce electron emission from a charged surface of ferroelectric sample; under the field of 10^8 V/cm the ionization processes occurring at this surface are initiated.

Electron emission from ferroelectrics, excited by an external electric field, is known since eighties. The first experimental results concerning low density (below 10^{-7} A/cm^2) electron emission were reported for $PbGe_5O_{11}$ and TGS single crystals. Electron emission with current density exceeding a few A/cm^2 was produced on PLZT ceramic sample by a short (10^{-7} s) HV pulse. Later, many research groups at laboratories all over the world have investigated these high density electron emission phenomena because of their potential applications in different areas of technology, for example in vacuum electronics as a new type of cold cathode. For these purposes many kinds of perovskite oxide-based ceramic samples with selected compo-sition and phase sequences were examined under different experimental conditions.

In a presented talk a new area of applications of electron emission from ferroelectrics for design of FEED (Field Effect Ferroelectric Electron Emitter Device) Flat Panel Display and FEED Flat Lamp are presented and discussed.

Photoinduced phenomena in the doped $Bi_{12}SiO_{20}$ crystals

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The sillenite crystals $Bi_{12}MO_{20}$ (with M = Si, Ge, Ti and other) are known as photorefractive materials of a high photosensitivity (~ 10^{-6}J ·cm^{-2}). Those work successful as functional media in different types of light-modulating and other devices of solid-state electronics and in holographic systems of optical information record and storage. So, the study of photoinduced phenomena and their modification by doping is very important in these applications.

Nominally pure and doped BSO crystals have been grown by Czochralski method. Doping agents were introduced in mixture as oxides. Content of the additive in crystals was from 0.02 to 0.1 mass %.

We have obtained spectral, kinetic and temperature characteristics of photochromic effect, light-induced photoconductivity and photoluminescence at T = 4.2, 15, 80, 300 K.

It was established that mechanisms of the photochromic effect, light-induced photoconductivity and photoluminescence are significantly different. The photochromic effect and photoluminescence are determined by intracenter transitions in deep centers in form of doping Al, Ga, Sn, Mo, Fe ions replacing Si ions in oxygen tetrahedrons or Mn, Cr, V, Cu, Ag ions replacing Bi ions in deformed oxygen octahedrons. The light-induced photoconductivity is determined by filling - emptying of shallow levels, forming tails of density of states near the edges of conduction band and valence band. We have obtained schemas of the photoinduced change of charge in deep centers: Al, Ga, Sn, Mn, Cr, Fe, V, Mo, Cu, and Ag. The pattern of the photoinduced charge redistribution was determined: $Al^{3+}\rightarrow Al^{4+}$, $Ga^{3+}\rightarrow Ga^{4+}$, $Sn^{3+}\rightarrow Sn^{4+}$, $Cr^{2+}\rightarrow Cr^{3+}$, $Mn^{4+}\rightarrow Mn^{3+}$, $V^{2+}\rightarrow V^{3+}$, $Fe^{2+}\rightarrow Fe^{3+}$, $Cu^{3+}\rightarrow Cu^{2+}$, $Ag^{+}\rightarrow Ag^{2+}$, $Mo^{5+}\rightarrow Mo^{4+}$.

It was shown that zonal transport of photocarriers at the condition of quick and slow (depending of the additive type) recombination is a general trait of photochromic effect and light-induced photoconductivity. We have revealed unnormal oscillating dependencies of low-temperature (80K) light-induced photoconductivity kinetics in BSO:Al and BSO:Ga crystals, big Stokes shift of luminescence spectrums. It was found that photoinduced effects accompanies strong electron-photon interaction.

Multiferroic behaviour of $CuMP_2(S,Se)_6$ type crystals

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$CuInP_2S_6$, $CuCrP_2S_6$ and $CuBiP_2Se_6$ crystallizes in a layered two-dimensional structure of $CuMP_2(S,Se)_6$ type. The structure is formed by double sheets of sulfur (or selenium) atoms sandwiching the metal cations and P–P groups which occupy the octahedral voids defined by the sulfur (or selenium) atoms. In these crystals depending from metal in M position are observed many types of feroic behaviour: ferrielectric phase transition ($CuInP_2S_6$), antiferroelectric ($CuCrP_2S_6$ and $CuBiP_2Se_6$), antiferomagnetic ($CuCrP_2S_6$) and many others. In this contribution we summarize the last results obtained in our laboratory on broadband dielectric investigations of these crystals. We demonstrate that ferrielectric phase transition in $CuInP_2S_6$ and antiferrielectric phase transition in $CuBiP_2Se_6$ follows necessarily with dipolar glass freezing at low temperatures. The coupling between antiferomagnetic and antiferroelectric properties was found in mixed $Cu(In_xCr_{1-x})P_2S_6$ crystals below pecolation threshold [1]. By further increasing of indium concentration dipolar glass phase appears in $Cu(In_xCr_{1-x})P_2S_6$. The phase transitions in other $CuMP_2(S,Se)_6$ type crystals also will be discussed in this contribution.

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Rochelle salt in an electric field not parallel to the ferroelectric axis

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Dielectric properties of the Rochelle salt crystal exposed to external electric fields parallel or not parallel to the ferroelectric a axis have been investigated in several papers [1-8]. In the prolonged transverse electric field a gradual disappearance of the hysteresis loop has been observed experimentally in the ferroelectric phase situated between two paraelectric ones. A mathematical formula for gradual decay in time of the remanent polarization P_r has been proposed [6]. The lack of the remanent polarization or its noticeable reduction, accompanied by a relatively small coercive field change, as well as quite new temperature dependences of the reduced remanent polarization can be observed even after the non-parallel field has ceased to be applied. The original properties can be easily restored, however, by annealing the crystal above the critical temperature. This phenomenon, observed also in the triglycine sulphate (TGS) and triglycine selenate (TGSe) ferroelectrics - called transverse field effect - is particularly interesting in the Rochelle salt where there exists the lower paraelectric phase. Although a similar polarization reduction in the transverse electric field has been obtained theoretically in the Rochelle salt [5,7], there is no information in the literature, to our knowledge, about the permanence of the effect. On the other hand, as follows from [9], a permanent but irreversible decrease in P_r not accompanied by any changes in the coercive field could be possibly observed under high pressure.

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Fundamental studies of ferroelastics ($Cs_3Bi_2I_9$): new physical phenomena

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Ferroelastics is a peculiar new class of crystalline solids in which the spontaneous strain of a crystal lattice is appeared relatively of initial one as a consequence of structure phase transition from more symmetrical (paraelastic) phase into less symmetrical (ferroelastic) phase. One of ferroelastics is the $Cs_3Bi_2I_9$ layered semiconductor having high anisotropy of chemical bonding: a strong ion-covalent bonding in the separate layer sandwich and a weak Van der Waals interaction between the neighbouring sandwiches.

The review report deals with the experimental and theoretical studies of new phenomena registered. The following problems were solved towards this purpose:

- A nontraditional for the layered substances temperature shift of the fundamental absorption edge Eg(T) of $Cs_3Bi_2I_9$ was found. It is shown that this shift is described very well by the Varshni formula.
- The transition region from 150 to 220 K was registered. It is shown that this region may be identified as the heterophase structure region where ferroelastic and paraelastic phases coexist.
- A change of exciton-phonon interaction from a weak to strong as temperature increases was found. The effect is explained on the basis of a model which takes into account the reconstruction of the crystal lattice from non-layered to layered one.
- The temperature value T* =150 K may be considered as characteristic one below of which the crystal loses the nature of layered substance.
- Raman spectra of $Cs_3Bi_2I_9$ were studied in heating regime over temperature range 5-300 K but any soft mode or softening of modes were not observed. The interpretation of Raman spectra is given.
- The structure phase transition in $Cs_3Bi_2I_9$ at T_c = 220 K was registered. It is shown that this transition is the first order transition which is close to the second order one.
- A new giant thermodynamical optical effect near the ferroelastic phase transition point was found and explained on the base of Landau-Khalatnikov theory.

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A low density plasma-assisted electron and ion emission from TGS crystals (a short review)

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An electron and ion emission accompanying non-thermal plasma processes, initiated at the surface of pure and doped TGS single crystals by a drive ac electric field (500 Hz) not exceeding 10^4 V/cm have been investigated by means of time and energy distribution measurements. From the obtained data it follows that the emission process is influenced by properties of studied material, its temperature and amplitude of the used electric field.

Taking these findings [1-4] into account we suggest that pure and doped TGS crystals can operate as a simple pulsed source of electrons and ions (cold cathode) and would be of use for design of different kinds of plasma-based devices operating with high-*k* ferroelectric (dielectric)-based materials.

The examples of the time and energy distributions are displayed in Fig. 1.

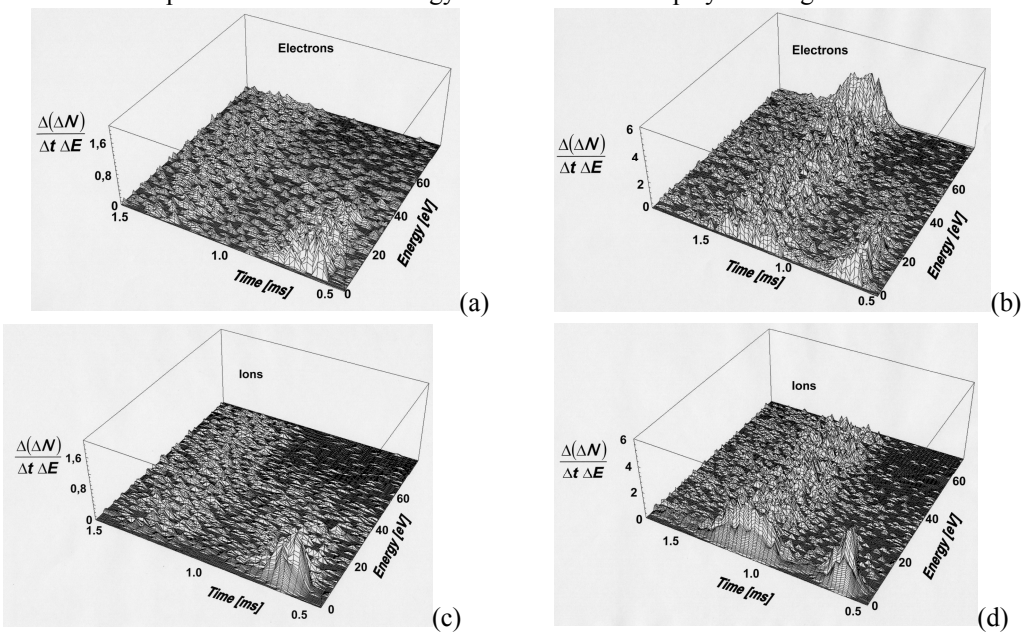

Fig. 1. Time and energy distributions of electrons and ions emitted from the pure TGS crystal sample taken for amplitudes of the driving field $1.55 \cdot 10^3$ V/cm (a, c) and $1.83 \cdot 10^3$ V/cm (b, d), frequency of electric field 500 Hz, temperature of the sample 298 K.

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Coexistence of dipole glass State with ferroelectric or antiferroelectric phases in the mixed ferro-antiferroelectric systems

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It is well known that at low temperatures in the spontaneously ordered materials with compete interactions between particles the specific states of matter take place. Such state are usually named spin glass (for ferromagnetic), or dipole glass (for ferroelectric) ones. In the above mention materials at relatively low temperatures and for intermediate concentration due to the system frustration long range ordering disappears and only short range correlations between nearest particles remains. Among different compounds in which the dipole glass state is observed the ferro-antiferroelectric solid mixtures with hydrogen bonds of $Rb_n(NH_4)_{1-n}H_2AsO_4$ type are present [1,2]. The problem of microscopic origin of dipole glass state, the conditions for existence pure ferroelectric and antiferroelecrtic phases both the coexistence mixed dipole glass state and long ordered phases are now intensively studied.

In the present lecture we will demonstrate a microscopic approach for dipole glass parameter determination in the wide regions of temperature and concentration. The approach is based on the using of single and pair correlation functions of nearest neighbours. The two-particle cluster approximation and the replica method [3,4] for the free energy of investigated system calculation has been exploited. The central point of the presentation are the correct phase diagram of mixed system and the dipole glass parameter behaviour versus temperature or concentration, both the coexistence of dipole glass state with ordered phases [5]. The problem of a precursors of the dipole glass state area, where a “slight” dipole glass phase properties of the system appears, will be discussed too.

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The influence of the weak optical activity on a optical properties of polar crystals

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It is well known that the optical activity is purely associated with the symmetric part of the gyration tensor. Antisymmetric part of the gyration tensor describes a so-called weak optical activity. Only a few reports of the latter phenomenon may be found in the literature.

We tried to descript the weak optical activity in crystals and to analyze the manifestations of this phenomenon. It was found that the weak optical activity should manifest itself in changing of the refractive indices and optical birefringence of a medium. Increments of both the refractive indices and the birefringence which appear due to the weak optical activity are quite small and depend on the signs of neither the optical activity vector nor the light wave vector. Assuming that the antisymmetric part of the gyration tensor is of the same order of magnitude as the symmetric one ($\sim 10^{-5}$ in common cases), we arrive that the birefringence increment should be of the order of 10^{-7}. The ellipticity of the eigen extraordinary wave in this case should also be very small ($\sim 10^{-7}$). Also we analyze the behavior of the refractive indices and the ellipticity of eigen waves under the conditions of coexisting gyration and weak optical activity. Quantitative relations describing the appropriate parameters are derived. It was shown that the ellipticities of eigen waves become different and one of that waves acquires a complicated (longitudinally-transverse) elliptical polarization state. This represents a new type of electromagnetic eigen waves in crystals. Since this difference appears owing to the presence of the weak optical activity, one can suggest a purely polarimetric technique for revealing this phenomenon.

We have obtained phenomenological relation for the Poynting vector of electromagnetic wave propagating in crystals that possess a so-called weak optical activity. It has been revealed that the Poynting vector has some transverse component that describes transverse shift of the optical beam. Such a beam drift could be explained following from the quantum properties of photon. The carried out analysis of electromagnetic wave polarization after passing through a crystal with a weak optical activity allow propose possible configuration of the experiment for the experimental detection of this effect.

The methods for piezooptic effect studies on the basis of 2D stress distribution

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The piezooptic coefficients π_{qm} are usually measured with significant errors, which often exceed tens of per cent [1]. The main cause of high measurement errors for the piezooptic coefficients is due to inhomogeneous 3D distribution of stress components taking place, instead of a homogeneous stress state usually assumed by an idealised model for uniaxially pressed parallelepiped-shape samples [1]. As a result, the values obtained experimentally for the piezooptic coefficients differ from their true values. It is evident that a real 3D stress distribution in samples depends strongly on the loading conditions and, moreover, the worst still is that these conditions differ from one experiment to another or from laboratory to laboratory.

A possible alternative to the approach described above is suggested by the loading methods that induce inhomogeneous though a priori known 2D stress distributions in samples. A well-known four-point bending of a bar [2], diametrically-stressed disk methods [3] and torsion method [4] are among them. In this work we describe these methods combined with digital imaging laser interferometry and polarimetry for determination of the piezooptic coefficients. It is shown that with using of these methods the error of determination of piezooptic coefficients is reduced to few percents.

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Critical behaviour of mixed $Cs_x(NH_4)_{1-x}LiSO_4$ crystals

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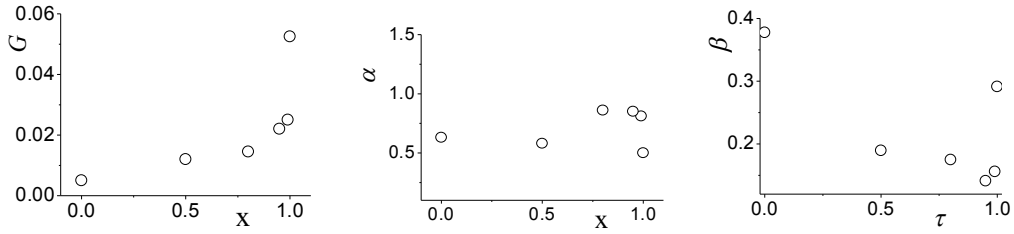
$A_1A_2BX_4$ compounds (with A_1 and A_2 being monovalent ions) represent one of modelling objects widely studied in ferroic physics (see, e.g., [1]). Among these, NH_4LiSO_4 reveals a rich sequence of phase transitions (PTs), including a ferroelectric one at ~ 460 K (the point symmetry change $mmm \rightarrow mm2$), while $CsLiSO_4$ shows a ferroelastic PT at ~ 200 K ($mmm \rightarrow 2/m$). It is known [2] that pronounced critical effects are seen in the optical birefringence of the mixed crystals $Cs_x(NH_4)_{1-x}LiSO_4$. Moreover, doping of pure $CsLiSO_4$ with a small amount of NH_4 (1% or less) leads to notable changes in the shape and magnitude of pre-transitional birefringence anomalies [2]. However, quantitative features of this behaviour have not yet been reported. The aim of this work is to process and interpret quantitatively the experimental data [2] for different concentrations x, using the phenomenological approach developed in the work [3].

Basing on temperature dependences of the birefringence derivatives, we have obtained the Ginzburg number G that governs the width of the critical region, as well as the critical indices and of the order parameter (β) and the heat capacity (α). Some of the results are shown in Fig. 1.



a) b) c)

Fig. 1. Concentration dependences of parameters G (a), α (b) and β (c) derived basing on our analysis of the birefringence in $Cs_x(NH_4)_{1-x}LiSO_4$ crystals.

One can see that small changes in x in the close vicinity of x = 1 have indeed drastic effect on all the parameters under analysis. In general, the increase observed for the Ginzburg number with increasing x is readily understood as being due to passing from the ferroelectric PT (at small x) to the ferroelastic one (at x ~ 1). Moreover, a substantial part of G should be ascribed to the effect of structural imperfections. Although some of our data on the critical index β are close to those reported by the authors [2] themselves, essential discrepancies also take place, which have become a subject of thorough consideration. Issuing from the both α and β values obtained (see Fig. 1), we conclude that the PTs for all the concentrations x are close to the tricritical point.

