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INVITED AND ORAL

PRESENTATIONS

Structure and magnetic properties of doped and undoped $Pb_3Mn_7O_{15}$

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The wide variety of physical properties in doped perovskite manganites stimulates the study of other Mn oxide families without perovskite structure, but with a mixed valence state of the Mn ions (Mn^{3+}/Mn^{4+}). The quasi 2D crystal $Pb_3Mn_7O_{15}$ is of interest because of presence of the mixed valence state in undoped case. First bulk measurements indicated a pronounced correlation between changes of electronic transport properties and variations of the magnetic system. One can expect that doping allows changing Mn^{3+}/Mn^{4+} ratio, local structure and, as result, magnetic and others physical properties. In addition, the stereoactive ions Pb^{2+} with $6s^2$ lone pair may provide the conditions for the occurrence of ferroelectric state and, possibly, for coupling between electric polarization and magnetism

We performed the study of the nominally undoped $Pb_3Mn_7O_{15}$ single crystal and ones doped with Fe, Ge and Ga ions. It was found that structure of the undoped $Pb_3Mn_7O_{15}$ in temperature range 2-300 K is orthorhombic with the *Pnma* space group. With increasing temperature the crystal transform from the orthorhombic to the hexagonal (*P63/mcm* space group) structure [1]. Around 250 K the charge ordering occurs in the crystal, when the Mn^{3+} and Mn^{4+} ions are arranged in the specific order among crystal sites [2]. $Pb_3Mn_7O_{15}$ has complicated, strongly frustrated magnetic structure. Below 160 K the short-range magnetic order starts forming within Mn layers. At $T_N=70$ K the compound reveals the transition to the long-range magnetic order. The magnetic state can be characterized as canted antiferromagnetic with moments lying in the basal plane of the crystal [3]. Below 20 K the crystal undergoes one more magnetic transition that corresponds to spin reorientation.

All the crystals doped with iron ions ($Pb_3(Mn_{1-x}Fe_x)_7O_{15}$, x=0.05, 0.1, 0.15, 0.2) belong to the hexagonal *P6₃/mcm* space group over the entire temperature range [4]. At small (x=0.05) dopant concentrations, the value of magnetization and T_N decrease insignificantly. With increasing x, the three-dimensional magnetic ordering does not occur and temperature dependences of magnetization at x≥0.1 exhibit spin-glass-like features in the low-temperature region. The exchange interactions in $Pb_3Mn_7O_{15}$ and $Pb_3(Mn_{0.85}Fe_{0.15})_7O_{15}$ were analyzed within an indirect coupling model. The latter allowed qualitative explanation of the variation in the magnetic properties of the $Pb_3Mn_7O_{15}$ single crystal upon doping with iron ions.

The structure of the $Pb_3(Mn_{0.95}Ge_{0.05})_7O_{15}$ and $Pb_3(Mn_{0.95}Ga_{0.05})_7O_{15}$ crystals is orthorhombic with the *Pnma* space group over the entire temperature range. Substitution of Mn^{4+} for Ge^{4+} ions does not result to significant change of the magnetic properties. Insignificant decrease of T_N and the effective magnetic moment occurs. On the contrary, Ga^{3+} ions exert strong influence on the magnetic properties of $Pb_3Mn_7O_{15}$. At doping, T_N decreases by 10 K, but paramagnetic Curie temperature decreases in almost half as much. The magnetic anisotropy is changed significantly too. The analysis of the exchange interactions showed that the different effect of the Ge and Ga ions is provided by the different distributions of the dopants over the nonequivalent Mn-related sites in the crystal.

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Investigation of structure peculiarities and non-linear properties of TM-doped strontium barium niobate crystals

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Strontium Barium Niobate $Sr_xBa_{1-x}Nb_2O_6$ (SBN) crystals are of interest because of their electrooptic, non-linear and thermoelectric properties. It is known that SBN solid solution is disordered as chemically as in the positions of Sr/Ba ions. Introduction of heterovalent ions into the matrix leads to further lattice disordering and strong modification of SBN physical properties. We report on the influence of chromium and nickel doping ions (TM-dopants) on the barium and strontium content in $Sr_xBa_{1-x}Nb_2O_6$ solid solution by comparing of structure peculiarities both nominally pure $Sr_{0.61}Ba_{0.39}Nb_2O_6$ (SBN:61) and SBN:61 doped with Cr^{3+}(0.005 at.%) and Ni^{3+}(0.03; 0.50 at.%). The investigated crystals were grown by modified Stepanov technique, doping ions were added into the melt in form of oxides. The crystals have been studied by X-ray diffraction methods. The chemical composition was determined taking into account the statistical distribution of strontium in two (Sr(1) and Sr(2)) sites and the vacancies in niobium Nb(2) and oxygen sites in the tetragonal tungsten bronze type structure. It was shown that doping of SBN leads to a change in the content of Ba^{2+} and Sr^{2+} ions in SBN crystal compositions and to their redistribution over the crystallographic sites. XRD analysis of crystal microparts (local regions) allows determining all possible types of point defects which may be present in the crystal structure. Full-profile Rietveld method gives an average real structure, which is more correct for the investigation of bulk properties. The full-profile Rietveld method have been used for the refinement of crystal composition, in particular, Sr content (in Sr1 sites) as well as Ba and Sr content (in Sr2 sites) in structures of undoped and TM-doped SBN crystals. Change in the structural parameters should affect the structural-dependent properties. To establish a relationship between structure, composition, and physical properties, the values of nonlinear second-order susceptibilities, $\chi^{(2)}$, were obtained based on the temperature dependences of the SHG intensity in the SBN samples studied. It should be noted that the nonlinear properties were investigated in the ground samples which were previously used for structural analysis. The investigation of second harmonic generation (SHG) of 1.064 μm laser radiation was performed on the ground SBN samples with average particle size of 2-4 μm, which corresponds to the maximum coherence length of the SHG process in SBN crystals at 1.064 μm. The single-mode single-frequency radiation from pulse-periodic YAG:Nd laser (pulse energy, 10 mJ; pulse duration, 12 ns; pulse repetition rate, 5 Hz) with Q-switch by phototropic $LiF:F_2^-$ crystal was used for SHG study. Sample investigation was carried out in the temperature range of 5-90 °C. As a result, it was found that an increase in dopant concentration in the composition of the SBN crystals, i.e. an increase and decrease in the *a* and *c* unit cell parameter, respectively, reduces the $\chi^{(2)}$ value. On the basis of established relationship between the unit cell parameters and Sr content in Sr1 sites in SBN structures it can be revealed that the $\chi^{(2)}$ value should decreases with increasing Sr content in Sr1 sites.