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Aging effect in $K_{1-x}Li_xTaO_3$ crystals

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We will present aging effect and low temperatures properties in quantum paraelectric potassium tantalate $K_{1-x}Li_xTaO_3$ crystals with x=0.0018 and 0.0035 (the nominal concentration in the melt x=0.005 and 0.010) investigated via temporal and temperature dependences of the dielectric response at low temperatures down to 1.7K. The substitution of K^+ ions by off-center Li^+ in $KTaO_3$ is considered as the source of induced polar clusters of short range order at low temperatures for $K_{1-x}Li_xTaO_3$ crystals [1-3]. The measurements were performed in the range of frequency of the *ac* electric field from 100 Hz to 2 MHz by Agilent E4980A Precision LCR Meter.

The isothermal evolution of the linear susceptibility satisfactorily follows a stretched exponential law [4-6]:

$$\chi(t) = \chi_\infty + \Delta\chi \exp\left\{-(t/\tau)^\beta\right\}$$

After aging samples at 4.2K the low temperature susceptibility $\chi(T,\nu)$ down to 1.7 K were investigated.

Acknowledgments

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Resistive switching in $BiFeO_3$ single crystal

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Recently, multinary oxide materials with perovskite structure have attracted much attention due to their ability to provide switching of the electrical resistance between insulating and metallic behavior by the application of an external electric field [1-3]. We found $BiFeO_3$ (BFO) single crystal to be very promising candidate for terabit memory devices.

A JEOL JSPM-4210A AFM setup equipped with Pt/Ir coated silicon tip operating in contact mode was used to obtain simultaneously the topographical and DC conductivity maps of the sample investigated. The reversal in the direction of the current flow was observed with the sign of electric field. The similarity to other transition metal oxides points to the responsibility of oxygen vacancies migration for the conductivity.

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Linear and non-linear dielectric response of sodium-bismuth titanate

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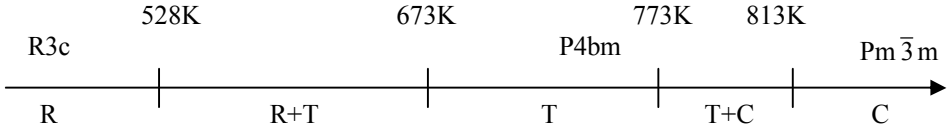
Sodium-bismuth titanate $Na_{0.5}Bi_{0.5}TiO_3$ (NBT) belongs to a lead-free perovskite materials [1]. NBT displays the following sequence of phases transitions [2]:



where: R - rhombohedral phase, T - tetragonal phase and C-cubic phase. R+T and T+C denote temperature regions of coexistence of the particular phases. Changes of symmetry of NBT result in changes of polar state of this material. Below 475 K a ferroelectric state exists. However, detection of the ferroelectric phase transition via measurement of a linear dielectric susceptibility is very difficult. On the other hand nonlinear dielectric susceptibilities are very sensitive tools for detection of the phase transitions and probing the resulting polar states of the investigated material.

The aim of this work is measurement [3] and analysis of the linear, χ_1 and the nonlinear dielectric susceptibilities, χ_2 and χ_3, defined by the following relationship between polarization of the sample, P, and an electric field, E, [4]:

$$P(E) = \varepsilon_0 \left(\chi_1 E + \chi_2 E^2 + \chi_3 E^3 + ... \right).$$

Both nonlinear susceptibilities clearly mark ferroelectric phase transition.

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Chemical capacitance proposed for manganite-based ceramics

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The measured value of effective electric permittivity ε_{eff} of several compounds, e.g. $(BiNa)(MnNb)O_3$ [1,2], $(BiPb)(MnNb)O_3$ [3], and $BiMnO_3$ increases from a value ~10-100 at the low temperature range (100-200 K) up to the high value reaching value 10^{-5} at high temperature range (e.g. 500-700 K). This feature relates to the semiconductor behaviour of the electric conduction. The reported activation energy values varies within ~0.2-1.0 eV Such features suggest the manifestation of the thermally activated space charge carriers, that influence the measured capacitance. The measured high-value effective permittivity of the several manganite compounds can be ascribed to the chemical capacitance expressed in terms of the chemical potential $C_\mu = e^2 \partial N_i/\partial\mu$. When the conduction electrons with density $n_{cb} = N_{cb} \exp(\mu_n - E_{cb})/k_BT$ are considered, the chemical capacitance $C_\mu^{(cb)} = e^2 n_{cb}/k_BT$ depends markedly on temperature. Hence, the experimental results obtained for the manganite compounds are discussed in framework of this model [4, 5, 6].

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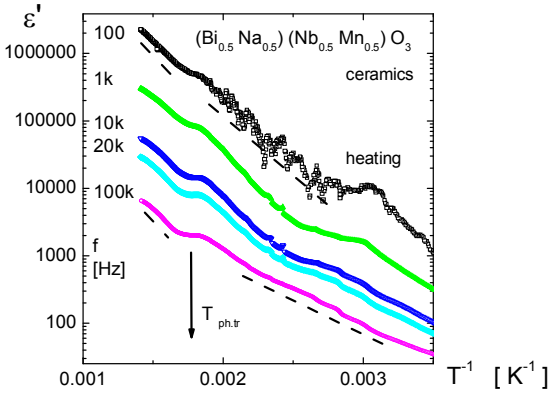

The effective electric permittivity *vs.* reciprocal temperature obtained for $(Bi_{0.5}Na_{0.5})(Mn_{0.5}Nb_{0.5})O_3$ ceramics.

Acoustic wave velocities and elastic properties of $Sn_2P_2S_6$, $Sn_2P_2(Se_{0.28}S_{0.72})_6$ and $Pb_2P_2S_6$ crystals

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The present report is devoted to experimental study and analysis of the acoustic properties of $Sn_2P_2(Se_{0.28}S_{0.72})_6$, $Sn_2P_2S_6$ crystals at ferroelectric phase transition. On the basis of experimentally obtained temperature dependencies of velocities of transverse and longitudinal acoustic waves the temperature dependencies of all components of elastic stiffness tensor were obtained. The temperature behavior of elastic stiffness coefficients have been analyzed with using of Landau-Khalatnikov approach. The acoustic slowness surfaces were obtained and analyzed from point of view of searching of the slowest acoustic wave. The results of study of the acoustic properties of $Pb_2P_2S_6$ crystals are also presented.

Critical behavior of a one-component order parameter in an external field

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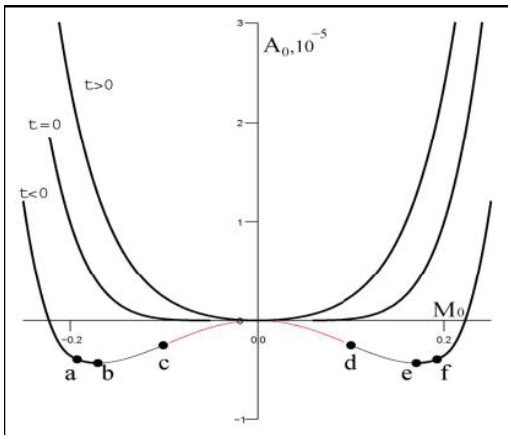
Basic principles of phenomenological theory for second order phase transitions (PT) were formulated by Landau in late 30-40s. The key assumption of the theory is that near the critical point the free energy can be expanded in a power series in the order parameter, the equilibrium value of which is found to obey the minimum condition for free energy. As is now known, this expansion is well defined in the neighborhood of Tc except for a narrow interval determined by the Ginzburg criterion. The above mentioned expansion is often called Landau's free energy. It turns out that similar quantity can also be derived (not constructed) in a theory considering PT at microscopic level. In the collective variables (CV) method proposed in [1] to describe the criticality of spin systems such a quantity appears in a natural way.



In the present work we extend results obtained earlier by the CV method for physical characteristics of 3D Ising-like model to the presence of an external field and look at what is going on when the field changes sign. As a result, we obtain the Gibbs free energy, Helmholtz free energy (see Figure), and the order parameter and establish the regions of stability, metastability, and unstability on the order parameter – temperature plane for the system under investigation. In addition, the way of implementation of the well-known Maxwell construction is proposed [2] at microscopic level.

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Crystals with an alkylammonium cation – a new class of multiferroic compaunds

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The crystalline ferroics with an alkylammonium cation possess series of interesting properties and are actively studied using different experimental methods. First of all, they are characterized by the complex sequences of phase transitions that are accompanied by different kinds of structural transformations connected with dynamics of organic cations and inorganic anions. For the technical applications it is important that those materials often posses magnetic ordering and electric polarization. This implies manifestations of so-called cross-effects, for example, change of the electric polarization under applied magnetic field or change of magnetization under applied electric field. Those effects have an unique application potential for the magnetoelectric memory cells and for the electric field controlled magnetic sensors etc.

Ethylammonium copper chloride, $(C_2H_5NH_3)_2CuCl_4$, belongs to the family of layered perovskite-type compounds. Being 2D Heisenberg ferromagnet with s=1/2 below T_c =10.2 K and ferroelectric below 247 K this crystal becomes a member of the rare class of magnetic multiferroic compounds with dominating ferromagnetic interactions in which electric polarization is not induced by magnetic spin reorientation but ferroelectric and magnetic order is formed independently.

For $[N(C_2H_5)_4]_2CoClBr_3$ crystal a clear magnetodielectric interaction which consists in substantial influence of the magnetic field on the dielectric permittivity near the ferroelectric phase transition was revealed.

Considering the abundance of compounds with general formula $(C_nH_{2n+1}NH_3)_2MX_4$, where M is a divalent metal, e.g., Mn^{2+}, Cd^{2+}, Fe^{2+}, Cu^{2+} and X is a halogen, the present results warrants screening other similar magnetic materials where electric order induced by hydrogen bonding can coexist with (ferro) magnetic phases and help to enrich the rare family of room-temperature multiferroics.

Unified lattice dynamics model for hydrogen-bonded crystals

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Contribution presents a semi-phenomenological atomistic model applicable for the lattice dynamics simulation of the hydrogen-bonded dielectric crystals. The model potential function takes into account the long-range Coulomb, short-range Born-Mayer-type, covalentl and hydrogen-bonded interatomic interactions. The lattice dynamics of CsH_2PO_4, CsD_2PO_4, RbD_2PO_4, $PbHPO_4$, $PbDPO_4$, TlH_2PO_4 and TlD_2PO_4 crystals was simulated in different structural phases based on this atomistic model. The wide set of the lattice dynamical characteristics, namely phonon frequencies in Brillouin zone centre, phonon dispersion relations, density of phonon states, partial density of states, dispersion of atomic mean-square displacements and structure factors were simulated in various phases of these compounds. The good agreement between the calculated and experimental data reveals the reliability of the current simulation.

The peculiarities of the structural phase transitions occurred in the crystals being under investigation were revealed. It was established that the ferroelectric phase transitions in RbD_2PO_4 and $PbHPO_4$ crystals are caused by the proton-phonon and phonon-phonon interactions. The internal bending mode of PO_4 tetrahedral groups may be treated as the probable candidate evoking the appearance of spontaneous polarisation in $PbHPO_4$. According to our simulation, the ferroelastic phase transition in TlH_2PO_4 occurs due to the interaction between the soft B_{3g} optic and B_{1u} acoustic mode. The hydrogen H_1 atoms placed on the shorter hydrogen bonds play the key role in the ferroelastic phase transition in TlH_2PO_4, whereas the D_2 atoms located on the longer hydrogen bonds exert the main effect on the antiferroelectric phase transition in TlD_2PO_4.

Investigations of phase transitions in $[(CH_3)_2CHNH_3]_4Cd_3Cl_{10}$ crystal

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Phase transitions of tera(isopropylamine)decachlorotricadmate (II) $[(CH_3)_2CHNH_3]_4Cd_3Cl_{10}$ crystal have been investigated by thermal and infrared measurements. Differential scanning calorimetry showed the sequence of phase transitions and symmetry of particular phases at 355 K, 294 K and 260 K. This results was confirmed and is similar to those obtained during thermal expansion and dielectric investigations. The infrared spectra of powdered $[(CH_3)_2CHNH_3]_4Cd_3Cl_{10}$ crystal in KBr were studied in the wide temperature range between 11 K and 388 K. The temperature changes of wavenumber, half – width, center of gravity and intensity of the bands were analyzed to clarify cationic and anionic dynamics contribution to the phase transitions mechanism. The results obtained from DSC and infrared measurements showed additional phase transition at 120 K.

Exotic domain walls in $BaTiO_3$

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Recently, the investigation of different types of domain walls in ferroelectric $BaTiO_3$ has been done within the Ginzburg-Landau-Devonshire phenomenological model [1]. In the framework of this model the existence of Bloch walls was predicted in orthorhombic and rhombohedral $BaTiO_3$. Later we have analysed the Bloch walls in rhombohedral phase by phase-field simulations [2].

This work continues the studying of "exotic" domain walls in low-symmetry phases of barium titanate using the phase-field simulation method. In particular, we shall report about the properties of chiral domain walls and walls with non-crystallographic orientation (S-walls).

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Thermodynamics and relaxation properties of $Rb_{1-x}(NH_4)_xH_2PO_4$ type mixed crystals. Problems and outlook.

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We propose a pseudospin model for the $Rb_{1-x}(NH_4)_xH_2PO_4$ ($Rb_{1-x}(ND_4)_xD_2PO_4$) type mixed crystals, which takes into account the energy levels of protons (deuterons) around a PO_4 group with random parameters, random long-range interaction, random local deformational field and piezoelectric coupling.

We explore the temperature dependences of heat capacity, local polarization of hydrogen bonds, Edwards-Anderson parameter, as well as of the real and imaginary parts of longitudinal and transverse dielectric permittivities in a wide range of sample compositions $x=[0,1]$ for the $Rb_{1-x}(ND_4)_xD_2PO_4$, $Rb_{1-x}(NH_4)_xH_2PO_4$, $K_{1-x}(NH_4)_xH_2PO_4$ and $Rb_{1-x}(NH_4)_xH_2AsO_4$ mixed systems. The theoretical phase diagrams obtained from the calculated dielectric permittivity are close to the experimental ones. Deviation of the theory from experiment takes place for all systems at compositions were the transition between "pure" states is observed.

For pure crystal of RbH_2PO_4 type and $NH_4H_2PO_4$ type we obtained the permittivity of mechanically free $\varepsilon_{33}^{\varepsilon}$ and clamped $\varepsilon_{33}^{\sigma}$ crystals, piezoelectric coefficients, and elastic constants. The calculations of the temperature dependences of these characteristics confirm the experimentally obtained significant difference between the values of $\varepsilon_{33}^{\sigma}$ and $\varepsilon_{33}^{\varepsilon}$ in the RbH_2PO_4 type crystals and the very small difference between these quantities for $NH_4H_2PO_4$ type ones.

For mixed crystal of $Rb_{1-x}(NH_4)_xH_2PO_4$ type we discuss the manifestation of piezoelectric coupling in temperature and frequency dependence of the dielectric permittivities. We also discuss possible ways of developing the theory of presented systems.

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Optical vortices operation using ferroelectric materials

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The interest to real-time operation by a spin (SAM) and orbital angular momentum (OAM) of photons is caused by promising applications of this phenomenon in quantum computing, cryptography and quantum teleportation. We have found that the efficiency of SAM to OAM conversion of optical beams in crystals can be gradually operated by the applied torsion moment or electric field. It has been shown that the torsion stresses can produce conical spatial distributions of the optical birefringence and can lead to appearance of the spin to orbital conversion of optical angular momentum. It was found that SAM-to-OAM conversion can appear only in the crystals of which symmetry groups contain three-fold axes. These crystals belong to the cubic or trigonal systems, being described by the point symmetry groups m3m, m3, 23, 432, $\bar{4}3m$, 3m, $\bar{3}m$, 32, 3 and $\bar{3}$. The well known ferroelectric materials such as $LiNbO_3$, $Pb_5Ge_3O_{11}$ etc. are among these crystals. The phase front of an initially nearly plane wave propagating through the system 'right-handed circular polarizer–twisted crystal–left-handed circular polarizer' should reveal a screw dislocation. The emergent optical beam in this case would bear an optical vortex with the topological charge equal to unity [1]. This method allows for direct operation of the OAM by changing the applied mechanical force. Moreover, the OAM can be efficiently operated via a Pockels effect occurring in the case when a conically shaped spatial distribution of external electric field is created in a crystal [2]. The last method allows for direct operation of the OAM by electrical driving signals. It is shown that a pure screw dislocation of the phase front appears when an electric field is applied to the crystals of the groups 3m, 32, 3, $\bar{6}$ and $\bar{6}m2$, 23 and $\bar{4}3m$. We have also demonstrated experimentally the appearing of an optical vortex whenever a conically shaped electric field was applied to $LiNbO_3$ and $Bi_{12}GeO_{20}$ crystals. On the basis of analysis of acoustogyration and acoustooptic diffraction of light in gyrotropic crystals from the viewpoint of conservation of optical angular momentum it has been shown that the availability of optical angular momentum in the diffracted optical beam can be necessarily inferred from the requirements of angular-momentum conservation law. As follows from our analysis, circularly polarised diffracted wave should bear a doubly charged vortex [3]. The efficiency of the spin-to-orbit momentum conversion is governed by the efficiency of acoustogyration or acoustoptic diffraction of light. The mentioned phenomena can be used for spatial operation by the beams bearing optical vortices.

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On the tricritical behaviour and (p, t, x) diagram of the $Sn_2P_2(Se_xS_{1-x})_6$ solid solutions.

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We have studied the temperature behavior of the acoustic properties of the $Sn_2P_2(Se_{0.28}S_{0.72})_6$ and $Sn_2P_2S_6$ crystals at the region of ferroelectric phase transition. The temperature dependence of the acoustic wave velocity v_{55} for both crystals was studied at the action of high hydrostatic pressures. The temperature dependences of coefficients of elastic stiffness for the $Sn_2P_2(Se_{0.28}S_{0.72})_6$ and $Sn_2P_2S_6$ crystals have been obtained and analyzed on the base of mean field theory.