The results obtained by XRD and XRPD analysis, in general, do not contradict each other. It is important for the successful detection or/and confirmation of congruent melting composition, evaluation of deficiency of O sites and dopant content (based on the values and behavior of U_{iso} thermal parameter), and establishment of composition-structure-property correlations.

Magneto-Controlled Jahn-Teller Transitions in Slightly Doped Lanthanum Manganites

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By combining the results of ultrasonic spectroscopy at $0.7 - 1.0$ GHz, magnetization up to 2 T, resistivity data for $La_{1-x}Sr_xMnO_3$ ($0.1 < x < 0.18$), we constructed the phase diagrams that describes magnetic, transport, and structural properties as well as relationship between them as a function of composition and temperature ($140 - 400$ K). We demonstrated that with increasing Sr content, the Curie temperature increases linearly while the temperature of an orbital ordering transition to state with a large coherent Jahn-Teller (JT) distortion decreases ($x < 0.15$). We observed two phase-transition, which is directly connected to the JT structural distortions [1]. The upper peaks in orthorhombic phase at $T_{JT} = 270$ K ($x = 0.125$) and $T_{JT} = 180$ K ($x = 0.15$) are possible due to incoherent JT distortion to cooperative JT distorted phase at the lower temperatures. The low-lying peaks at 150 K and 120 K respectively are caused by the reverse transitions in the incoherent JT phases. When the transition to the ferromagnetic state occurs in a phase with a large cooperative JT distortion ($x \le 0.15$), a strong magneto-lattice coupling is observed. The cooperative JT distortion is dramatically reduced in the ferromagnetic phase. These observations are consistent with a competition between ferromagnetism and JT distortion that is mediated by a colossal spin-charge-lattice coupling [2]. For these JT structural phase transitions of a first order was discovered the pronounced influence of an applied magnetic field B_{ext}. For $B_{ext} = 2$ T, the upper T_{JT} decreases with increasing magnetic field; as opposite, the lower T_{JT} increases with increasing B_{ext}. Thus the pronounced magnetic field dependence of these JT phase transitions demonstrates strong relation between charge mobility, the JT effect, and magnetism in the doped manganites [3,4].

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Explosive Crystallization of PZT Microstructures by Multipulse Femtosecond Infrared Radiation

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Pulsed laser annealing is a useful approach to crystallize PZT thin films at low substrate temperatures. However, widely used excimer lasers provide only limited thicknesses (<300 nm) crystallized in this manner due to the limited thermal diffusion length of the absorbed laser pulse in the film. For some applications, such as thin film MEMS, a higher thicknesses is required. In addition, the mode structure of excimer laser spot does not allow localizing crystallization in the submicron region.

Femtosecond laser processing both inorganic and organic materials is a rapidly advancing area of ultrafast laser applications. It is dramatically different from conventional laser processing which uses either a continuous wave (CW) laser or longer micro- or nanosecond pulsed lasers. The big difference comes from the basic principle or mechanisms of laser-induced material removal processes. For long-pulsed lasers, ablation of materials occurs through melt expulsion driven by the vapor pressure and the recoil pressure of light. For ultrafast lasers, energy deposition occurs on a timescale that is short compared to atomic relaxation processes. The laser energy is absorbed by the electrons, leaving the ions cold, and only after the laser pulse is gone does thermalization take place. As a result, compared to micromachining with CW and long-pulse lasers, ultrafast lasers have several advantages: micro-sized structure creation, no collateral damage to the surroundings, clean process look, no material property change, and capability for transparent material sub-surface engraving.

In this paper, the process of the local laser heating and crystallization is studied experimentally and theoretically. TEM images taken after different durations of the annealing process allows to consider the crystallization propagation within the film under the multipulse femtosecond laser annealing. Theoretical analysis of the process and its comparison with the experimental time dependence of the SH intensity suggests the mechanism of crystallization.

We proposed to use for annealing of ferroelectric film on platinized substrate a single-mode multipulse femtosecond laser with a wavelength that falls in the transparency range of the PZT film. Contrary to excimer-laser annealing, in this case laser irradiation is absorbed by underlying platinum layer and the heating of the film is carried out by the platinum. The heating is carried out locally with a Gaussian distribution of temperature along the radius of the laser spot. The use of femtosecond laser allows diagnosing the formation of the ferroelectric phase during the process of annealing based on optical second harmonic generation (SHG), which is an effective method for studying phase transitions, including the crystallization of perovskite phase.

We found that under certain conditions crystallization occurs vary rapidly, within subseconds. This time scale allows to use while the process modeling an approach which is generally applied to description of rapid thermal annealing. However, in-plane localization of the heat source within micrometer requires in the description of the process to take into account not only temporal but spatial derivatives as well.

Microstructure, phase state and ferroelectric properties of thin PZT films at morphotropic phase boundary

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Thin films of $Pb(Zr_{1-x}Ti_x)O_3$ (PZT) solid solutions are excellent materials for applications in microelectromechanical systems and infra-red and magnetoelectric arrays [1,2]. To increase an efficiency of the device performance, it is desirable to use PZT solid solutions at morphotropic phase boundary (MPB) where the ferroelectric film parameters reach their maximum values. It is suggested that the extreme properties of the films are associated with the presence of monoclinic modification of ferroelectric phase in a fairly narrow concentration region ($x \approx 0,46$-$0,48$) at room temperature [3-4].

In the work, to study the phase state of thin PZT films at MPB we used two-stage technology – (a) RF magnetron sputtering of ceramic $Pb(Zr_{0,54}Ti_{0,46})O_3$ target onto "cold" $Pt/SiO_2/Si$-substrate and - (b) sequence annealing of the samples at high temperatures in the air to form perovskite phase. Fine variations of Zr/Ti ratio (in the range of 1-2%) were reached by changing as the distance between the substrate and the target and the working gas mixture ($Ar + O_2$) pressure. The elemental composition and microstructure of the films were studied by scanning electron microscope EVO-40 (Zeiss), atomic force microscope "Smena" and near-field microscopy. Crystal structure was analyzed with X-ray spectroscopy (DRON-7) and energy electron diffraction. To study dielectric properties an impedance meter E7-20 was used.

It is shown microstructure, phase state and physical properties of fabricated thin-film samples to depend strongly on as an annealing temperature T_{ann} (550-650 ^{o}C) as a thickness of PZT layer (300-800 nm) and Zr/Ti ratio. The phase analysis has revealed the quantitatively different coexistence of rhombohedral, monoclinic and tetragonal modifications of ferroelectric phases at room temperature which changed at heating. The correlation between phase state and dielectric properties (frequency, field and temperature dependencies of dielectric permittivity) are studied. An abnormally large dielectric permittivity observed at MPB is discussed. A method for determining inclined MPB boundary based on analysis of temperature dependencies of dielectric permittivity is evaluated.

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Magnetoelectric Effects in 3d-Ion Implanted BaTiO$_3$ Crystals

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There has been a great interest in multiferroic materials due to their attractive physical properties, multifunctionality, and wide applications in various fields of information technology, radioelectronics, optoelectronics, and microwave electronics [1]. In these materials the coupling interaction between ferroelectric and ferromagnetic substances could produce a magnetoelectric effect in which change in magnetization is induced by an electric field orthe change in electric polarization is induced by an applied magnetic field [2]. It is well known that a strong magnetoelectric effect could be realized in the composites consisting of magnetostrictive and piezoelectric substances. In this context the production and research of new composite multiferroic structures based on ferroelectric crystals with ferromagnetic inclusions is of great interest.

In this work we report on the synthesis of nanocomposite materials obtained by nanosized inclusions of magnetic 3d-metals (Fe and Co) in surface layer of barium titanate (BaTiO$_3$) ferroelectric crystal by using ion-beam implantation technique and the results of investigations of magnetoelectric effects in these structures.

The samples were prepared by implantation with 40 keV Co$^+$ and Fe$^+$ ions into (100)-face oriented single crystalline plates of BaTiO$_3$ (*CrysTec GmbH*, Germany) at the fluences between 0.5×10^{17} and 1.5×10^{17} ion/cm^2 and with ion current density of 8 µA/cm^2. The implantation was carried out at room temperature and residual vacuum of 10^{-5} Torr by using the ion-beam accelerator *ILU*-3 (Kazan Physical-Technical Institute of RAS). Then the samples have been characterized by scanning electron microscopy (SEM) with X-ray EDS element microanalysis, coil magnetometry, ferromagnetic resonance (FMR) and magnetocapacitance measurements.