Our results of the temperature dependence of the acoustic wave velocity v_{55} at high hydrostatic pressures reveal that tricritical point exists on the pressure–temperature phase diagram of $Sn_2P_2S_6$ crystals. It was found that its coordinates are P_{TC}=4335.7bar and T_{TC}=259K. It follows from the (p,T)-phase diagram obtained by us that the Curie temperature decreases linearly with increasing hydrostatic pressure and no phase transition splitting is observed on the phase diagram. The behavior of the acoustic wave velocity and the critical exponents are almost unchanged at pressures less than 2.3kbar, although it changes drastically in the pressure region 2.3kbar<p<4.3kbar.

The investigation results of the temperature dependence of the longitudinal ultrasonic wave velocity v_{55} for $Sn_2P_2(Se_{0.28}S_{0.72})_6$ crystals at different hydrostatic pressures shown that it essentially differ for $Sn_2P_2(Se_{0.28}S_{0.72})_6$ from those found for the pure $Sn_2P_2S_6$ crystals. The different temperature and pressure behaviors of the same sound velocity in the both crystals suggest that, contrary to the pure $Sn_2P_2S_6$ compound, the $Sn_2P_2(Se_{0.28}S_{0.72})_6$ solid solutions should ‘move away’ from the tricritical point with increasing hydrostatic pressure. Using our experimental data concerned with the baric shifts of the Curie temperature for the both crystals we have constructed a partial (P, T, x)-phase diagram for the $Sn_2P_2(Se_{0.28}S_{0.72})_6$ solid solutions. It is readily seen from (P, T, x)-phase diagram that the lines of the phase transition for the both crystals are parallel. The latter fact suggests that this part of the (P, T, x)-phase diagram represents a plane. Hence, the tricritical points in the both crystals should be connected by some straight line or a curve in the (P, T, x)-space.

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POSTER PRESENTATIONS

Study of the phase transition in polycrastalline $(Ba_{0,90}Pb_{0,10})(Ti_{0,90}Sn_{0,10})O_3$

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The results of dielectric measurements of polycrystalline $(Ba_{0,90}Pb_{0,10})(Ti_{0.90}Sn_{0.10})O_3$ (BP10TS10) sample are presented. A broadening maximum of permittivity ε'(T) at temperature T_m=367K was observed. No T_m temperature dependence from frequency of the external electric field in this material is typical for diffuse phase transition (DPT). The T_m corresponds to the temperature maximum of dielectric losses (tgδ), ac conductivity (σ'_{ac}) and minimum of real part the electrical modulus (M'). In the paraelectric phase, at the Burns temperature (392K) was observed a change in the value of the parameter γ describing the diffuse phase transition. The γ value decreases from 1,66 to 1,24 with a change in the measured temperature range. This suggests that at high temperatures, the substitution of Pb and Sn ions have less influence on diffuseness of phase transition. Measurements of dielectric quantities were performed by means dielectric spectroscopy in the frequency range between 20 Hz and 1 MHz.

The ceramic-ferrite composites based on $PbFe_{1/2}Nb_{1/2}O_3$

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A ceramic-ferrite composites based on $PbFe_{1/2}Nb_{1/2}O_3$ powder and ferrite powder (zinc-nickel ferrite - NiZnFe and zinc-manganese ferrite - MnZnFe) have been obtained in presented work. The volume fraction of ceramic powder in the composite was equal to 90%, while the ferrite powder fraction was 10%. The synthesis of components of ceramic-ferrite composite have been done by a powder calcination method. Final densification have been done by a free sintering.

For obtained ceramics XRD investigations were performed as well as investigations of microstructure, EDS, dielectric, magnetic, internal friction and electrical hysteresis loop. The results of these investigations shown that the combination of ferroelectromagnetic PFN with magnetic ferrite caused an increase of the value of dielectric permittivity of the composite accompanied by the increase of dielectric losses. So, the addition of the ferrite (NiZnFe, MnZnFe) as an additional component improves the magnetic properties of PFN-ferrite composite. Taking into account the fact that the electric conductivity of zinc-manganese ferrite (MnZnFe) is higher the zinc-nickel ferrite (NiZnFe) seems to be better material for obtaining composites based on ferrite and ceramic powder.

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Thermally stimulated conductivity of MDM and MDSCM structures on basis of polar $Li_2B_4O_7$ single crystal

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For constructing of solid-state detectors of thermal neutrons by current pulses using structures of metal-dielectric-metal (MDM) or metal-dielectric-semiconductor-metal (MDSCM) type it is necessary to perform investigations of electro-physical parameters of such structures. Owing to high sensitivity of lithium-6 and boron-10 isotopes to thermal neutrons the most efficient working substance for such detectors are $Li_2B_4O_7$ single crystal plates which just act as dielectric in MDM or MDSCM structures. Therefore, the presented work is devoted to investigations of thermally stimulated conductivity of MDM and MDSCM structures, where M – Cu thin films, D – thin plates from $Li_2B_4O_7$ single crystal of X and Z crystallographic orientation, and SC – ZnO and Eu_2O_3 thin films.

It was ascertained that at temperature change and applied constant electric voltage there are observed current steps through such structures, especially in temperature range below the room temperature. The current steps are observed for structures on basis of both crystallographic orientations of $Li_2B_4O_7$ single crystal plates, but in somewhat different temperature ranges. Also it was fixed a response of the given structures on pressure changes in the gas environment, in particular, on vacuumization process.

The observed phenomena are explained by presence of two polar directions in $Li_2B_4O_7$ single crystals and connected with this pyroelectric properties [1,2]. There have been analyzed an influence of such uncontrollable current steps on results of the thermal neutrons detection by our MDM and MDSCM structures on basis of $Li_2B_4O_7$ single crystals, and the ways for minimization of this influence.

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Broadband dielectric studies of Bi doped $SrTiO_3$ ceramic

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Piezoelectric ceramics and single crystals containing lead have been widely used as actuator, transducer, and sensor materials. However, the toxicity of lead oxide has led to a demand for alternative materials that are more environment friendly. $(Sr_{1-1.5x}Bi_x)TiO_3$ - strontium bismuth titanate (SBT for short) is the one of such compounds.

The ferroelectricity in incipient ferroelectrics like $KTaO_3$ or $SrTiO_3$ can be induced by application of strong enough electric field, uniaxial stress or substitution of A-site ions by isovalent or heterovalent ions. Scanavi [1] discovered that $(Sr_{1-1.5x}Bi_x)TiO_3$ ceramic with small to moderate Bi content exhibits dispersion similar to relaxor ferroelectrics. Further dielectric studies on SBT ceramic (up to $x \leq 0.17$) [2, 3] showed that Bi doping induces formation of local antiferrodistortive and polar regions. This causes a complex relaxational dynamics below the phonon frequency range. The aim of this work - extend the investigations of dielectric dispersion in SBT to GHz range and to calculated distribution of relaxation times.

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Ultrasonic investigation of phase transitions in $PbFe_{1/2}Nb_{1/2}O_3$ ceramics

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Lead iron niobate $PbFe_{1/2}Nb_{1/2}O_3$ (PFN) undergoes transitions to antiferromagnetic and ferroelectric phases at about 145 K and 380 K respectively [1]. We have investigated dielectric and acoustic properties of PFN ceramic inside 120 K – 450 K temperature interval. The $PbFe_{1/2}Nb_{1/2}O_3$ ceramics were obtained by conventional ceramic technology. Powders lead ferrotantalate were synthesized from the corresponding oxides by solid phase thermal chemical reactions. Dielectric response showed single dielectric permittivity maximum caused by ferroelectric phase transition around 380 K, but no dielectric anomalies associated with magnetic phase transition at low temperatures were observed, as sometimes is reported in literature. Formation of the polar phase was confirmed by ultrasonically detected piezoelectric signal. Ultrasonic investigations using pulse-echo method showed two anomalies in temperature dependencies of ultrasonic velocity and attenuation, associated with magnetic and ferroelectric phase transitions. Also a cooling-heating hysteresis of several degrees was observed for the determined ferroelectric phase transition temperatures.

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The influence of chromium impurity on optical and electronic properties of cobalt

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The refraction n and absorption χ indices of polycrystal Co-Cr alloys with 10, 20 and 35% of chromium concentrations were measured in a wide spectral region 0.23÷2.8 μm (0.44÷5.36eV) at room temperature by spectral ellipsometric methods. Based on these data, it is calculated the permittivity ε and reflection coefficient R at normal incidence of light. It is analyzed the dispersion relations of optical conductivity $\sigma(h\nu)$, which is proportional to the interband density of electronic states. Using mathematical modeling, dispersion curves of residual optical conductivity $\Delta\sigma$ $(h\nu)$ are calculated.

It is established that new impurity bands formed in the electronic spectrum of the solvent Co when impurities Cr added. The new bands are responsible for the extra absorption in Co-Cr alloys. It is suggested the localization of impurity energy levels in Co-Cr alloys at different energies above the Fermi level.

Key words: cobalt-chromium alloys, electronic structure, impurity band, energy subzone, frequency of collisions, concentration of electrons, intraband junction, density of electronic states, optical conductivity spectrum.

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Structure of tantalum and niobium pentoxide ceramics treated by concentrated light flow

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Ceramic Nb_2O_5 and Ta_2O_5 refractory oxides obtained by conventional techniques have a macro-crystalline structure, are particularly brittle of feeble plasticity and weak crack resistance limiting practical applications. Mechanical characteristics of the ceramics can be improved to obtain material of the smallest (micro- and nano-meter scale) structure by employing advanced treatment techniques. Atomic force microscopy (AFM) and Raman studies of the effect of concentrated light flow (CLF) on nano-, micro- and macro-structures, and disordering of the structural units in ceramic tantalum and niobium pentoxides are reported.

High-energy concentrated light transforms the structure of Nb_2O_5 and Ta_2O_5 ceramics at different scales starting from fractal macro-, micro- and nano-structures and ending by altering of the character of chemical bonding and the degree of coordination in the structural polyhedrons. The complex transformations radically change the physical characteristics of Nb_2O_5 and Ta_2O_5 including mechanical properties and thermal expansion. The differences in reaction of Nb_2O_5 and Ta_2O_5 ceramics to CLF (a larger proportion of the nano-meter structures in Ta_2O_5 ceramics, chemical bonding, and coordination of structural polyhedrons) can be accounted for by different melting temperature of the oxides and the difference in covalent bonding of Nb-O and Ta-O.

Concentration and thermal phase transitions in perovskite solid solutions

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Solid solutions (SS) of $Li_{0.12}Na_{0.88}Ta_yNb_{1-y}O_3$ are of interest as ceramic materials of lithium super-ionic (SI) conductivity. Ordering of Li^+ and Na^+ cations and deformations of oxygen octahedrons in the SS structure at the ratio of Na : Li = 7 : 1 provide specific channels of conductivity formed of Na^+ cation vacancies. Position and broadening of the transition to the SI state vary over a wide temperature range (~ 670 ÷ 730 K) depending on the degree of ordering of the structural units in the niobium and tantalum sub-lattices. The change of the geometry of the oxygen octahedrons and the type of dipole ordering in the $Li_{0.12}Na_{0.88}Ta_yNb_{1-y}O_3$ SS is accompanied by a variety compositional phase transitions (PT).

Phase transitions and structural disordering of the $Li_{0.12}Na_{0.88}Ta_yNb_{1-y}O_3$, SS preceding transition to the SI state is studied by Raman spectroscopy. A series of compositional phase transitions and structural reordering in $Li_{0.12}Na_{0.88}Ta_yNb_{1-y}O_3$ SS is observed at y ≈0.25; 0.6; 0.8. At the ferroelectric to antiferroelectric PT occurring in the $Li_{0.12}Na_{0.88}Ta_yNb_{1-y}O_3$ SS at 570÷620 K, the Raman band corresponding to stretch of the oxygen bridge disappears. Thermal disordering caused by highly mobile lithium ions, proceeds gradually and relatively uniformly. The increase of translational mobility of the light lithium ions is facilitated by disorientation of the oxygen octahedrons BO_6 on the whole and by considerable deformation significantly altering the octahedron symmetry. Static disordering in the Nb^{5+} and Ta^{5+} sub-lattice occurring under varied tantalum content decreases the temperature of the ferroelectric to antiferroelectric PT promoting transition to the SI state. However, our data suggest that transition to the SI state is spread over a broad range of temperatures and does not show up as a stepwise change in the Raman spectrum.

Influence of point defects on the bulk modulus and electronic structure of $BiMnO_3$

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$BiMnO_3$ is a multiferroic in which the ferroelectric order coexists with ferromagnetic order in the temperature range from 0 to about 105K [1].

Ab initio calculation of DFT were carried out in an approximation GGA using PBE parameterization and the spin polarization inside the SIESTA package [2,3]. A unite cell with 40th atoms were modelled for ideal and defected system.

The results of calculations for the hypothetical-high temperature cubic structure including the electronic structure and the bulk modulus were presented. It was shown that the relaxed cubic system was energetically stable with and without spin polarization.

For a monoclinic structure of the ideal monocrystal BiMnO3 as well as for oxygen defected were determined: the electronic structure and bulk modulus, total density of states DOS and a gap energy. For both types of structure were showed the characteristics of p(V) and E(V) fitted to the Muhrnagan equation of the state.

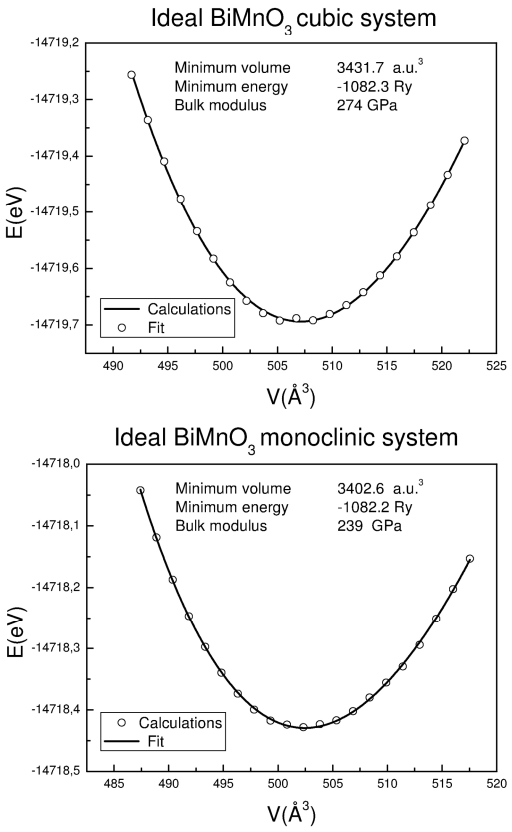

Fig. 1: Total energy as a function of the volume of elementary cell

The obtained results indicate an influence of oxygen point defects on the mechanical properties (e.g. bulk modulus) as well as on the electron structure of the steady state of the $BiMnO_3$ crystal and are in a good agreement with other calculations [4].

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Study of dielectric hysteresis in $Sn_2P_2S_6$ ferrolectric crystals

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A novel method of measurements the ferroelectric hysteresis loop which use the modified "double-wave" scheme [1] was used for study the domain switching process in the ferroelectric $Sn_2P_2S_6$ single crystals. This is some modification of the known Sawyer-Tower scheme, the main advantage of which is a possibility to separate the "pure" hysteresis loop, determined by the domain reversal only, from the contributions of parasitic currents, which are extremely strong in the semiconductive materials like $Sn_2P_2S_6$. The basic idea of this method is to make the switching process in two steps, by applying the switching voltage as two triangle-like pulses of the same sign. The first pulse stimulates the domain reversal together with the accompanying dielectric displacement and current, whereas during the second one the switching is absent. The "purified" hysteresis loop can be obtained by extraction of the signal on the second step from the first one.

The scheme is realized on the base of the computer-controlled AD card and the high-voltage amplifier, and includes the LabView program realizing the algorithm. The applying voltage repetition rate can be varied in a wide range, from the lowest values up to 1 kHz, that makes possible to obtain more detailed information about switching, screening and charge transfer processes in the studied samples.

The measurements by this method were carried out on the nominally pure $Sn_2P_2S_6$ and doped (Sb, Bi) samples with different electric conductivity, and are compared with results obtained with the high-resistive ferroelctrics (TGS). The corrected hysteresis loop is analyzed using the model approach. These data are compared with the loops obtained by the holographuic method, i.e. the registration of the hysteresis loop based on the photorefractive properties of the $Sn_2P_2S_6$ crystals [2].

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Spray drying as a method of producing TGS powders

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Spray drying is typically used as a method for removing water or other liquid from the liquid stream, in pharmaceutical technology. In this article spray drying method was used, for the first time, to obtain ferroelectrics TGS powders. The microstructure of the powders was observed by SEM and AFM. X-ray diffraction analysis was carried out to verify the correctness of lattice parameters values. Dielectric response was studied in the frequency range from 100 Hz to 1 MHz. The results of the measurement will be shown.

Structural phase transitions in ferroelectric crystals and thin films investigated by VUV spectroscopic ellipsometry with synchrotron radiation

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It is well known that the structural phase transitions in solids are accompanied by changes in band structure which in turns are reflected by anomalies in the temperature behavior of optical properties. Recently, Spectroscopic Ellipsometry (SE) proves it efficiency in studying various structural phase transitions [1, 2]. SE is independent of the absolute intensity of the incident light eliminating the disadvantages of other non-destructive and contactless optical techniques such as dependence on the intensity of the light source (reflectometry), and vibration and atmospheric disturbances (interferometry). The high sensitivity of this method makes it attractive in particular for investigation of thin and even ultra-thin films.

In this work we present our last results of study $Sr_xBa_{1-x}Nb_2O_6$ (SBN), $Pb_5Ge_3O_{11}$ (PGO), KH_2PO_4 (KDP), KD_2PO_4 (DKDP) ferroelectric crystals and $PbTiO_3$ thin films by VUV SE using synchrotron radiation as a light source (Berlin electron storage ring for synchrotron radiation BESSY II). Due to extremely small size of probing light spot in comparison to conventional ellipsometers, small aperture of the detector and brilliance of the synchrotron radiation, not only changes in the linear behavior but also clear anomalies can be detect in the temperature dependences of the complex effective dielectric function $\langle\varepsilon\rangle(E)$ and intensity of reflected light $I_R(T)$ at certain fixed photon energy when a change of the phase state occurs. Particularly interesting are anomalies observed in the temperature-and-optical dependencies of $PbTiO_3$ thin films epitaxially grown on $SrTiO_3$ substrate at the temperature 105 K corresponding to the well-known phase transition in $SrTiO_3$ crystal.

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Studies of fluctuation effects in the optical birefringence of $NaNO_2$ and $KFeF_4$ crystals

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It is known that $NaNO_2$ crystal reveals a parent-to-incommensurate ($T_i \approx 438.4$ K) and an incommensurate-to-ferroelectric ($T_C \approx 436.9$ K) phase transitions (PTs), whereas an isostructural PT ($T_C \approx 385$ K) and, maybe, an incommensurate one depending on sample quality should exist in $KFeF_4$ (see, e.g., [1, 2]). Since many details of those PTs need to be understood in much more detail, our aim consists in quantitative interpretation of the birefringence data [1, 2] using the techniques described in part in the work [3].

We have solved a longstanding debate on the temperature width of the critical region in $NaNO_2$ [4]. The mean Ginzburg number G obtained for the incommensurate PT ($G \approx 4\times10^{-4}$) testifies an extremely narrow critical region. The critical index of the heat capacity found close by the PT point is equal to $\alpha=0.4$ (see Fig. 1), which agrees fairly well with the estimations made from the heat capacity data [5] (0.38 for the paraphase). At the same time, the log-log curve for the spontaneous birefringence shows a continuous change of its slope, indicating availability of a crossover region.

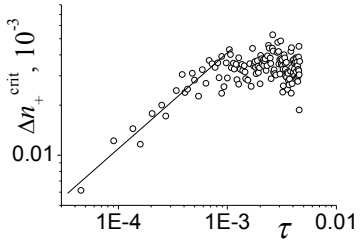

Fig. 1. Log-log plot of the critical birefringence part Δn_+^{crit} in the parent phase of $NaNO_2$ crystal (see the data [1]) versus the reduced temperature $\tau = (T - T_i)/T_i$.

As for $KFeF_4$ crystals, analysis of temperature derivatives of the birefringence has revealed no hypothetic PT into the incommensurate phase. On the other hand, the characteristics of their PTs are found to depend essentially on the perfection of single crystals (see Table 1). Most probably, the value $\alpha \approx 0.5$ obtained for the reduced temperatures $10^{-3} \div 10^{-1}$ while processing the critical birefringence part implies the availability of symmetry-conserving local-temperature defects or the Gaussian fluctuations.

Table 1. Some characteristics of the PT for different samples of $KFeF_4$ crystals.

Crystal growth technique	Sample quality	Curie point T_C, K	Birefringence fluctuation tail, 10^{-5}	Ginzburg number G	Critical index β
flux (F)	higher	385.04	1.8	0.0015	0.19
Bridgman (B)	middle	385.31	3.8	0.0050	0.19
Hydrothermal (H)	lower	394.49	4.5	0.0175	0.21

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Dielectric relaxation of the nanostructured ZnO films.

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Zinc oxide (ZnO) manifests many advantages, as compared to other wide band gap semiconductors, such as high-thermal/chemical stabilities and the possibility of wet chemical etching. It is a technologically important material exhibiting multifunctional properties for various applications in optoelectronic devices applications, such as solar cells, transparent conducting electrodes, light emitting devices, gas sensors and heat mirror [1,2]. ZnO is unique material that demonstrates a large variety of nanostructures. Modification of the crystallites' sizes of nanocrystalline ZnO leads to the change of the arbitrary interfaces volume and its drastic influence on the dielectric properties, conductivity of a sample especially in a radio-frequency range.

The thin films were deposited on the glass substrates with ITO buffer layers by the standard RF-magnetron sputtering using ZnO targets in the argon atmosphere. The two types of films were prepared. The first sample was obtained by sputtering on the substrate heated to 573 K, whereas the second sample was manufactured without substrate heating. The dielectric measurements were carried out using traditional method of capacitor capacitance measurement. The capacitance was measured using LCR–meter HIOKI 3522-50 LCF HiTester at the frequency range of 4 Hz-100 kHz. Additionally, the dielectric parameters of ZnO films were measured at temperature 350 K and frequency range of 100 kHz-2 MHz. The nitrogen cryostat with UNIPAN 680 temperature control system was used for the dielectric measurements.

The dispersion of the dielectric permittivity of both samples was observed. In the first stage the dielectric dispersion of such nanostructured zinc oxide films at temperature range of 120-380 K was studied. We observed the relaxation process in these materials at the temperature range of 220-350 K within the above mentioned frequency window. The second relaxation process was recognized in the frequency range of 100 kHz – 2 MHz in vicinity of 350 K. The nature of the low-frequency relaxation process is connected with space-charge polarization on the grain boundary [3,4]. It is realized due to the high defect concentration within the interfaces of the ZnO nanograins in comparison with a bulk material. It was shown that the structural irregularity of a sample and crystallite sizes are reflected considerably in the effects of polarization of the nanostructured film ZnO at low frequencies. The high-frequency relaxation process corresponds to the thermal polarization involving the electrons localized at the oxygen vacancies. The performed investigations reveal that that the substrate temperature during deposition of the transparent ZnO films by the method of RF magnetron sputtering is one of the key parameters affecting the structural, electrical, and optical properties of synthesized films.

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Textured $Bi_4Ti_3O_{12}$-PVC ceramic-polymer composites

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Textured $Bi_4Ti_3O_{12}$ -PVC composites were fabricated. Bismuth titanate $Bi_4Ti_3O_{12}$ is a ferroelectric with an Aurivillius structure. Ceramics powders of bismuth titanate were prepared by the sol-gel method using bismuth nitrate pentahydrate $Bi(NO_3)_3 \cdot 5H_2O$ and tetrabutyl titanate $Ti(OC_4H_9)_4$ as precursors. The $Bi_4Ti_3O_{12}$ -PVC composites were fabricated from ceramics powders and polymer powders by hot-pressing method. The composite surface images were obtained by AFM tapping mode (NT-MDT Solver P47).

On the possibility of structural transformation in Tl_4HgI_6 crystals: linear thermal expansion data

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While searching new materials for optoelectronic devices, many researchers pay close attention to A_4BX_6-group compounds. The object of our interest is single crystals of Tl_4HgI_6 (see, e.g., [1, 2]). In this work we report mainly on experimental results concerned with thermal expansion properties of Tl_4HgI_6.

Tl_4HgI_6 crystals have been grown with a Bridgman-Stockbarger technique. Basing on our X-ray studies made on powders, we conclude that the crystals belong to the tetragonal centrosymmetric space group P4/mnc. Thermal linear expansion has been measured using a quartz dilatometer. The results are displayed in Fig. 1.

It is seen from Fig. 1a that Tl_4HgI_6 single crystals show both positive and negative values of the relative linear expansion $\Delta L/L$. The latter anomalous property is peculiar for comparatively narrow temperature regions of ~ 10 K around 449 K (heating run) and 409 K (cooling run). Moreover, a clear temperature hysteresis of about 40 K exists. It would be natural to ascribe the above behaviour to some structural transformation. To the best of our knowledge, this is the first experimental report on the phase transition in Tl_4HgI_6. Furthermore, the observed linear expansion is large enough, when compare to standard values typical for many single crystals. Notice that the linear thermal expansion coefficient α is of the order of 10^{-5} for the most of temperatures, although it dips down to as large values as $\sim 10^{-2}$ in the close vicinity of a hypothetic structural transformation (see Fig. 1b).

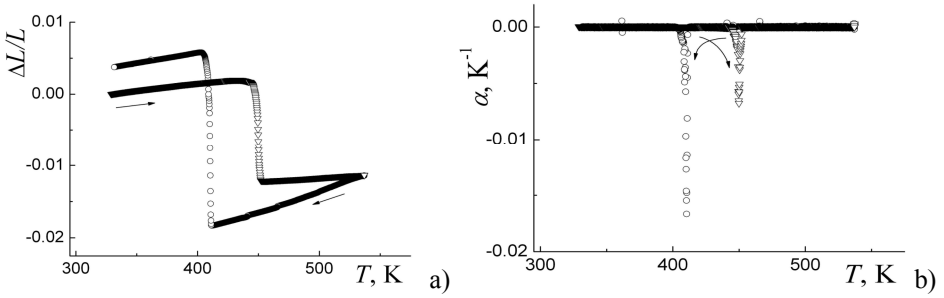

Fig. 1. Temperature dependences of relative linear elongation along *c* axis (a) and thermal expansion coefficient (b) for Tl_4HgI_6 crystals, measured in both heating and cooling regimes.

We present also an explanation of a possible structural transformation in Tl_4HgI_6, considering the temperature changes of the lattice parameters and the inter-atomic distances known from the literature.

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Microstructure, calorimetric and dielectric investigation of hafnium doped barium titanate ceramics

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The barium hafnium titanate samples $BaHf_xTi_{1-x}O_3$ (BHT-x) $(0 \le x \le 2,5)$ were prepared by a conventional ceramic technology. The room temperature X-ray powder diffraction profiles show a single phase with perovskite structure. The performed SEM and EDS studies reveal that the samples are perfectly sintered and the material is chemically homogeneous. The examined samples are of good quality, the grains are well shaped and there is a very small amount of a glassy phase. The thermal behaviours of the $BaHf_xTi_{1-x}O_3$ ceramics were studied using Differential Scanning Calorimetry. The measurements were made using a Netzsch DSC F3 Maia calorimeter in the temperature range from 120 K to 600 K under the argon atmosphere. The BHT-x specimens consisted of single piece of ceramic of the average mass 20 mg and were placed in an alumina crucible. DSC measurements showed the influence of *Hf* addition on character of phase transitions in $BaTiO_3$ structure. The results were compared with for pure $BaTiO_3$.

The dielectric measurements were performed by means of QUATRO KRIO 4.0 temperature system together with precise LCR Agilent 4284A meter, BDS 1100 cryostat and WINData 5.62 Novocontrol software. The heating and cooling agent used was nitrogen. The data were taken at stabilized temperature points within the range from 500 K to 140 K with 5 K step. Measurements of dielectric permittivity, dielectric loss tangent and electric conductivity were performed using standard dielectric spectroscopy in the frequency range between 20 Hz and 1 MHz.

Phase transitions in the polytypes of $TlInS_2$ and $TlGaSe_2$ ferroelectric crystals

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Isomorphic ternary chalcogenide compounds $TlInS_2$ and $TlGaSe_2$ are ferroelectrics-semiconductors, in which structural phase transitions (PT) occur in the temperature range T=100÷300 K. These crystals are characterized by the pronounced layered structure and under normal conditions belong to the monoclinic system (the space group C^6_{2h}). Weak connections between layers in the $TlInS_2$ and $TlGaSe_2$ crystals are the reason of existence of their polytypes, which differ in number of the packages along the C axis, i.e. by unit cell parameter c: c, 2c, 3c, 4c … It has been reported in many papers that for these compounds the results differ significantly for samples from different ingots. In particular, it concerns characters and temperature positions of ferroelectric PTs. Such features were connected with the possible influencing of polytypism. In this connection complex researches $TlInS_2$ and $TlGaSe_2$ samples which belonged to different polytypes (C and 2C) were performed in the temperature range T=100÷300 K. For the selected samples measurements of their dielectric permittivity and crystalline lattice structure changes were conducted. It has been established that C-$TlInS_2$ and 2C-$TlInS_2$ polytypes differ by character of ferroelectric PTs and concern to the various types of incommensurate systems. It is shown that C-$TlInS_2$ crystals concern to improper ferroelectrics with an incommensurate phase (T_i≈ 215 K). The ferroelectric PT takes place at the temperature T_c= 197 K in this polytype and accompanied by quadrupling of the unit cell along the C axis. We found that the ferroelectric PT in 2C-$TlInS_2$ polytype, unlike C-$TlInS_2$, is characterized by the other order parameter. Such ferroelectric PT takes place at higher temperature T_c= 202 K. If take into account the features of ferroelectric PT in the two different polytypes of $TlGaSe_2$ crystals, reported by us earlier, the our experimental results prove the crystals of C-$TlInS_2$ and C-$TlGaSe_2$ are the ferroelectrics with an incommensurate phase of type I, and the crystals of 2C-$TlInS_2$ and 2C-$TlGaSe_2$ polytype belong to another type – the type II.

Detailed studies of polycritical region of $TlInS_2$– type crystals

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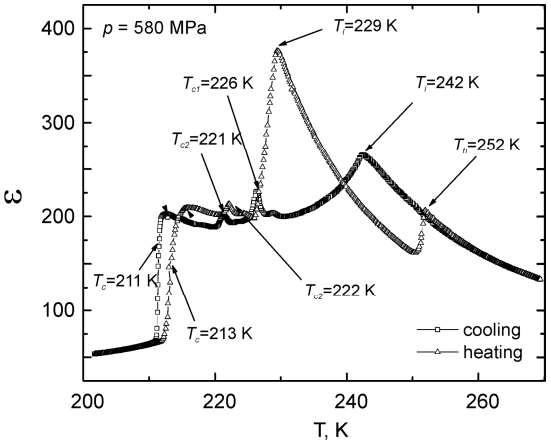
Layered ferroelectrics are interesting for investigation since their characteristics are determined by quasi-two-dimensionality and strong structural anisotropy. This class of materials includes $A^{III}B^{III}C^{VI}_2$ chalcogenides (A = Tl, B = In, Ga, C = S, Se), among which $TlInS_2$ ferroelectric crystal is especially interesting since it possesses a complex sequence of phase transitions in the temperature interval 190–216 K and reveals polycritical phenomena in the (p, T)-diagram in the pressure range $580 \le p < 660$ MPa.

$TlIn(S_{1-x}Se_x)_2$ single crystals were grown by Bridgman technique. Dielectric constant and dielectric loss were measured at the measuring field frequencies of 1 MHz along the [100] crystallographic direction.



Studies of dielectric constant and spontaneous polarization in the cooling mode at different pressures were performed. The polycritical points are observed at the coordinates p = 585 MPa, T = 240 K), (p = 610 MPa, T = 223 K). (p = 620 MPa, T = 215 K) in $TlInS_2$ crystal.

The extrapolation of the dielectric constant dependence shows the evidence for a polycritical point at (p = 740 MPa, T = 345 K).

Detailed studies of dielectric constant transformation in the pressure range $580 \le p < 660$ MPa were performed. Possible types of polycritical points in the (p, T)- diagrams are discussed.

Low-frequency dielectric dispersion in doped $Sn_2P_2S_6$ ferroelectric crystals

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The $Sn_2P_2S_6$ ferroelectrics are attractive materials for many optical and dielectric applications. Their basic parameters substantially depend on the defects and impurities that stimulated the study of the doped and modified by post-growth treatment crystals.

The spectra of dielectric permittivity ε in the frequency range of 20 Hz -100 kHz and temperatures between 100 K and 400 K were measured with different $Sn_2P_2S_6$ samples. There are the nominally pure vapor-transport samples, crystals, obtained by Bridgman's method with deviation from stoichiometry, as well as a number of the doped crystals $Sn_2P_2S_6$:Ag(Sb;Bi), and crystals annealed in various atmosperes. It was found that the non-stoichiometric samples demonstrate a Debye-type dielectric response in the low-frequency region (below 1 kHz), and the parameters of dispersion (the dielectric contribution Δε and the relaxation time τ) strongly depend on the dopant type and the sample stoichiometry. These parameters were estimated for all these samples and at various temperatures, in the both para- and ferroelectric phases. In addition, the additional dielectric anomalies, most probably connected with the ferroelectric domains, were found the low-temperature region (below 150 K).

The dielectric spectra of the Ag-doped $Sn_2P_2S_6$ sample demonstrate a substantial ion-migration contribution to the dielectric permittivity. It was found that the annealing in hydrogen substantially changes the dielectric spectra, leads to increasing the electric resistivity, and also changes the shape of dielectric anomaly near the phase transition point. The degradations of the dielectric parameters with time (during weeks) is also observed, that probably occurs due to desorption of the previously absorbed hydrogen atoms Besides, the first data on the impact of the light pre-illumination on the dielectric spectra on different $Sn_2P_2S_6$ crystal are studied.

Dielectric properties of $Ba_2NdFeNb_{4-x}Ta_xO_{15}$ ceramics

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$Ba_2NdFeNb_{4-x}Ta_xO_{15}$ materials belong to the so called tetragonal tungsten bronze (TTB) structural family. The main characteristic feature of TTB structure is three types of open channels that develop within its octahedral framework, which allows performing a wide range of substitutions, either in these channels or within the octahedral framework itself. Interesting dielectric behaviours were discovered for this family, namely the ferroelectric to relaxor crossovers in the $Ba_{6-2x}Eu_{2x}Fe_{1+x}Nb_{9-x}O_{30}$ [1] or $Ba_2Pr_xNd_{1-x}FeNb_4O_{15}$ [2].

We have investigated $Ba_2NdFeNb_{4-x}Ta_xO_{15}$ (x= 0.3, 0.6 and 2) solid solutions using broadband dielectric spectroscopy and ultrasonic pulse-echo method. Nb substitution with Ta considerably alters dielectric response of this system. $Ba_2NdFeNb_{4-x}Ta_x\ O_{15}$ compounds with x up to 0.3 displays ferroelectric behaviour with $T_C \approx 325$ K (on heating). Further increase of x causes formation of relaxor state in these solid solutions and lowers corresponding dielectric permittivity dispersion temperature region.