Remarkable shift of FMR line has been observed on applying dc electrical field on the sample. These results revealed a strong magnetoelectric coupling between the ion-synthesized magnetic nanoparticles and the ferroelectric matrix of BaTiO$_3$. Maximal magnetoelectric constant of 14.5 Oe·cm/kV was observed in Fe-implanted BaTiO$_3$. Another evidence of magnetoelectric coupling is magnetocapacitance effects observed clearly in 3d-ion implanted plates of BaTiO$_3$. The relative changes in capacitance reached to 6.3% upon applying the magnetic field with of the strength of 2T.

Thus, our studies show that ion-beam synthesized nanocomposite BaTiO$_3$:Fe(Co) layers reveal ferromagnetic properties and strong magnetoelectric effects at room temperature that makes them useful for magnetoelectric applications.

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Computer modeling the phase states and phase transitions in 2D S=1 (pseudo)spin systems

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We made use of a special algorithm for CUDA architecture for NVIDIA graphics cards, a nonlinear conjugate-gradient method to minimize energy functional, and Monte-Carlo technique to directly observe the forming of the ground state configuration and phase transformations for the 2D anisotropic S=1 spin and pseudospin systems described by a general Hamiltonian

$$\hat{H} = \sum_{i}\left(\Delta_i \hat{S}_{iz}^2 - h_i \hat{S}_{iz}\right) + \sum_{i>j} I_{ij}^{\parallel}\hat{S}_{iz}\hat{S}_{jz} +$$

$$\sum_{i>j} I_{ij}^{\perp}(\hat{S}_{i+}\hat{S}_{j-} + \hat{S}_{i-}\hat{S}_{j+}) + \sum_{i>j} J_{ij}^{\perp}(\hat{T}_{i+}\hat{T}_{j-} + \hat{T}_{i-}\hat{T}_{j+}) + \sum_{i>j} t_{ij}\left(\hat{S}_{i+}^2\hat{S}_{j-}^2 + \hat{S}_{i-}^2\hat{S}_{j+}^2\right)$$

where $\hat{T}_{\mp} = \left\{\hat{S}_z, \hat{S}_{\mp}\right\}$. The Hamiltonian can describe both conventional spin S=1 systems with a single- and two-ion bilinear and biquadratic anisotropy in an external field and unconventional systems such as extended bosonic Hubbard model with truncation of the on-site Hilbert space to the three lowest occupation states: n = 0, 1, 2 (semi-hard-core (shc) bosons). For the shc-bosons the Hamiltonian describes the on-site (Δ-term) and inter-site ($I^{//}$-term) density-density coupling, magnetic field corresponds to chemical potential, while the last terms describe the one-particle and two-particle inter-site transfer. The technique used allowed us to examine earlier implications and uncover novel features of the (pseudo)spin phase transitions, in particular, look upon in the on-line regime the nucleation of the odd domain structure with antiphase domain walls and specific vortex-like topological defects for large square lattices, 300×300 and more. Furthermore, we could simulate different forms of impurity potentials and examine its effect on the (pseudo)spin phases. In addition to classical mean-field and Monte-Carlo methods we made use of two different quantum Monte-Carlo (QMC) technics, the standard stochastic series expansion (SSE) with loop updates and a continuous time world-line QMC for square lattices. In the talk we demonstrate great potential of the technics for visual simulation of different specific features of the (pseudo)spin systems including domain structure, domain walls and its transformation under magnetization/charge doping.

Dependence of the ESR spectrum YbMnO$_3$ on the synthesis features

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Polycrystalline samples of ytterbium manganites YbMnO$_3$ were synthesized according to two different ceramic technologies (YbMnO$_3$-I and YbMnO$_3$-II). These technologies differ in the sintering time and annealing temperature. The X-ray analysis of the synthesized manganites (I and II) showed that both samples belong to the space group P6$_3$cm and they are in single-phase state. The analysis of the XRD peak intensities demonstrated only the slight deviation in oxygen content and Yb/Mn ration between two samples. Electron spin resonance (ESR) was much more sensitive to such small differences in the crystal structure.

ESR measurements were carried out in the temperature range of 100 - 320K at the frequency of 9.48GHz. The ESR spectrum of ytterbium manganite YbMnO$_3$ (I and II) consists of one broad exchange-narrowed resonance line in all temperature range for both samples. At the same time the fitting of the ESR spectrum of YbMnO$_3$-I gives the g-factor above 2.1 (Fig. 1a), which is unusual for Mn^{3+} ions. The g-factor of YbMnO$_3$-II changes from 1.99 to 3.3 (Fig. 1b), that corresponds to middle g-factors of Mn^{3+} and Yb^{3+} ions systems, respectively. This temperature dependencies g-value and linewidth suggests the strong exchange interaction between Mn^{3+} and Yb^{3+} ions. The ESR linewidth is about 800 Oe in room temperature in both cases, that is 2.3 times less that in La$_{0.95}$Sr$_{0.05}$MnO$_3$ or in GdMnO$_3$, where the linewidth of the ESR line at room temperature is several thousand oersted, and the effective g-factor is less than 2 [1, 2]. Moreover, the ESR spectrum of YbMnO$_3$-I splits in two lines in W-band, when the ESR spectrum of YbMnO$_3$-II still consists of one exchange-narrowed resonance line. The possible reasons of the phenomenon are under discussion.
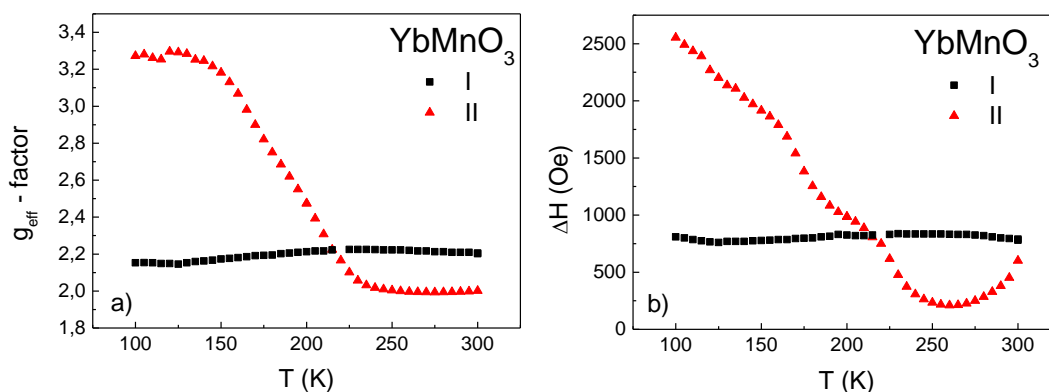
Fig. 1. Temperature dependence of g-factor (a) and ESR linewidth (b) in YbMnO$_3$