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Pressure behaviour of the order parameter of phase transitions in $TlIn(S_{1-x}Se_x)_2$ crystals

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A considerable interest to $TlInS_2$-type semiconductor crystals stems from their physical properties enabling these materials to be treated as a potential base for functional elements of electronics, pressure and temperature gauges, pyroelectric detectors. Besides the interest to the studies of $TlIn(S_{1-x}Se_x)_2$ crystals is determined by polycritical phenomena revealed in *x,T*- and *p,T*-phase diagrams of these compounds.

Here we report on the studies of the behaviour of the order parameter of phase transitions in $TlIn(S_{1-x}Se_x)_2$ single crystals along the *p,T*-diagram. These studies are based on the experimental measurements of birefringence and pyroelectric coefficient, with the accounting of fact that for ferroelectrics the anomalous part of birefringence is proportional to squared of the spontaneous polarization.

The studies of birefringence and pyroelectric coefficient of $TlIn(S_{1-x}Se_x)_2$ ($x<0.1$) single crystals are carried out in the temperature interval 80-400 K and hydrostatic pressure range up to 700 MPa.

Found that with the pressure increase the birefringence and pyroelectric coefficient anomalies shifts towards higher temperatures. The relevant pressure coefficients are determined. Decrease of the anomalous part of birefringence is observed with hydrostatic pressure, it is the evidence for the decrease of the spontaneous polarization value. Such behaviour is in agreement with the pressure studies of the temperature dependence of spontaneous polarization, which determined on the base of the studies of pyroelectric current. The observed birefringence anomalies and the pressure behaviour of birefringence in the incommensurate and ferroelectric phase are discussed.

Modeling of homologous series of flower phases of TMA molecules

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Self-assembled molecular monolayers nowadays are successfully applied in various fields of molecular electronics and nanobiomedicine. Different, sometimes quite exotic molecular structures, as well as phase transitions between these structures, have been found studying self-organization of molecular systems. Especially interesting are H-bonded molecular networks. Recently, very interesting reports of two-dimensional molecular networks, composed of organic molecules of trimesic acid (TMA) on graphite and Au(111) were published. Triangular TMA molecules are characterized by rather simple and strict geometrical three-leg form originating from the central phenyl ring. The ordering of these molecules is controlled by dimeric or trimeric H-bonding at the vertices of the triangle. TMA molecules form porous honeycomb lattice and a series of other polymorph structures (called "flower" phases), which originate from combination of these H-bondings. Here we present the model for ordering of TMA molecules into the flower phases. The model accounts for dimeric and trimeric intermolecular interactions and three states (two main orientations and a vacancy state) of a molecule on a rescaled triangular lattice. As a result, we obtain the ground state phase diagram for homologous series of flower phases. Corresponding phase diagrams for different ratios of main interaction parameters at finite values of temperature are obtained using Monte Carlo calculations.

Broadband dielectric properties of $0.5BaTiO_3$–$0.5KNbO_3$ composite

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Restriction of usage lead in many countries has driven to extensive search for new lead-free materials for piezoelectric applications. However, they still need improvement to be able to replace traditional ceramics.

A nanostructured composite of two ferroelectric materials would have lattice distortions at interfaces of phases, which can increase polarization of the material [1], [2], leading to enhanced piezoelectric properties.

It was shown recently, that in case of $0.5BaTiO_3$ – $0.5KNbO_3$ composite ceramics, an enhanced piezoelectric response is observed compared to solid solution of the same composition [3]. This makes the material interesting for a thorough investigation.

The samples were measured in 30 – 500 K temperature range and 100 Hz – 40 GHz frequency band during cooling with 1 K/min temperature rate. The measurements revealed several anomalies of dielectric permittivity, which could be attributed to phase transitions of $BaTiO_3$. Furthermore, several glass-like relaxational processes were observed, with their origin being still unknown.

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Spectral ellipsometry study of $[(CH_3)_2CHNH_3]_4Cd_3Cl_{10}$ and $[C(NH_2)_3]_4Cl_2SO_4$ crystals in spectral range of electronic excitations

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The pseudo-dielectric function $<eps(E)> = <\varepsilon_1>(E) + i<\varepsilon_2>(E)$ of the organic-inorganic crystals $[(CH_3)_2CHNH_3]_4Cd_3Cl_{10}$ and $[C(NH_2)_3]_4Cl_2SO_4$ are studied by the spectral ellipsometry method in the photon energy range of 3 – 10 eV and in the temperature range of 265 – 400 K comprising different structural phases of the crystals. The $[(CH_3)_2CHNH_3]_4Cd_3Cl_{10}$ crystal exhibits several temperature dependent phase transitions at 353 K, 294 K, and 259 K [1]. The guanidinium ($C(NH_2)_3$) containing ferroelectric crystal $[C(NH_2)_3]_4Cl_2SO_4$ is characterized by two phase transitions at 356 K and 352 K [2].

Three spectral bands are found in the dielectric function $<\varepsilon_2>(E)$ of $[(CH_3)_2CHNH_3]_4Cd_3Cl_{10}$ and two analogous bands are present in $[C(NH_2)_3]_4Cl_2SO_4$ ($G_4Cl_2SO_4$) in the range of 3 – 10 eV. Relatively small temperature anomalies of the dielectric permittivity $\varepsilon(T)$ in the ranges comprising phase transition points of the crystal studied have been revealed and discussed.

Results of calculations of the electronic band structure and dielectric functions $\varepsilon_2(E)$ of the crystals studied based on the density functional theory (DFT) with using VASP code are presented and discussed together with corresponding experimental data of pseudo-dielectric functions obtained.

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Electronic structure and mechanical properties for ferroelectric $Sn_2P_2Se_6$ crystals

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Information obtained from first principles about the electronic structure of solids makes it possible to predict physical properties of semiconductor materials from their chemical composition. Despite the fact that $Sn_2P_2Se_6$ crystals have long been studied it is not enough data on the electronic structure and mechanical properties in literature. The aim of this work is the calculation of mechanical parameters based on theoretical approach developed in the works of W.A. Harrison [1, 2] and orthonormal tensor basis method [3].

The results of calculation of shear modulus, bulk modulus and Poisson ratio for structural units present in $Sn_2P_2Se_6$ crystals have been given. The applicability of the proposed approach to the calculation of binding energy, the relative displacement parameter, thermodynamic and acoustic Gruneisen parameters and account of anisotropic component of the mechanical parameters has been considered.

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The low-frequency relaxation of $Na_{0.5}Bi_{0.5}TiO_3$-$BaTiO_3$ crystals

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At present time investigations of ferroelectric relaxors with $A'_{1-x}A''_xBO_3$ and $AB'_{1-x}B''_xO_3$ - type structure are intensified due to excellent dielectric and electromechanical properties and possibility to control these properties by doping and changing of forming components. $Na_{0.5}Bi_{0.5}TiO_3$ (NBT) and $Na_{0.5}Bi_{0.5}TiO_3$-$BaTiO_3$ (NBT-BT) solid solutions with morphotropic phase boundary are very useful as lead-free containing ceramics with high piezoelectric coefficients and electromechanical coupling factors. These materials are exhibiting ferroelectric relaxor behavior which is associated with structure phase transitions and unusual local structures, particularly compositional and positional disorder. In scientific literature there is enough information about structure and phase transitions of NBT and NBT-BT. But the data, given in numerous papers, are often inconsistent and contradict each other. It is connected with influence of technology factors on the ceramics synthesis procedure and the method of crystal growth.

Therefore, the main purpose of this work is study the dielectric properties of NBT-BT signal crystals near MPB and to carry out comparative analysis with literature dates.

The crystals of (1-x) NBT- $xBaTiO_3$ system (x=0, 0.05, 0.06 start mixture) have been grown by Czhochralski method. The dielectric studies of the samples with platinum electrodes have been carried out for frequencies 0.1, 0.3, 1, 10, 100 kHz in the wide temperature region (25^0C-540^0C).

The temperature dependence of dielectric permittivity $\varepsilon=f(T)$and $tg\delta=f(T)$ in the crystals of NBT-BT system remains typical for pure NBT, which exhibits anomaly near 200^0C (below- ferroelectric rhombohedral phase) and broad maximum ε near 320^0C (above- ferroelastic tetragonal phase). The anomalies of ε typical for pure NBT displaced to low temperatures with addition $BaTiO_3$ and diffuse of ε_{max} is increased. The increase of $BaTiO_3$ content lead to increase maximum ε and the temperature region of dielectric permittivity hysteresis also changed.

The dispersion of ε is observed at frequencies 0.1, 0.3, 1 kHz in the wide temperature region. The dependences $\varepsilon=f(T)$ of studied crystals shows three anomalies between room temperature and 540^0C. The dissipation factor $tg\delta$ increases with increasing temperature. The behavior $tg\delta=f(T)$ is attributed to increasing conductivity. The study of NBT indicates the low frequency dependence of dielectric permittivity at high temperature (at~ 540^0C) . However it is not connected with cubic-tetragonal phase transition and disappears after not long annealing [1]. It is may be supposed that low frequency dispersion of NBT and NBT-BT crystals concerns with some lattice defects possibly due to the oxygen nonstoichiometry.. The dielectric properties of thermal treated crystals have been investigated. The mechanism of low frequency relaxation ε of NBT and NBT-BT crystal is discussed.

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Microscopic theory of thermodynamic and dynamic properties of Rochelle salt. Taking into account piezoelectric coupling

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The recently proposed four-sublattice model for Rochelle salt is modified by taking into account piezoelectric coupling with shear strains ε_4, ε_5 and ε_6. Our model is a generalization of the four-sublattice model proposed in [1] and Mitsui model with taking into account the piezoelectric coupling [2]. Within a mean field approximation we calculate and study the spontaneous polarization, longitudinal and transverse static dielectric permittivities of mechanically free and clamped crystals, coefficients and constants of piezoelectric strain and stress, and also the elastic constants of these crystals.

Dynamic characteristics of the crystals are explored within a nonequilibrium statistical operator method with taking into account dynamics of strains via Newtonian equations of motion. In the case of frequency-independent kinetic parameters these results are shown to be in agreement with those obtained by us in the framework of the Glauber method. The obtained results for longitudinal characteristics substantiate and generalize the results of [2]. The set of the theory parameters providing the best fit to the available experimental data calculated characteristics is found. Phenomena of crystal clamping by high frequency electric field, piezoelectric resonance, and microwave dispersion, typical for piezoelectrics, are described.

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On the phase transitions in $RbIn(MoO_4)_2$

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Double molybdates and tungstates have attracted a great deal of interest in recent years because of ferroelastic phase transitions and their application potential . Some of the crystals doped with ions, such as Cr^{3+} and Fe^{3+} turned out to be promising materials for tunable laser applications in the micro-wavelength region and micro- and nano-sized cryogenic fluorescent thermometer.

At room temperature $RbIn(MoO_4)_2$ can exist in two modifications: an orthorhombic one of the symmetry Pnma, and trigonal of symmetry P-3m1 [1]; the latter is the object of our studies. By EPR method of Fe^{3+} and Cr^{3+} admixture ions a phase transition at about 163 K has been found in this crystal [2]. Temperature anomalies in the EPR spectra indicate that below this temperature a few other structural phase transitions take place in it [3].

The contribution deals with the detailed EPR and polarizing light microscopy studies of $RbIn(MoO_4)_2$ in the temperature range 77-300K. The spontaneous birefringence and the orientation of optical indicatrix principal axes were investigated. Also relations between ferroelastic domain structure and the EPR spectra in $RbIn(MoO_4)_2$ are considered.

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The surface images of monoclinic domains in TDM/T by AFM

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The atomic force microscopy is a very useful technique for visualising the ferroic crystals surface topography. It has been shown that the variety of domain structures due to the lattice distortion associated with the ferroic phase transitions can result in a complex morphology of their crystal surfaces [1-3].

In the present paper we will focus our attention on the AFM images of the surface topography of ferroelastically twinned crystals $KFe(MoO_4)_2$, $NaFe(MoO_4)_2$ and $KSc(WO_4)_2$. The purpose of this paper is to visualise the undulation of their surfaces caused by domain configurations.

$KFe(MoO_4)_2$, $KSc(WO_4)_2$ and $NaFe(MoO_4)_2$ belong to a family of trigonal double molybdates and tungstates and show a crystal system change from the trigonal to the monoclinic one [4]. The AFM observations of these crystals have been performed at room temperature in their ferroelastic phases. It has been shown that the crystal surfaces bend at the domain boundaries by the angles which can be explained in terms of the monoclinic distortion.

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Crossover between ferroelectric and relaxor behaviour in $(1-x)Ag_{0.9}Li_{0.1}NbO_3$ - $xBi_{0.5}K_{0.5}TiO_3$ ceramics

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Lead based relaxor ferroelectric single crystals and ceramics with the perovskite structure, like PMN, PZN, PLZT and PMN-PT have been widely studied and met promising applications e.g., as very efficient piezoelectric materials. Nowadays, is generally accepted that diffusive and frequency dependent dielectric anomaly in relaxors is caused of dynamics of polar nanoregions, with appears near the Burns temperature (T_B). Due a toxicity of lead one very important topic is searching of lead free relaxor ceramics and crystals, which exhibit piezoelectric properties similar to PMN-PT. On the other hand the investigations of broadband dynamics of polar nanoregions are rather, because it is very difficult to perform dielectric investigations of relaxors in frequency range 1 GHz – 1 THz near and below T_B. In this work we presented dielectric properties of $(1-x)Ag_{0.9}Li_{0.1}NbO_3$ - $xBi_{0.5}K_{0.5}TiO_3$ (ALNBKT) ceramics in very wide frequency (20 Hz – 4 THz) and temperature ranges (500 K – 20 K). The ALNBKT ceramics depending on BKT concentration exhibit ferroelectric, relaxor or crossover behaviour. For ALNBKT with 0.05 $Bi_{0.5}K_{0.5}TiO_3$ ceramics the frequency-independent maximum of complex dielectric permittivity at low frequencies shows ferroelectric phase transition. For ALNBKT with 0.15 $Bi_{0.5}K_{0.5}TiO_3$ ceramics typical relaxor behaviour was observed. The dielectric dispersion of these ceramics appears in microwave and THz frequency range at high temperatures. On cooling the dielectric dispersion becomes broader and it splits into two parts below the dielectric permittivity maximum temperature at 1 kHz. The low frequency dielectric dispersion part anomalously slows down and at low temperatures its part appears without our frequency range. However, the high frequency part remains at microwave and THz frequencies. The distribution of relaxation times has been calculated from the dielectric spectra. The longest relaxation times diverge according to the Vogel-Fulcher law, while the most probable relaxation time diverges according to the Arhenius law. Such dielectric behaviour is typical for ferroelectric relaxors. At very low temperatures (below 100 K) the relaxation dielectric dispersion almost vanishes in THz range. Here the resonant soft mode was observed. The microscopic origin of polar nanoregions in lead free $(1-x)Ag_{0.9}Li_{0.1}NbO_3$ - $xBi_{0.5}K_{0.5}TiO_3$ relaxors is also discussed. The ALNBKT ceramics with 0.1 $Bi_{0.5}K_{0.5}TiO_3$ exhibit crossover between ferroelectric order and relaxor disorder.

Magnetic transitions in the antiferromagnetic magnetoelectric $LiCoPO_4$ crystal: birefringence, heat capacity and magnetic properties

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$LiCoPO_4$ is crystallized in the orthorhombic olivine structure (*Pnma* group). Below T_N=21.6 K the crystal becomes strongly anisotropic and nearly quasi-2D antiferromagnet. Magnetic symmetry group has no the inversion center. The $LiCoPO_4$ crystal exhibits a unique set of physical properties, viz., strong linear magnetoelectric effect at $T<T_N$=21.6 K, large uniaxial magnetic anisotropy, super weak ferromagnetism, near quasi-2D magnetic behavior, and a large Li-ionic conductivity, which makes it attractive for fundamental and applied studies. In spite of the fact that $LiCoPO_4$ has long been known as a magnetoelectric with considerable constants of the linear magnetoelectric effect and that it is studied by many researchers basically in this aspect, a number of its properties are up till now considered abnormal and have no explanation. Among them, in particular, magnetic structure, super weak ferromagnetism and magnetic hysteresis loop of a field-induced birefringence.

With the purpose to obtain the additional information about AFM properties we have carried out the thermal, polarization optic and magnetic measurements of this phosphate crystal. The presented report contains: temperature dependences of a spontaneous and magnetic field induced birefringence of linearly polarized light and a specific heat capacity measured in a magnetic field, and a differential magnetic susceptibility in pulse magnetic field directed along an easy axis of antiferromagnetic $LiCoPO_4$. Comparison of temperature behavior of specific heat and birefringence shows, that magnetic contribution to specific heat and temperature derivation of linear birefringence near T_N can be satisfactorily described by logarithmic divergence, as expected for a quasi-2D antiferromagnetic Ising system, and that non-critical temperature anomalies of linear birefringence caused by 2D and 3D spin fluctuations have the opposite signs. We pay attention to the revealed features of behavior of birefringence and heat capacity in magnetic field – the hysteresis of magnetic birefringence and global character of hysteretic loop and the new peak on temperature dependence of heat capacity arising only at magnetic field and testifying about the new first-order phase transition induced by magnetic field. The measurements of a differential magnetic susceptibility in pulse magnetic field directed along an easy axis revealed that antiferromagnetic order is being step-by-step destroyed by magnetic field. Three phase transitions were observed: the two first-order ones at H_1 = 118 kOe, H_2 = 224 kOe and the second-order one at H_3 = 283 kOe (T = 1.7 K). It was found that magnetization varies smoothly and almost linearly in the magnetic field interval (H_2, H_3). Taking into consideration that uniaxial magnetic anisotropy of $LiCoPO_4$ exceeds exchange energy this behavior may indicate on formation of a collinear modulated magnetic structure with magnetic-field-dependent long-range period that change in magnetic field quasi-continuously.

Hydrostatic pressure effects in Rochelle salt

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Within the framework of the previously proposed [1] modification of the two-sublattice Mitsui model that includes the shear strain ε_4 and the diagonal strains ε_1, ε_2, ε_3 we study the influence of hydrostatic pressure on the phase transitions and physical properties of Rochelle salt crystals. The hydrostatic pressure variation of dielectric permittivity is described using a derived expression for the permittivity of a partially clamped crystal.

A good agreement with experiment is obtained for the pressure variation of the Curie temperatures and static permittivity. The theory however, deviates from the only available experimental data on the pressure dependence of spontaneous polarization; some additional measurements are required here.

The pressure dependences of the intra- and inter-sublattice interaction constants and the asymmetry parameter in Rochelle salt are explored. These parameters, as well as the effective dipole moments, are found to increase with hydrostatic pressure. This is consistent with the ideas of the four-sublattice Mitsui model [2,3], where the dipole moments in Rochelle salt are considered as 3D vectors, assuming they rotate under pressure in such a way that their projection on the a-axis increases.

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Piezoelectric resonance in Rochelle salt: the contribution of diagonal strains

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Within the framework of the previously proposed [1] modification of the two-sublattice Mitsui model that includes the shear strain ε_4 and the diagonal strains ε_1, ε_2, ε_3 a dynamic dielectric response of Rochelle salt rectangular X-cuts is considered. To describe the coupled dynamics of the pseudospin subsystem and lattice strains, the Glauber-like dynamics of the pseudospins is combined with the classical equations of motion of elementary crystal volume. The problem is reduced to a system of second-order partial differential equations that is solved numerically by the finite element method. A simplified but explicitly solvable system of equations for the lattice strains is obtained as well, yielding the explicit expressions for the resonant frequencies of crystal vibrations of the ε_4 shear mode and in-plane extensional modes associated with the strains ε_2 and ε_3.

Experimentally observed phenomena of crystal clamping by high frequency electric field, piezoelectric resonance, and microwave dispersion are described. The temperature variation of different vibration modes is explored. It is shown that the lowest resonant frequency is always associated with the ε_4 shear mode.

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Devitrification of the $Li_2O–7×GeO_2$ glass

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Lithium heptagermanate crystal $Li_2Ge_7O_{15}$ (hereafter LGO) is of interest due to ferroelectric phase transition at T_C = 283 K. The authors of [1] have shown that thermal treatment of LGO glass allows to obtain glass- ceramic materials with crystallites in nano meter range. Study of the ferroelectric phase transition in LGO nanostructured glass-ceramic seems to be promising.

LGO in glass state was obtained by fast quenching of stochiometric compound $Li_2O–7×GeO_2$ [1]. On heating of LGO initial glass, two exothermic peaks were observed on DSC curves at T_1=838K and T_2=918K (20K/min heating rate) [2]. In order to elucidate the origin of the DSC peaks, the LGO glass- ceramics have been heat treated and obtained in three states: – the samples *a* in initial glass state; – the samples *b* of intermediate composition, obtained by heating of glass up to 868K between T_1 and T_2 and further cooled to room temperature; – and the samples *c* treated by heating of glass up to temperatures above T_2. X-Ray diffraction study (CuKα radiation) has shown that the *a* samples have homogeneous glass structure. The samples of *b*-series consist of $Li_2Ge_7O_{15}$ and $Li_6Ge_8O_{19}$ crystallites (fig.1) in accordance with [3, 4]. The samples *c*, overheated above the temperature T_2 of the second DSC peak, fully consist of $Li_2Ge_7O_{15}$ crystallites [3].

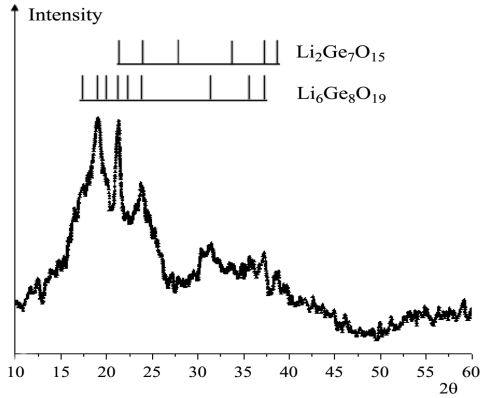

Fig.1. X-ray diffraction pattern of the sample *b*

X-Ray study allows to conclude that devitrification of the $Li_2O–7×GeO_2$ glass occurs in two stages. At first, on heating above T_1 the nuclei with $Li_6Ge_8O_{19}$ structure arise, and then above T_2 a whole samples volume crystallizes to LGO structure. This conclusion is in agreement with the results of conductivity σ measurements in *a*, *b* and *c* samples [1]. It has been shown that σ in *b* samples in one order exceeds conductivity of *a* samples and in two orders exceeds σ in the polycrystalline *c* samples. It is known, that conductance of $Li_2O–x×GeO_2$ compounds is mainly determined by interstitial lithium ions transport [5]. Therefore, high conductance of *b* samples [1], can be attributed to nucleation of $Li_6Ge_8O_{19}$ crystallites with high relative content of Li ions.

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Ceramic - ferrite composites of based on PZT type ceramic powder

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A ceramic-ferrite composites based on PZT powder have been obtained in presented work. The main aim of combination of ferroelectric and magnetic powders was to obtain material showing both electric and magnetic properties. Ferroelectric ceramic powder (in amount of 90%) was based on the doped PZT-type solid solution while magnetic component of the composite was nickel-zinc ferrite $Ni_{1-x}Zn_xFe_2O_4$ (in amount of 10%). The synthesis of components of ceramic-ferrite composite was performed using the solid phase sintering. Final densification of synthesized powder has been done using free sintering.

For obtained ceramics the XRD, the microstructure, EDS, dielectric, magnetic, internal friction and electrical hysteresis loop investigations were performed. Obtained results shown the correlations between the magnetic subsystem and the electrical subsystem of the composite ceramic - ferrite. Such properties of obtained composites give the possibility to use them in memory applications of new type.

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Relaxation currents in morphotropic region of $Pb[(Fe_{1/3}Sb_{2/3})_xTi_yZr_z]O_3$ ferroelectric ceramics

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PZT ferroelectric ceramics exhibits good dielectric, piezoelectric and piroelectric properties, and potential technical applications need its accurate electrical characterization. The complex perovskite-type compound $Pb[(Fe_{1/3}Sb_{2/3})_xTi_yZr_z]O_3$ with x + y + z = 1, x = 0.1 and y = 0.43 – 0.47 has been obtained by the $Fe_{1/3}Sb_{2/3}$ cation modification. Previously, dc and ac conductivities of this compound have been studied [Phase Transitions. 2009, 82: 899-909 and Ferroelectrics. 418, 2011: 52-99]. Now, the studies on the dielectric relaxation currents in morphotropic regions are presented for samples with y = 0.44 –46.

The measurements have been performed at three poling fields, i.e. (a) 0.02kVcm^{-1} that is much lower than the coercive force (8kVcm^{-1}), (b) 10kVcm^{-1}, i.e. above the coercive force and (c) much higher fields (20kVcm^{-1}). There were measured transient polarization and depolarization currents. For a low poling field, these currents do not differ from each other but for higher fields the difference increases with increasing poling field.

Time dependence decaying currents can be expressed in the form of the two-power law:

$$J(t) = \frac{A(T)}{\left(\frac{t}{\tau_p}\right)^n + \left(\frac{t}{\tau_p}\right)^m} \tag{1}$$

The exponent n < 1 corresponds to short time limit and 1 < m < 2 to long time one. The relaxation time τ_p corresponds to the region where the loss peak frequency ω_p appears. This expression is well known as Jonscher, Dissado and Hill universal dielectric response function. The analysis of depolarization current data obtained at various temperatures (298 – 473 K) show that relaxation time τ_p varies exponentially with temperature:

$$\frac{1}{\tau_p} = \frac{1}{\tau_0}\exp\left(-\frac{E}{kT}\right) \tag{2}$$

The activation energies calculated for samples with y = 0.44, 0.45 and 0.46 equals to 0.26, 0.24 and 0.22 eV, respectively. These energies differ only slightly from the activation energies calculated from the temperature dependence of conductivity at low temperatures presented in an earlier paper [Ferroelectrics. 1994;154: 247-252]. The defect dipole $\left(Fe_{TiZr} - V_{\ddot{O}}\right)$ complex and the double minimum Dissado-Hill potential models are proposed to explain the observed relaxation behavior in $Pb[(Fe_{1/3}Sb_{2/3})_xTi_yZr_z]O_3$ ferroelectric ceramics.

Ferroelectric 8/65/35 PLZT:Nd^{3+} ceramics as photonic applicable material

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The optical properties of Nd^{3+} ions in the host matrices such as transparent glass-ceramics depend on chemical composition, heat treatment conditions and preparation methods [1]. As it was reported for PLZT:Nd^{3+} ceramics, three luminescence bands are located in the near-infrared region [2]. They correspond to $^4F_{3/2}$ - $^4I_{9/2}$ (890 nm), $^4F_{3/2}$ - $^4I_{11/2}$ (1060 nm) and $^4F_{3/2}$ - $^4I_{13/2}$ (1330 nm) transitions of Nd^{3+}. In the presents work optimal conditions of 8/65/35 PLZT:Nd^{3+} preparation by MOM technique as well as activator concentration were determined in relation to photonic applications. Our study gives a detailed account of the relationships between doping and preparing conditions on the basic physical and dielectric and optical properties of obtained ceramic materials.

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Vibrational spectroscopic properties of a $[C(NH_2)_3]_4Cl_2SO_4$ ferroelectric crystal containing guanidinium cation – an experimental and theoretical study

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Tetraguanidinium dichloro-sulfate crystal, $[C(NH_2)_3]_4Cl_2SO_4$, abbreviated as $G_4Cl_2SO_4$ was investigated. The sequential phase transitions [PTs] have been found in the crystal. At room temperature the compound belongs to the orthorhombic space group $Cmc2_1$ [1], numbered as III, which is a ferroelectric one. On ascending temperature it shows two successive phase transitions of the first order at 353 K to the intermediate orthorhombic phase [1] numbered as II and 357 K to the paraelectric tetragonal phase [1] numbered as I, respectively. On descending temperature it shows only one PT, at 354 K, from the phase (I) to the phase numbered as II [2]. The vibrational infrared spectra of powdered $G_4Cl_2SO_4$ crystal in Nujol and Fluorolube mulls were studied in the wide range of temperature, from 298 K to 377 K. The temperature changes of wavenumber, width, centre of gravity and intensity of the bands were analyzed to clarify the molecular mechanism of the phase transition. It was shown that the low-(room) temperature phase is the same as the phase (II). Information about hydrogen bonds was obtained. The time dependence of IR vibrations in the phase II was observed and it is connected with slow transition III→II [2].

Theoretical calculations were made based on Density Functional Theory (DFT), with the B3LYP method using 6-311 + G(df,dp) basic set. Calculated normal vibrational modes of the molecules, their frequencies and intensities were compared with these recorded in experiment.

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Dielectric properties of PLZT-x/65/35 (2≤x≤13) under mechanical stress, electric field and temperature loading

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We investigated the influence of uniaxial pressure (0-1000 bars) applied parallely to the *ac* electric field on dielectric properties PLZT-x/65/35 (2≤x≤13) ceramics. It was revealed significant influences of the external stress on these properties. Applying uniaxial pressure leads to a change of the peak intensity of the electric permittivity (ε), of the frequency dispersion as well as of the dielectric hysteresis. The peak intensity of ε becomes diffused/sharped and shifts to a higher/lower temperatures with increasing the pressure. It was concluded that applying uniaxial pressure induces similar effects as increasing the Ti–ion concentration in PZT system. We interpreted our results based on the domain switching processes under the action of combined electromechanical loading.

Raman study of polarization switching in PMN-PT single crystals

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Large electromechanical coupling constant, piezoelectric coefficient and strain level of poled PMN-PT single crystals have attracted lots of interest [1, 2]. Recently, we have studied behaviour of these crystals under bias electric field up to 1kV/mm.

In particular, polarization switching of PMN-PT single crystals has been studied by dielectric and Raman spectroscopy measurements. In this contribution we shall focus on the unusual switching mechanism observed in 0.68PMN-0.32PT single crystals.

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Pre-transitional effects in well known ABO_3 perovsites

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Pre-transitional instabilities in oxidic ferroelectric ABO_3 perovskite single crystals (in a form of local polar regions) have been theoretically predicted to appear in temperature range (Tc, Tc+1.1*Tc). It was already experimentally proved for $BaTiO_3$ single crystals, in which ferroelectric phases evolve below Tc, by the electric permittivity, electrostrictive deformation, Brillouin scattering and birefringence measurements. Up to know such pre-transitional instabilities have not been investigated for single crystals with the antiferroelectric or ferroelastic transitions. Hence, preliminary data will be presented for $PbZrO_3$ crystal, which reveals - except a narrow temperature range below TC - the antiferroelectirc properties.

Moreover, for $SrTiO_3$ crystal - which has been intensively investigating for tens of years - birefringence above phase transition at 104K (of the order of 10^{-5}) has been detected. This brings information about an origin of instabilities different than in the case of barium titanate and lead zirconate. These instabilities are considered as rotational dynamic clusters that compete with precursor effects stemming from the polar soft mode and appear on different length scales as compared with $BaTiO_3$.

Absorption spectra of $TlIn(S_{1-x}Se_x)_2$ single crystals under hydrostatic pressure.

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$TlInS_2$-type crystals are layered ferroelectric semiconductors with an incommensurate phase and a complex sequence of structural phase transformations. It should be noted that in the (p, T) phase diagram of $TlInS_2$ crystal pressure-induced structural transformations to non-polar phases are observed. Besides, a Lifshitz-type point is possibly observed in the (x, T) phase diagram of $TlIn(S_{1-x}Se_x)_2$ solid solutions at $x = 0.05$ [1].

We report on the studies of temperature and pressure dependences of absorption spectra for $TlIn(S_{1-x}Se_x)_2$ ($x < 0.15$) samples in the temperature range of 170–300 K. $TlIn(S_{1-x}Se_x)_2$ single crystals were obtained by Bridgman technique. The measured long-wavelength tails of the optical absorption in $TlIn(S_{1-x}Se_x)_2$ obeys the Urbach rule. On the temperature behavior of absorption edge for current samples are shown different convergent groups of lines $\ln\alpha(h\nu)$. Characteristic parameters such as steepness parameter $\sigma(T)$, Urbach's energy $E_u(T)$, and effective phonon energy ($h\nu_p$) were obtained.

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Using the crystalline disk method for measurements of piezooptic coefficients. The case of $LiNbO_3$ crystals

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In this work suggested a highly precise method for determining piezooptic coefficients. The technique is based on creating 2D distribution of mechanical stresses in a crystalline disk compressed along its diameter, which is known in advance.

Using the relevant theoretical relations that describe piezooptic effect in the crystals belonging to the point symmetry group 3m and specific example of crystals that belong to this point symmetry group ($LiNbO_3$), we have determined the differences of coefficients such as $\pi_{11}-\pi_{12}, n_o^3\pi_{11}-n_e^3\pi_{31}, n_e^3\pi_{33}-n_o^3\pi_{13}$.

We have proven theoretically that the above piezooptic parameters can be successfully determined after measuring the optical phase difference. Also coefficients π_{44} and π_{41} can be calculated basing on the measurements of the optical indicatrix rotation angle. The technique suggested in our work has been verified on the example of the parameter $\pi_{11}-\pi_{12}=\pi_{66}$ for the $LiNbO_3$ crystals. The mean absolute value of $\pi_{11}-\pi_{12}=\pi_{66}$ is equal to $(0.20\pm0.01)\times10^{-12}\,\mathrm{m}^2/\mathrm{N}$, so that our experimental error does not exceed 6%.

Influence of isomorphous substitution of metals on the phase transitions and dielectric properties of DMAMeS (Me=Al, Ga, Cr) ferroelectrics

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Crystals of dimethylammonium metal sulphate hexahydrate $NH_2(CH_3)_2Me(SO_4)_2\times6H_2O$ (DMAMeS, Me = Al, Ga) have been widely studied recently using different experimental methods because of their interesting physical properties and sequence of phase transitions (PTs).

In particular it has been found that DMAMeS are ferroelastic at room temperature. At T_{c2}=152 K and T_1=75 K DMAAS undergoes a proper ferroelectric and antiferroelectric phase transitions correspondingly. In a region between T_1=75 K and T_{c1}=110.5 K a coexistence of these two phases was observed. DMAGS crystal is characterized by antiferroelectric → ferroelectric (at T_{c1}=119 K) and ferroelectric → ferroelastic (at T_{c2}=136 K) PTs [1].

We present results of study of dielectric properties of the DMAMeS crystals doped with chromium in the vicinity of ferroelectric PTs within frequency range of 10^2-10^5 Hz, where the dispersion caused by the motion of domain walls was revealed.

The temperature dependences of the dielectric permittivity manifest sharp peaks at T=152.4 K for the pure DMAAS. The point of PT was found to be shifted toward T=154.5 K and T=150.5 K for DMAAS:Cr^{3+} for chromium concentration of 6,5% and 10% respectively. Doping of the DMAGS crystal with chromium (6%) causes only 1 K decrease of the ferroelectric PT temperature.

Influence of chromium doping on the ferroelectric PT temperatures can be explained by changes of dipole clusters sizes and dynamics in vicinity of the ferroelectric phase.

[1] *V. Kapustianyk*. Physics of Crystalline Ferroics with an Organic Cation. Lviv 2006, 438 p.

High-pressure studies of the dipole glass state in $CuCr_xIn_{1-x}P_2S_6$ layered crystals

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It was determined that in solid solutions $CuCr_xIn_{1-x}P_2S_6$ at concentrations $x<0.2$ and $x>0.8$ occurs a transition into ferrielectric and anti-ferroelectric monoclinic phase. In the solid solutions with $0.2<x<0.8$ the dipole glass state is formed due to the structural disorder that is induced by substitution of atoms in the cation sublattice [1].