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Off-resonant Raman quantum memory for light in impurity crystals

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Developing optical quantum memories is one of the most important problems of modern quantum optics and quantum information (see the reviews [1–3]). Effective memory devices which are able to store and reconstruct quantum states of the electromagnetic field are supposed to be necessary for scalable optical quantum computing and long-distance quantum communication. The most promising approaches to the problem use the interaction of light with optically dense media. Currently, one of the most commonly discussed materials are rare-earth-ion-doped solids [4], in which the phase relaxation time at cryogenic temperatures may be as long as several hours [5]. In particular, efficient storage has been demonstrated recently in Y_2SiO_5 crystal doped by Pr^{3+} [6–8] and Eu^{3+} [9] ions.

In the present work the possibility of implementing quantum memory schemes based on off-resonant Raman interaction of a weak signal field (e.g., single-photon wave packet) and a strong control field in impurity crystals is discussed. In particular, Y_2SiO_5 crystal doped by odd Nd^{3+} or Er^{3+} isotopes is considered as the most promising material. It is shown that the schemes based on the control-field angular scanning [10, 11] or spatial chirp [12] can be implemented in this crystal via cavity-enhanced Raman interaction. In doing so, quantum storage and retrieval requires neither temporal modulation of the control field amplitude nor additional electric (or magnetic) field for modulating atomic levels.

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Thermophysical properties of multiferroic bismuth ferrite with rare-earth elements

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We research the thermal diffusion, thermal conductivity, and heat capacity of $Bi_{1-x}Re_xFeO_3$ multiferroics (Re – rare-earth element; x=0 - 0.20) in temperature intervals from 130 K to 1200 K. The substitution of a small amount of rare earth elements for bismuth leads to a change in temperature anomalies of the thermal diffusion and the thermal conductivity in an antiferromagnetic phase transition region, an increase of the heat capacity in a wide temperature range, and a temperature displacement of the antiferromagnetic transition. It is established that the temperature dependence of the excess heat capacity is related to the Schottky effect for three level states that appear as a result of structure distortions in the rare earth doped compositions.

The analysis of the results obtained in this work together with the structural and acoustic data indicates, that local distortions of the crystal lattice, which are caused by the distortions of oxygen octahedra of FeO_6 and polar shifts of $Bi^{3}+$ and $Fe^{3}+$ ions from their initial positions, constitute the main mechanism of the scattering of phonons in $BiFeO_3$ and $Bi_{1-x}Re_xFeO_3$ multiferroics. It has been found that doping with a rare-earth element leads to a significant change in the temperature anomalies of the thermal diffusion and heat conductivity near phase transitions, namely, to the smearing of the ferroelectric transition T_c and the appearance of a minimum in the region of the antiferromagnetic transition T_N.

The dominant mechanisms of phonon heat transfer in the region of ferroelectric and antiferromagnetic phase transitions have been revealed. The temperature dependence of the mean free path of phonons has been determined.

Low frequency relaxation dynamics of $Na_{1/2}Bi_{1/2}TiO_3$

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Sodium bismuth titanate $Na_{1/2}Bi_{1/2}TiO_3$ (NBT) belongs to perovskite-type materials with its two different isovalent ions Na and Bi at the A-site of the ABO_3 structure. It has recently attracted attention as environmentally friendly lead-free relaxor ferroelectrics, which exhibits very attractive piezoelectric properties [1,2]. Results of most detailed studies of the dielectric properties of NBT in a wide temperature range on medium measuring frequencies were presented in [3]. However, the interpretation of these data is discussed until now, and the question of carrying out a thorough study of the NBT dielectric response on the middle and low measuring frequency remains actual. In this report, the results of detailed study of the single crystal NBT dielectric properties in wide frequency and temperature ranges are presented.