Mixed ferro-antiferroelectric $CuCr_xIn_{1-x}P_2S_6$ are suitable objects for the study of an influence on the structural disorder of ferroelectric and antiferroelectric phase transitions and transition to relaxor glass states.

Investigation of properties of ferroelectrics under hydrostatic pressure are useful to find out microscopic mechanism responsible for the glasslike behavior.

In this work we report and discuss the influence of high hydrostatic pressure on the relaxation behavior of layered crystals $CuCr_xIn_{1-x}P_2S_6$ with different concentrations. It is shown that an increase in hydrostatic pressure leads to an increase of real and imaginary parts of dielectric permittivity in the relaxation region. At the same time the pressure increases the relaxation time and decreases the activation energy. It was also found that the transition temperature of the glassy state with higher pressure decreases.

1. Maior M.M., Motrja S.F., Gurzan M.I., Prits I.P., Vysochanskii Yu.M. DipoleGlassyState in Layered Mixed Crystals of $Cu(In,Cr)P_2(S, Se)_6$ System // Ferroelectrics. - 2008. - V. 376. - P. 9-16.

Effect of MnO_2 addition on dielectric properties of barium titanate ceramics

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The effect of doping MnO_2 on the structure, microstructure and dielectric properties of $BaTiO_3$ (*BT*) were studied. For this purpose MnO_2 – doped $BaTiO_3$ ceramics, were prepared by a conventional ceramic method. The performed EDS investigations revealed that the $BaTi_{1-x}Mn_xO_3$ *(BTM-x)* samples were perfectly sintered. They contained a little glassy phase and their grains were well shaped. The electric measurements of the samples were performed using the LCR Agilent 4284A meter and a temperature control system Quatro Krio 4.0. Temperature and frequency dependence of the dielectric permittivity, dielectric loss tangent and electric conductivity were investigated in the temperature range from 140 K to 500 K and frequency between 20 Hz and 1 MHz. It was shown that all investigated electrical parameters depend on frequency of electric field and amounts of manganese substitution. In order to better understand of the character of the phase transition in $BaTi_{1-x}Mn_xO_3$ the thermal behavior were also studied. A differential scanning calorimetry (DSC) measurement was carried out using Netzsch DSC F3 Maia calorimeter in wide range of temperature (140 K ÷ 500 K) at a heating rate of 10 K/min.

Appearance of an optical vortex under the torsion stresses in $LiNbO_3$ crystals

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It was found that the twisting of $LiNbO_3$ crystals causes a birefringence distribution revealing nontrivial peculiarities. In particular, this distribution have a special point at the center of the cross section perpendicular to the torsion axis where the zero birefringence value occurs. It has also been ascertained that the surface of the spatial birefringence distribution has a conical shape, with the cone axis coinciding with the torsion axis [1]. We revealed that an optical vortex, with a topological charge equal to unity, appears under the torsion of $LiNbO_3$ crystals. It has been shown that, in contrast to the *q*-plate, both the efficiency of spin-orbital coupling and the orbital momentum of the emergent light can be operated by the torque moment.

[1] I.Skab, Y.Vasylkiv, V.Savaryn, and R.Vlokh. JOSA A. **28**, 633 (2011).

Studying of the spin-to-orbital momentum conversion operated by electric field in $LiNbO_3$ and $Bi_{12}GeO_{20}$ crystals

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An optical conversion of spin angular momentum to orbital angular momentum (SAM-to-OAM) that appears in $LiNbO_3$ and $Bi_{12}GeO_{20}$ crystals under the effect of conically shaped external electric field due to a Pockels effect has been studied both experimentally and theoretically. We have revealed the appearance of a doughnut mode and an optical vortex in the system consisting of a right-handed circular polarizer, a sample subjected to conical electric field, and a left-handed circular analyzer [1]. It has been found that the presence of natural optical activity leads to notable decrease in the efficiency of the SAM-to-OAM conversion.

[1] Y.Vasylkiv, O.Krupych, I.Skab and R.Vlokh. Ukr. Journ. Phys. Opt. **12**, 171 (2011).

Technology and properties of PMN-PT-PS-PFN:Li the material for multilayer ceramic capacitors

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We present the technology of obtaining and the properties of multicomponent material 0.61PMN-0.20PT-0.09PS-0.1PFN:Li (PMN-PT-PS-PFN:Li). Obtained by us solid solution can be used the material for multilayer ceramic capacitors MLCC. PMN is known as a classic relaxor while the solid solutions PMN-PT exhibit the properties changing from relaxor to normal ferroelectric ones depending on the content of PT. The addition of PFN into PMN-PT decreases the temperature of final sintering what is very important during technological process of obtaining of MLCC. Pure PFN exhibits however relatively high electric conductivity which can be decreased by the addition of Li.

Two alternative methods were used for obtaining of PMN-PT-PS-PFN:Li. First was the one-step method in which final solid solution has been obtained from simple oxides and carbonates. The second method was two-step one. In two step method the intermediate compounds $MgNb_2O_6$ and $FeNbO_4$ were obtained and next mixed with PbO, TiO_2 and Li_2CO_3. Finally from such obtained powders the ceramic samples of PMN-PT-PS-PFN:Li were sintered. The XRD, microstructure, ferroelectric, dielectric and electromechanical properties have been investigated for such obtained ceramic samples. It was stated that using two step method we obtain material with lower content of unwanted non-perovskite phases. There are also significant differences in electric properties of samples from both groups.

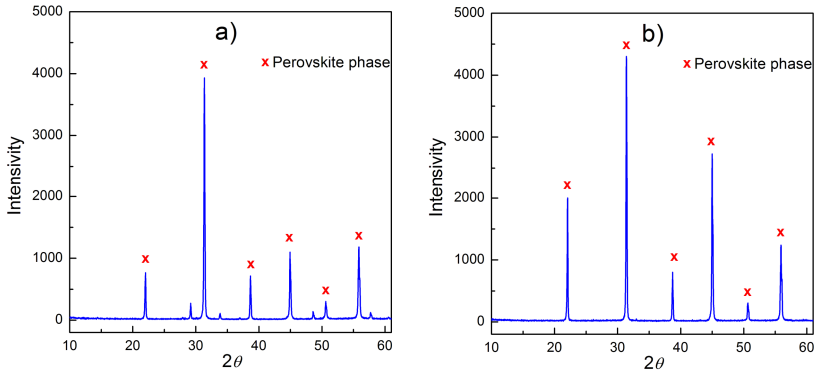

Fig.1 XRD patterns for PMN-PT-PS-PFN:Li ceramics: a) one-step method, b) two-step method

Study of the influence of uniaxial pressure on the electric behaviour $Li_{0.015}Na_{0.985}NbO_3$ ceramic

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The sodium niobate $Na^{+1}Nb^{+5}O_3$ is one of the most studied ferroelectrics materials. It has ferroelectric, antyferroelectric or paraelectric properties in different temperature ranges. Some solid solutions based on $NaNbO_3$ have ferroelectric and good piezoelectric properties.

Solid solutions oxides with the formula $Li_{0.015}Na_{0.985}NbO_3$ were synthesized by a conventional solid-state reaction. X-ray measurements showed, that the investigated compound at room temperature characterised by lattice constants: a = 0.5479 *nm*, b = 1.5523 *nm*, c = 0.5559 *nm* and volume of elementary cell V = 0.48142 nm^3. The XRD results demonstrate that the lattice parameters *a, b, c,* and the volume of the unit cell V for $Li_{0.015}Na_{0.985}NbO_3$ decreased in comparison with pure $NaNbO_3$. The performed EDS investigations revealed that the $Li_{0.015}Na_{0.985}NbO_3$ samples were perfectly sintered. They contained a little glassy phase and their grains were well shaped. The electric measuremnts of the sample were investigated using BM595 and LCR 821 meter in temperature range of 300 K - 750 K (with a cooling rate of 4 K/min) without and under axial pressure up to 110 MPa. It was shown that electric behaviour of $Li_{0.015}Na_{0.985}NbO_3$ ceramics was sensitive to the applied compressive stress. The pressure shifts the phase transitions, decreases the thermal hysteresis and diffusness of permittivity characteristics. This behaviour of the samples suggests a possibility of practical application of this material.

Uniaxial pressure action on the phase transitions of TGS admixtured crystalls

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The influence of uniaxial mechanical stresses applied along the principal crystal-physical axes on the principal values of birefringence Δn_i is studied for TGS crystals with D-serine admixture.

The general features are as follows: the Δn_i changes are proportional to temperature; the derivative $\partial \Delta n_i / \partial T$ changes its value while passing through the Curie point; the uniaxial stresses change the absolute value of Δn_i, though remain a qualitative temperature character of Δn_i unchanged, and the phase transition (PT) point is shifted under the influence of the stress.

The PT temperature decreases for the cases of σ_x and σ_y stresses, while the σ_z stress increases the PT point. The total baric displacements of phase transitions: $\partial T_c / \partial \sigma_m$ = +0.0045 and +0.0030 K/bar, for the pure and D-serine doped TGS crystals, respectively.

PT shifts have been explained by influence of temperature and stresses on the shifts of structural elements taking place for the PTs. Those slight discrepancies may be caused by both a complex structure of TGS crystals and possible irregularities of introducing the admixtures into the crystal structure. While the doped crystal is growing, the admixture enters into the structure by means of substituting one of the glicynes. The notable shift in the PT point towards higher temperatures should be apparently caused by the influence of uniaxial stresses upon the ferroelectric domains. In case of TGS crystals, the latter represent “tubes” of an oval, more frequently lens-like, section, which is stretched along the direction perpendicular to the *c* axis.

A less value of the baric coefficients for admixtured D-serine TGS crystal when compare with the pure crystal, is associated with the fact that the domains in the doped crystals had large sizes though irregular shapes and smeared borders.

The baric changes in the refractive indices of $LiNH_4SO_4$ crystals

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Lithium ammonium sulfate, $LiNH_4SO_4$ (LAS), crystallizes by evaporation in two rhombic modifications α and β. In β modifications the crystal is pseudohexagonal and has space group C_{2v}^9 -$Pna2_1$ at room temperature.

It is established that the dispersion of $n_i(\lambda)$ for mechanically free and compressed crystals is normal in the spectral range 300–700 nm and sharply increases when approaches the absorption edge. The uniaxial pressures do not change the character of the curves $n_i(\lambda)$; it is only the dispersion of $dn_i/d\lambda$ that changes ($dn_x/d\lambda$=5.19×10^{-5} nm^{-1} and 5.12×10^{-5} nm^{-1}, $dn_y/d\lambda$=5.39×10^{-5} and 5.32×10^{-5} nm^{-1}, $dn_z/d\lambda$=5.34×10^{-5} nm^{-1} and 5.31×10^{-5} nm^{-1}, near 400 nm for, respectively, a mechanically free sample and a sample under a uniaxial pressure of σ_m = 200 bar).

Using the obtained dependences $n_i(\lambda, \sigma)$ and the molar mass μ and the crystal density ρ were calculate the peak wavelengths of the ultraviolet (UV, λ_{01}) and infrared (IR, λ_{02}) absorption bands, the corresponding effective oscillator strengths and refraction R and electronic polarizability α. It is showed that a pressure of ~200 bar increases α_i on average by ~4 ×10^{-26} cm^3, which coincides in order of magnitude with the baric change in the sample volume and linear sizes along the compression.

Differentiation of Lorentz–Lorenz formula, which describes the refraction R and electronic gives the relation

$$\frac{dR}{d\sigma} = -\left(\frac{\mu}{\rho^2}\frac{n^2-1}{n^2+2}\frac{d\rho}{d\sigma}\right)_n + \left(\frac{\mu}{\rho}\frac{6n}{(n^2+2)^2}\frac{dn}{d\sigma}\right)_N .$$

It was estimate the contributions to the baric changes Ri from the term with derivatives $\partial\rho/\partial\sigma$ and $\partial n/\partial\sigma$. Using known numerical values for LAS crystals, n_i, μ, ρ, $\partial\rho/\partial\sigma_m$ and $\partial n/\partial\sigma \approx 2 \times 10^{-6}$ bar^{-1}, we obtain the geometric factor is ~32% of the total baric increment R. The first term indicates the change in the number of dispersion centers in the volume (due to the change in volume with pressure), while the second term characterizes the change in the dispersion frequency, i.e., the polarizability through the change in the chemical bond character. Thus, competition of two factors occurs under uniaxial pressure: sample compression (and, as a result, increase in n_i) and change in the interatomic bond nature.

These changes make it possible to estimate the corresponding variations in the band gap according to the Moss relation

$$n^4 E_g = \text{const},$$

which yields

$$\frac{\partial E_g}{\partial\sigma} = -\frac{4}{n}E_g\frac{\partial n}{\partial\sigma} .$$

Using the known values $\partial n/\partial\sigma$, n_i, and E_g, we find that the baric shift of the band gap is $\partial E_g/\partial\sigma \sim 4.1 \times 10^{-5}$ eV/bar. The baric shift of the effective UV oscillator turned out to be fairly large ($\partial\lambda_0/\partial\sigma \approx 0.5–2\times10^{-2}$ A/bar ≈ 15 ×10^{-5} eV/bar), which may indicate that this oscillator is in the high-energy spectral region.

Phase transitions in $Cu_6PS_5I_{1-x}Cl_x$ superionic ferroelastics

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Cu_6PS_5X (X= I, Cl) superionic conductors belong to the compounds with argyrodite crystal structure and are characterized by high values of electrical conductivity and low values of activation energy. At room temperature Cu_6PS_5X (X= I, Cl) crystals belong to the cubic syngony ($F\bar{4}3m$ space group). At low temperatures Cu_6PS_5I crystal undergoes two phase transitions (PTs), one of them being a first-order superionic and ferroelastic PT at T_I=(144-169)K, the other – a second-order structural PT at T_{II}=(269±2)K. At $T_I<T<T_{II}$ Cu_6PS_5I crystal belongs to a cubic superstructure ($F\bar{4}3c$ space group), at $T<T_I$ – to the monoclinic syngony (Cc space group). In Cu_6PS_5Cl crystal, a PT from the cubic symmetry ($F\bar{4}3m$) to the monoclinic one (Cc) at T=170 K is observed. This PT in Cu_6PS_5Cl crystal has superionic and ferroelastic characteristics simultaneously.

The isoabsorption studies have shown that an anomaly, characteristic for Cu_6PS_5I crystal near the first-order PT at $T=T_I$ is revealed only in solid solution crystals with x=0.1 and x=0.2. With further anion substitution I→Cl at x>0.2 a stepwise anomaly near the first-order PT at $T=T_I$ is totally smeared out due to the compositional disordering of the $Cu_6PS_5I_{1-x}Cl_x$ mixed crystal lattice. A similar behaviour is observed for the second-order PT at $T=T_{II}$, i.e. the typical change of the slope in the $E_g^{\alpha}(T)$ plot at $T=T_{II}$ cannot be observed in solid solution crystal due to its smearing out. Thus, in order to determine the PT temperatures at $x\geq0.4$ the polarization studies were performed. At the transition from the isotropic (cubic) to the anisotropic (monoclinic) phase of Cu_6PS_5I crystal, an appearance of optical transmission in the polarizer–crystal–analyzer system is known to be observed. Thus, polarization studies enabled us to reveal a low-temperature PT accompanied by the change of symmetry from cubic to monoclinic in $Cu_6PS_5I_{1-x}Cl_x$ solid solution crystals. Note that with the increase of Cl content at $x\geq0.4$ the temperature hystheresis for the low-temperature PT disappears what is the evidence for the PT change from the first to the second order. Besides, an essential effect of anionic substitution on the PT temperature interval was found: with the increase of chlorine content a considerable smearing of the PT is observed.

Based on the experimental isoabsorption and polarization studies, a phase x,T-diagram diagram for $Cu_6PS_5I_{1-x}Cl_x$ mixed crystals was built. With the account of two PTs present in the Cu_6PS_5I crystal and only one in Cu_6PS_5Cl, the existence of a triple point in the (x,T) phase diagram of $Cu_6PS_5I_{1-x}Cl_x$ crystals was quite predictable. This triple point is the convergence of three PT lines: (i) a second-order PT line ($T=T_{II}$) at x<0.4, corresponding to the $F\bar{4}3m \rightarrow F\bar{4}3c$ space groups changes, (ii)a first-order PT line ($T=T_I$) at x<0.4, corresponding to the symmetry change $F\bar{4}3c \rightarrow Cc$, and (ii) a second-order PT line ($T=T_{II}$) at $x\geq0.4$, corresponding to the symmetry change $F\bar{4}3m \rightarrow Cc$.

Influence of size effect on phase transitions in Cu_6PS_5I superionic ferroelastic

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Cu_6PS_5I superionic conductor at a room temperature belong to cubic syngony (space group $F\bar{4}3m$). There are two low-temperature phase transitions (PT) in Cu_6PS_5I crystal, one of which at T_{II}=(269±2) K is structural second-order PT which is accompanied by the change of symmetry $F\bar{4}3m \rightarrow F\bar{4}3c$, and the other at T_I=144–169 K is the first-order PT which is simultaneously a superionic and ferroelastic, and it is accompanied by the change of symmetry $F\bar{4}3c \rightarrow Cc$.

Cu_6PS_5I single crystrals were grown using chemical vapour transport method. The microcrystalline powder with the average grain size of 50 μm were obtained by grinding of the synthesized material in an agate mortar. Cu_6PS_5I nanocrystalline powder was obtained by ball milling the material in a stainless steel cylindrical vial with hardened steel balls, the average grain size was 24 nm. X-ray diffraction analysis has confirmed that Cu_6PS_5I lattice structure is preserved for the micro- and nanocrystalline powders, though the diffraction peaks become broader and less pronounced with the decrease in size.