The measurements were carried out on single crystal $Na_{1/2}Bi_{1/2}TiO_3$. Sample has the shape of thin plate of 9x8x1 mm^3. This thin plate was cut out with the normal to its plane parallel to the (001). The dielectric response was studied at frequency range 0.1 Hz - 10 MHz and temperature region 300-1000 K using ultrabroadband dielectric spectrometer Novocontrol BDS80 with Novotherm-HT cryosystem. Experimental temperature dependencies of real (ε') and imaginary (ε'') parts of dielectric permittivity of single crystal NBT for several measuring frequencies obtained upon cooling are presented on Fig.
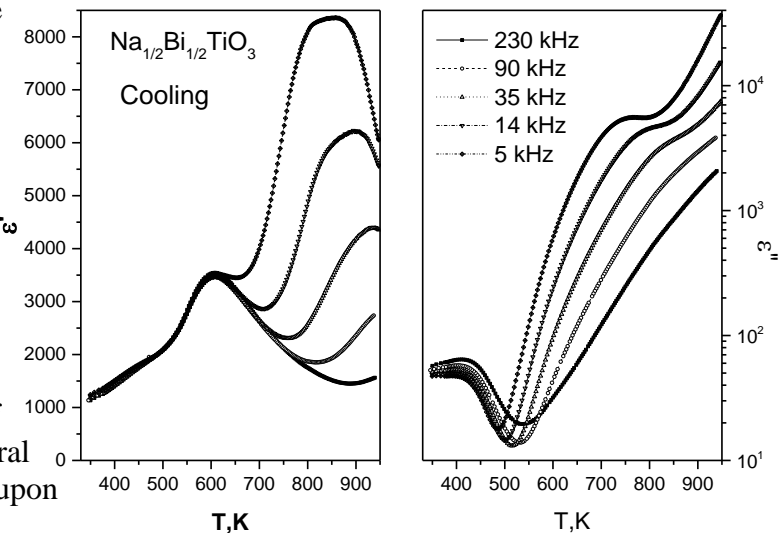
We have fitted the experimental frequency dependencies of the real and imaginary parts of permittivity by sum of the phenomenological Cole-Cole (CC) distributions of relaxation time for describing relaxation processes and term describing DC-conductivity in order to identify the relaxation processes and the temperature dependencies of their parameters. In our experimental frequency window, we were able to distinguish three relaxation processes described by CC distribution and have estimated the contribution of DC-conductivity. The temperature dependencies of the dielectric strength and mean relaxation time of CC processes were obtained. Activation energies of processes were estimated. The temperature dependence of the characteristic relaxation time of one of the processes don't described by the Arrhenius law, and obeys the Vogel-Fulcher law with T_f~370K. Thus, in the system exists freezing that previously has not been observed in NBT.

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Formation of nanodomains during the fabrication of SPE waveguides in periodically poled LiNbO₃ crystals

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The presented study of the domain structure change in periodically poled congruent lithium niobate crystals (PPLN) induced by soft proton exchange (SPE) has been done for explanation of the poor nonlinear performance observed in certain channel waveguides [1]. The complementary methods have been used for domain visualization: piezoelectric force microscopy (PFM) and scanning electron microscopy. The degradation of the nonlinear response of the waveguides has been attributed to formation of nanodomains in PPLN crystals.

The samples under investigation were prepared on a 0.5-mm-thick Z-cut congruent LN wafer, which was periodically poled by E-field technique with liquid electrodes and photoresist mask [2]. The SPE procedure was carried out in benzoic acid bath with 2.9% lithium benzoate at 300°C for 70 hours, using a SiO_2 mask on Z+ polar surface to fabricate the channel waveguides along the X axes. The planar waveguide Z- polar surface was used for determination of index profile.

The high-resolution PFM images of the static domain patterns allowed to visualize in the waveguide a dense structure of isolated nanodomains with lateral sizes down to 50 nm with aspect ratio ranging from 50 to 100 (Fig. 1) [3]. It is reasonable to assume that the nanodomains extend into the crystal bulk down to the depth ranged from 2.5 to 5 μm.
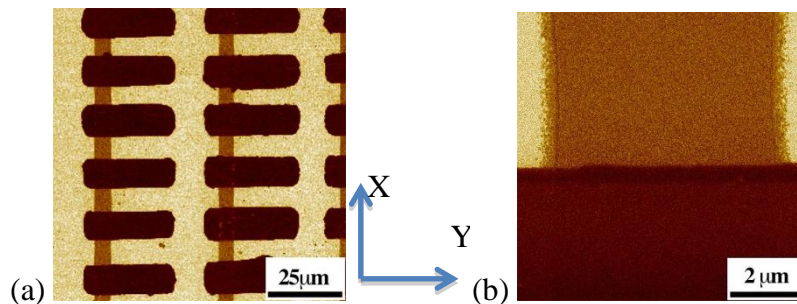
Fig.1. Domain structure of a PPLN crystal crossed by a SPE waveguide.

The formation of nanodomains can be attributed to switching under the action of pyroelectric field during cooling and gradient built-in field due to gradient of spontaneous polarization.

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Ab initio studying of spin states in the sodium cobaltates $Na_{2/3}CoO_2$

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Physics of the ordered phases in the cobaltates is a challenge for theory. The problem is to reconcile the metallic state of the CoO_2 planes strongly doped by 3d-electrons with the robust arrangement of the charge and magnetic states of the Co ions in Na_xCoO_2 ($2/3 <$ x $<$ 0.85). The compound $Na_{2/3}CoO_2$ provides a prototypical system to study this behavior. Experimentally, at low temperature, in the given cobaltate the triangular lattice $Co^{3.33+}$ separates in the non-magnetic sites $Co1^{3+}(t_{2g}^6)$ and the Kagome lattice, $Co2^{3.44+}$, accumulating the itinerant holes Co^{4+}.

The aim of the present work is the ab-initio investigation of the magnetic states of $Na_{2/3}CoO_2$ within the LDA+U approximation. The realistic distribution of the sodium ions was taken into account explicitly [1]. No imprints of the Kagome structure were detected among the low spin (LS) states with the on-site moments $\mu_{Co} < 1$ μ_B, related to the configurations $Co^{3+}(t_{2g}^6, s = 0)$ and $Co^{4+} (t_{2g}^5, s = 1/2)$.[2] However, we have identified the intermediate spin (IS) state of Co ions with pronounced Kagome structure with magnetic moments of about 1.55 μ_B, which has negligibly higher energy of about 50 meV per Co-ion at representative U = 5 eV.
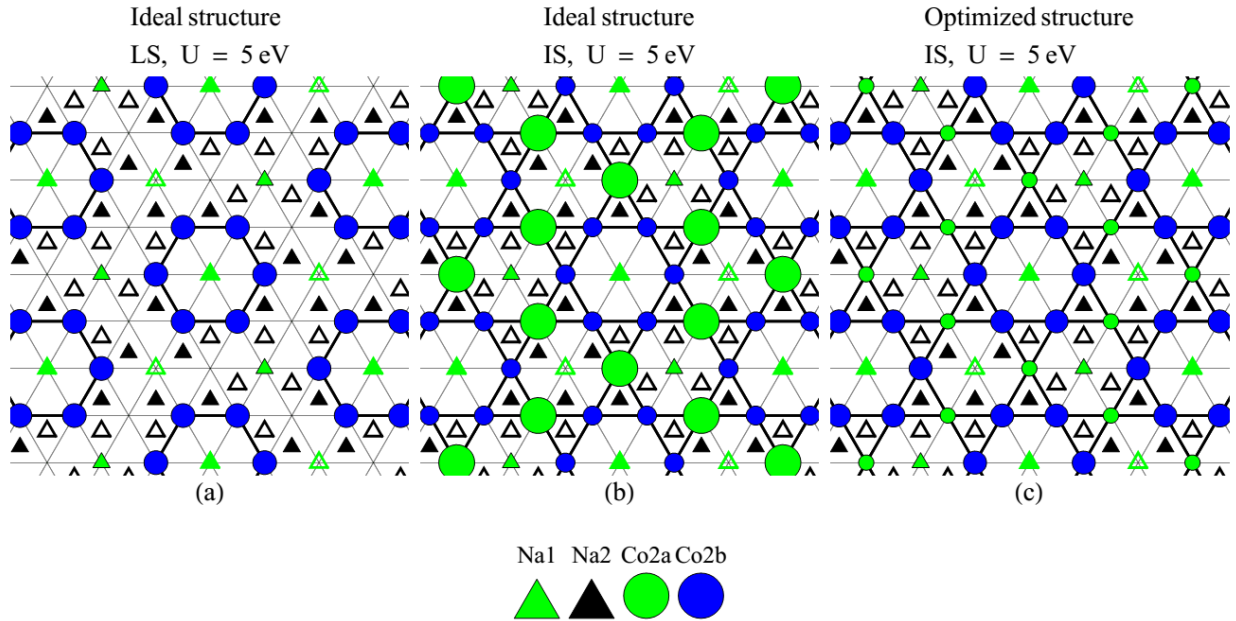
Figure 1. Spatial spin distribution in CoO_2 layer of ideal structure of $Na_{2/3}CoO_2$ in LS state at U = 5 eV (a), IS state at U = 5 eV (b) and in geometrically optimized structure in IS state at U = 5 eV (c). The cobalt radius proportional to its magnetic moment. Sodium ions above and below the CoO_2 plane are shown as filled and empty symbols.

Thus, the magnetic Kagome structure, detected in $Na_{2/3}CoO_2$ with the experiments (NMR and NQR) at radio-frequencies, could be an the indication of a proximity of the system to the transition between phases, where the collective LS- and IS-states become intermixed due to slow quantum and/or temperature fluctuations.

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Na order and Co charge disproportionation in Na_xCoO_2

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The influence of the dopant atoms on the electronic properties of conducting layers has initiated large debates in High Temperature Superconducting (HTSC) cuprates as well as in other complex layered oxides of transition elements. Whereas in many systems this influence is masked by miscellaneous effects, there are many experimental evidences that in the sodium cobaltates Na_xCoO_2 a large interplay between the Na atomic ordering and the electronic density on the Co sites occurs. In the Na_1CoO_2 compound Na atoms occupy only the so called Na2 positions (Na sites above a triangle of Co). This phase is a band insulator in which the Co sites are in filled-shell nonmagnetic Co^{3+} states. At x<1 the system becomes metallic, but only specific Na compositions can be obtained, which correspond to some Na orderings as observed by diffraction techniques. E.g. for x=0.5 the Na atoms are ordered in an orthorhombic superstructure commensurate with the Co lattice and a small charge disproportionation into $Co^{3.5\pm\varepsilon}$ (with ε<0.2) occurs on the two Co sites .