Heat capacity (70-300 K) measurements were performed by VERSALAB commercial device (Quantum Design) in zero applied magnetic fields. Heat capacity was measured using the two-τ model of the standard relaxation method. The typical for second-order PT maximum at temperature T_{II}=272.6 K and the insignificant peculiarity of knee-type at first-order PT temperature T_I=147.5 K are observed on temperature dependence of specific heat capacity for Cu_6PS_5I single crystal. One can notes the absence of sharp anomaly in the range of first-order PT. We remind that in the range of first-order PT in Cu_6PS_5I crystal the stepwise changes of optical pseudogap and dielectric permittivity, the anomaly of ultrasound velocity, appearance of domain structure and birefringence are observed. However, in the range of superionic-ferroelastic first-order PT only the deviation from the regular temperature behaviour of heat capacity, typical for corresponding phase, are took place. Probable, the absence of sharp anomaly in the range of above mentioned PT caused by its rather complete nature.

At transition to microcrystalline Cu_6PS_5I with size of 50 μm both PT are shifted to the high-temperature region and are revealed at T_{II}=276.3 K and T_I=178.2 K. Futher decreasing of microcrystals size and transition to nanometric region lead to the more PT shift to the high-temperature region: PT are observed at T_{II}=287.5 K and T_I=213.6 K.

Thus, the crystal size decrease and transition to nanoscale lead to: 1) a significant increase of the first-order PT temperature by 66.1 K and second-order PT temperature by 14.9 K; 2) smearing of second-order PT; 3) decrease of the specific heat capacity value in the maximum of second-order PT by 9 $J \times mol^{-1} \times K^{-1}$.

Influence of uniaxial pressure and aging on dielectric and ferroelectric properties of $BaTiO_3$ ceramics

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The effect of uniaxial pressure (0-2000 bar) and aging on dielectric and ferroelectric behaviour of $BaTiO_3$ ceramics were investigated. Applying uniaxial pressure leads to a reduction of the peak intensity of the electric permittivity (ε), of the frequency dispersion, polarization as well as of the dielectric hysteresis. The peak intensity of ε becomes diffused and shifts to a higher temperatures with increasing the pressure. The electrostrictive coefficient Q_{11} and differential permittivity were evaluated from obtained data. We interpreted our results based on the Cochran soft-mode and domain switching processes under the action of pressure. The aging effect followed a logarithmic law and is related to the relaxation of the domain structure towards an equilibrium configuration. The aging rate was found to decrease with increasing of frequency and is result of the pinning of polarization components by defects field.

EPR spectra in Pb_2MoO_5:Cu^{2+}: Superhyperfine interaction with ligands

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EPR spectra of Cu doping ions have been studied in Pb_2MoO_5 crystal which is promising for applications in acousto-optic devices. Monoclinic Pb_2MoO_5 single crystals (space group symmetry C_{2h}^3) were grown from the melts by Czhokhralskii method. EPR spectra were registered by using of serial EPR spectrometer operating in X- frequency band. EPR spectra testify for Cu^{2+} centres in $^2D_{5/2}$ (S=1/2, I=3/2) state. The angular dependencies of EPR spectra (fig.) were described by the spin-Hamiltonian (SH) including electron Zeeman and hyperfine (HP) interaction terms $\mathsf{H} = \beta\bar{\mathbf{B}}\mathbf{g}\hat{\bar{\mathbf{S}}} + \hat{\bar{\mathbf{S}}}\mathbf{A}\hat{\bar{\mathbf{I}}}$. At room temperature **g** and **A** tensors are nearly axial with the main values: g_X=2.058±0.001, g_Y=2.055±0.001, g_Z=2.349±0.001 and A_X=(11±2), A_Y=(22±5), A_Z=(130±1) in 10^{-4} cm^{-1} (the values for ^{63}Cu). The principal magnetic axis $\bar{\mathbf{Z}}$ coincides with intersection line of (010) and (-201) planes, whereas $\bar{\mathbf{Y}}$||[010].

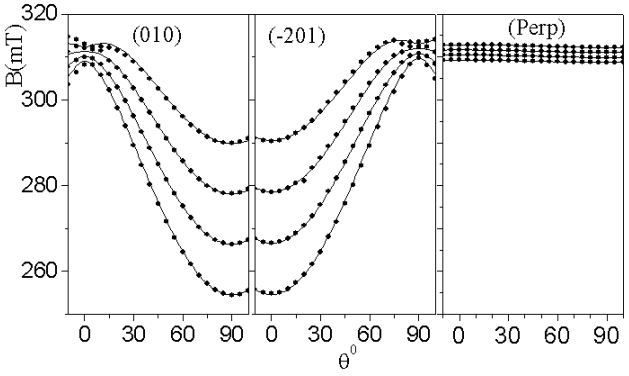

Fig. Angular dependencies of the lines positions of Cu^{2+} HP quartet in Pb_2MoO_5. Circles represent the experimental data for ^{63}Cu isotope, solid lines are calculated on the basis of SH with parameters given in the text

Each component of Cu^{2+} HP quartet shows an additional splitting that attributes for superhyperfine (SHP) interaction of Cu^{2+} electron spin S with the nuclear spins I^L of surrounding isotopes ^{207}Pb (I^L=1/2, natural content 22.6 %). SHP structure of EPR spectra is described by adding to SH of the corresponding term $\sum_i \hat{\bar{\mathbf{S}}}\mathbf{A}^{L_i}\hat{\bar{\mathbf{I}}}^{L_i}$ (i=1,…4). Analysis of the SHP line contour and directions of the magnetic axes of SHP tensor $\mathbf{A^L}$ allow to suppose that Cu^{2+} centers are located in the interstitial positions within structural cavities. Hence doping with Cu introduces extra positive charge into Pb_2MoO_5 lattice and reduces content of own positively charged defects, such as oxygen vacancies. EPR data allow to expect sufficient influence of Cu impurity on electrical and optical properties of Pb_2MoO_5.

Phase diagram and domain structure of the $Rb_{2x}Tl_{2(1-x)}Cd_2(SO_4)_3$ solid solutions

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The x, T – phase diagram for the $Rb_{2x}Tl_{2(1-x)}Cd_2(SO_4)_3$ solid solutions have been obtained from measurements of temperature dependences of the birefringence and from observations of the domain structure. Ferroelastic domain structure and movement of phase boundaries have been studied in the course of phase transitions in $Rb_{2x}Tl_{2(1-x)}Cd_2(SO_4)_3$ crystals [1]. We have revealed the two different scenarios of the ferroelastic phase transition in langbeinites:

(1) At the direct phase transition with the symmetry change 23*F*222, the domain structure most often appears in the form of heterophase structure, i.e. a sandwich-like structure consisting of layers of ferroelastic domains and paraelastic phase. The two types of conjugated domain walls can appear in this process:

(a) a pair of conjugated walls with the {110} orientation. The orientation of these walls coincides with the orientation of domain walls in the other ferroelastic langbeinites. It is explained in terms of residual walls existing between enantiomorphous twins that appear due to hypothetical phase transition with the symmetry change $\bar{4}$3m*F*23;

(b) a type of domain walls that play simultaneously a part of phase boundaries. There is a pair of these conjugated walls, with the orientation deviating from the {110} planes. The value of the deviation angle depends on the orientation minimum of elastic energy of the phase boundary. These phase boundaries have the same orientation as the domain walls inclined with respect to the {110} planes.

(2) At the indirect phase transition into ferroelastic phase (23*F*2*F*1*F*222), the crystal is usually transformed into single-domain state. The phase boundary movement appears during this phase transition, which testifies a first-order character of the phase transition. Then the phase boundary has either the exact {110} orientation or deviates from this orientation by the angle of ~10°. The orientation of the phase boundary is determined by the minimum of the density of elastic non-compatibility energy between the high-temperature phase and the ferroelastic phase.

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Field and deformation effects in quasione-dimensional CsD_2PO_4 type ferroelectrics with hydrogen bonds

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The modified proton ordering model of quasi-one-dimensional ferroelectric compounds with hydrogen bonds with taking into account linear on strains ε_i and ε_5 contributions into the energy of the proton system is proposed. On the basis of this model within the two-particle cluster approximation with taking into account short-range and long-range interactions, longitudinal electric field, and hydrostatic pressure $p=-\sigma_i$ we have calculated the thermodynamic potential. By minimizing it, we obtain a system of equations for strains ε_i and ε_5 and for the order parameter. Using these equations, the longitudinal dielectric permittivity of mechanically free and clamped crystals, coefficients of piezoelectric strain and stress, elastic constant at constant field are calculated. The molar entropy and heat capacity, associated with the proton system, are calculated by differentiating the thermodynamic potential.

In the framework of D.M.Zubarev nonequilibrium statistical operator method with taking into account dynamics of strains, a dynamic dielectric permittivity for both mechanically clamped and free crystals and relaxation times are found. Phenomena of crystal clamping by high frequency electric field, piezoelectric resonance, and microwave dispersion are described. A thorough numerical analysis of dependences of the calculated characteristics on the theory parameters is carried out. A set of these parameters for partially deuterated ferroelectrics, which allows to properly describe the available experimental data, is found.

The effects of the longitudinal electric field and the influence of hydrostatic and uniaxial pressures on the physical characteristics of partially deuterated crystal are studied. A good quantitative description of the corresponding experimental data by the proposed theory is obtained. It is determined that the considered modification of the model of quasi-one-dimensional ferroelectrics practically does not influence their spontaneous polarization, heat capacity, and longitudinal static dielectric permittivity, but leads to appearing of piezoelectric and elastic characteristics.

X-ray photoelectron spectroscopy and first-principles analysis of electronic structure of $Sn_2P_2S_6$:Ge ferroelectrics

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For $Sn_2P_2S_6$ ferroelectrics by first-principles calculations an analysis of the P_2S_6 cluster electronic structure and their comparison with crystal valence band in paraelectric and ferroelectric phases has been done and the origin of ferroelectricity has been outlined [1,2]. It was established that the spontaneous polarization follows from the stereochemical activity of the electron lone pair of tin cations that is determined by hybridization with P_2S_6 molecular orbitals. Increase of the chemical bonds covalence and their rearrangement are related to the valence band changes at transition from paraelectric phase to ferroelectric one.

Energetic levels and charge density redistribution together with structure relaxation were calculated [1] for tin vacancies acceptors states and for sulfur vacancies donor states in $Sn_2P_2S_6$ crystals. Taking into account of named donors and acceptors and with consideration of small electron polarons at Sn^+ cations and small hole polarons at S^- anions, the semiconducting and nonlinear optic properties of these crystals with deviations from stoichiometric content were explained [3].

X-ray photoelectron spectra of the valence band and core levels of $Sn_2P_2S_6$ crystals were investigated in the energy range 0 to 1400 eV for both paraelectric and ferroelectric phases. Ab-initio calculated values of the binding energies are close to the experimental ones [4]. Observed structure of the valence band also coincides with theoretical calculations [1,2].

Influence of Ge impurity on the core level binding energies and the electronic structure of the valence band of $Sn_2P_2S_6$ ferroelectric crystals was investigated by X-ray photoelectron spectroscopy together with electron spectra calculations in the framework of local density approximation of Density Functional theory. It was found that such impurity improves stereoactivity of the cation sublattice that is related to the ferroelectric phase transition nature. This founding agrees with rise of the ferroelectric phase temperature region at germanium introducing into crystal lattice.

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Impedance studies of sol-gel derived (Ba,La)TiO_3 ceramics

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Barium titanate has been investigated extensively because of scientific interest as well as various applications to electronic devices. Partial substitution of either Ba ions or Ti ions is often employed to modify the nature and temperature of the paraelectric-ferroelectric transition for particular application. In the present research $BaTiO_3$ was added as a shifter in order to move the Curie point of $BaTiO_3$ to lower temperatures. The $(Ba_xLa_{1-x})Ti_{1-x/4}O_3$ (BLT) amorphous gel was prepared by sol-gel process and calcined in the furnace to synthesize BLT nanopowder exhibiting the mole fraction $0.001 \leq x \geq 0.005$. The fine BLT ceramics was densified and sintered by free sintering method.

The electrical properties of (Ba,La)TiO_3 materials were studied by impedance spectroscopy. It is an effective characterization method for investigation of many ceramics systems including the ferroelectric systems. It was employed to analyze the properties of the intergranular and interfacial regions, their interrelations, their temperature and frequency dependences and the dc and ac phenomena in order to separate the individual contributions of electrode effects, bulk effects and the interfaces in the frequency domain from the total cell impedance. The equivalent circuit method was applied to fit the experimental data. The impedance analyzer of Quadtech 1920-type precision LCR meter was employed and measurements were carried out during heating up and cooling down.

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Optical anisotropy and birefringence of $K_{1-x}Rb_xSc(MoO_4)_2$

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Mixed $K_{1-x}Rb_xSc(MoO_4)_2$ crystals belong to a family of the trigonal double molybdates, compounds which have attracted a great deal of interest in recent years because of their simple structure and ability to undergo ferroelastic phase transitions. In $KSc(MoO_4)_2$ three structural phase transitions leading to ferroelastic phases of monoclinic symmetry are observed [1, 2]. For the low concentration of rubidium (x=0.03) the sequence of phase transitions resembles that revealed in pure $KSc(MoO_4)_2$ [3,4]. However for x=0.1 and 0.2 only one phase transition is observed down to the liquid nitrogen temperature [3,4]. Optical microscopic observation has revealed that the phase transition in mixed crystals is characterized by a change from uniaxial to biaxial upon cooling and appearance of ferroelastic domains.

The contribution presents results of the spontaneous birefringence measurements in the $K_{1-x}Rb_xSc(MoO_4)_2$ crystals using the Senarmont method. The temperature dependence of the birefringence Δn has been measured for the light propagation direction along the c-axis between 77 and 300 K. The disposition of optical indicatrix principal axes has been determined in the ferroelastic phases of all crystals under investigation. It has been shown that $\Delta n(T)$ is given by a relation $(Tc-T)^{\alpha}$ where the value of α changes with the concentration x. The last results are compared with the temperature dependence of the splitting of the EPR lines as found upon transition to the ferroelastic phase in these crystals [4].

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Special points on the x,T-phase diagram of $Sn_2P_2(Se_xS_{1-x})_6$ ferroelectrics

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We have studied optical and acoustic properties of $Sn_2P_2S_6$ and $Sn_2P_2(Se_{0.28}S_{0.72})_6$ ferroelectrics in order to verify the presence of a Lifshitz point on the concentration–temperature phase diagram of $Sn_2P_2(Se_xS_{1-x})_6$ solid solutions.

We have obtained temperature dependences of acoustic wave velocities and calculated respective values of elastic constants for both $Sn_2P_2S_6$ and $Sn_2P_2(Se_{0.28}S_{0.72})_6$ crystals. On the basis of these data we have constructed cross-sections of acoustic velocity surfaces by crystallographic planes for $Sn_2P_2(Se_{0.28}S_{0.72})_6$ crystals.

We have calculated critical exponents for the elastic stiffness coefficients temperature dependences as well as for the birefringence derivatives of $Sn_2P_2S_6$ and $Sn_2P_2(Se_{0.28}S_{0.72})_6$ crystals. Critical exponents of birefringence derivatives are equal to 0.41 for $Sn_2P_2S_6$ crystals and 0.48 for $Sn_2P_2(Se_{0.28}S_{0.72})_6$ crystals. The corresponding values for elastic stiffness coefficients temperature dependences are −0.44 and −0.47. So one can conclude that the thermodynamic conditions of $Sn_2P_2S_6$ crystals are very close to the thermodynamic conditions of a tricritical point, while $Sn_2P_2(Se_{0.28}S_{0.72})_6$ crystals meet these conditions.

We have also studied experimentally temperature behavior of the birefringence and the optical indicatrix rotation angle. According to the results of these studies $Sn_2P_2(Se_{0.28}S_{0.72})_6$ crystals are in the conditions of a tricritical point. Phase boundary movement was not observed at the temperature of the phase transition. Splitting of the phase transition was not found. It was shown that the most probable Se concentration at which the phase transition is splitting is above ~ 0.4. It was also shown that the phase transition splitting point could be described as a triple point, which is very close to a Lifshitz point. Thus two critical points should exist on the phase diagram of $Sn_2P_2(Se_xS_{1-x})_6$ solid solutions, namely a tricritical point and a triple one.

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Comparison of polarization switching in ferroelectric TGS and relaxor SBN single crystals.

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The mechanism of polarization switching in ferroelectrics has been intensively discussed in recent years, due to potential use of ferroelectric thin films in non-volatile memory elements and a broad range of electronic and optical devices [1]. In this report the comparative experimental analysis of the switching process in ferroelectric triglycine sulphate (TGS) and relaxor strontium barium niobate ($Sr_{0.61}Ba_{0.31}Nb_2O_6$; SBN:61) have been performed. Despite its complicated chemical and crystallographic form, TGS exhibit a wide range of features indispensable for the understanding of a very basic features of the mechanism of polarization switching [2]. Compared to conventional TGS, a unique property of relaxor SBN is the appearance of a very broad and frequency-dependent dielectric anomaly, near the ferroelectric phase transition [3]. The dielectric properties of relaxors can be attributed to the development of a quenched random fields, associated with the compositional/ structural disorder [3]. Microscopic studies of the switching process in conjunction with electric measurements , allowed as to establish a relationship between local properties of the domain dynamics and macroscopic responses such as polarization hysteresis loop , switching current and dielectric permittivity measurements . The microscopic features of 180 degree domain wall dynamics, in low electric fields, were investigated by nematic liquid crystal method.

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Equilibrium states of one-dimensional hydrogen-bonded proton conductor.

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We study the equilibrium states of one-dimensional hydrogen bonded proton conductor described with the orientational-tunnelling model that takes into account two-stage mechanism of proton transfer (according to Grotthuss) and short-range interaction between protons. This model can be applied to the subclass of superionic crystals where protons move quasi-one-dimensional chains. With exact diagonalization teqnique we calculate one-particle spectral densities for the finite cluster and analyze the conditions of appearance of the various states of the system, including charge density wave like state (where proton ordering is similar to the one observed in ferroelastic phases) and the state similar to superfluid (SF) phase (that can be analogues to superionic one). The corresponding diagrams of states are built and discussed.

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