We have synthesized and characterized different stable phases of sodium cobaltates Na_xCoO_2 with sodium content 0.65<x<0.80, including one of the most stable magnetic phases of sodium cobaltates with a well defined Néel temperature of T_N=22 K. We demonstrate that ^{23}Na NMR allows to determine the difference in the susceptibility of the phases and reveals the presence of Na order in each phase. Our detailed NMR /NQR studies allowed us to reveal the peculiarities of the x=2/3 phase. We could establish reliably the atomic order of the Na layers and their stacking between the CoO_2 slabs. We found that the Na^+ order stabilizes filled non magnetic Co^{3+} ions on 25% of the cobalt sites Co1 arranged in a triangular sublattice. The transferred holes are delocalized on the 75% complementary cobalt sites Co2 which unexpectedly display a planar cobalt kagomé structure [2].

^{59}Co NMR experiments give clear evidence that such Co charge disproportionation is a dominant feature of Na cobaltates for 0.65<x<0.80 [3]. Only a small fraction (≈25\%) of cobalts are in a non-magnetic Co^{3+} charge state whereas electrons delocalize on the other cobalts. We found that the magnetic and charge properties of the Co sites are highly correlated with each other as magnetic shift K_{ZZ} scale linearly with quadrupolar frequency v_Q [2]. Such correlations can be understood as both measured values v_Q and K_{ZZ} contain terms proportional to the quadrupole moment of the t_{2g} hole density distribution which involves as a coefficient the hole concentration on the Co site. Therefore this correlations reflects the fact that the hole contenton the Co orbitals varies from site to site in both phases and the hyperfine coupling (or the local magnetic susceptibility) scales with the on site delocalized charge. Such unusual charge differentiation in sodium cobaltates calls for better theoretical understanding of the incidence of the Na atomic order on the electronic structures of these compounds.

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Studies of Heat Capacity and Thermal Expansion of $Na_{1-x}K_xNbO_3$ and $Na_{1-x}Li_xNbO_3$ Solid Solution Ceramics

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Sodium niobate $NaNbO_3$ (NN) belonging to an extensive family of oxides with perovskite-type structure stands out in the large number of structural phase transitions (PT). The diversity of the instabilities of the NN lattice accounts also for the complex polymorphism of $Na_{1-x}K_xNbO_3$ and $Na_{1-x}Li_xNbO_3$ solid solutions. Although sodium niobate and its solid solutions have been the subjects of an extremely large number of studies, no truly comprehensive investigation of thermal characteristics in the region of the phase transitions as well as the effect of thermal prehistory of a sample on the stability of the distorted phases has been performed so far. A large number of PT's observed in NN and its solid solutions are manifested by very weak anomalies of the structural, electrophysical and optical parameters, and the data on the T-x diagrams based on the results obtained in the previous studies are fairly contradictory. Thermophysical methods are characterized by a high sensitivity and provide a possibility to detect any energy variations in a sample, irrespective of their nature Thus they permit investigation of transitions driven by ferroelastic, ferroelectric and antiferroelectric transformations.

We report the results of dielectric, heat capacity and thermal expansion studies of $Na_{1-x}K_xNbO_3$ and $Na_{1-x}Li_xNbO_3$ ceramics over a wide temperature range of 100-750 K.

The dielectric, calorimetric and dilatometric studies of $Na_{0.95}K_{0.05}NbO_3$ ceramic sample revealed anomalies in the behavior of related properties associated with consecutive phase transitions in the sequence T1 – S – G – Q – N. It has been shown that hydrostatic "chemical" pressure inducing rotational distortions is one of the most essential factors governing variations in the arrangement of phase boundaries.

The data about phase transitions and T-x phase diagram of $Na_{1-x}Li_xNbO_3$ solid solutions at small Li concentrations (x=0.00 – 0.10) are more contradictory and dependent on preparation methods, samples quality and thermal prehistory. Anomalies of heat capacity C_p and thermal expansion observed in our samples with x=0.05 are characteristic either for NN or for compositions with large Li concentrations. After multiple heatings up to 800 K we observed only the main anomalies at N → Q → S or N → Q → R phase transitions, characteristic for compositions with x ≥ 0.05. Moreover, annealing at 603 K lead to splitting of the anomaly corresponding to Q → R/S phase transition. At subsequent heating after cooling, heat capacity as well as thermal expansion exhibit only one anomaly.

Different mechanisms of structural distortions in the solid solutions studied are discussed.

Charged domain walls in lithium niobate
with inhomogeneously increased bulk conductivity

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The formation of the charged domain walls (CDWs) during electric-field polarization reversal has been investigated in lithium niobate (LiNbO$_3$) single crystals with the conductivity in the surface layers increased drastically by annealing single crystalline plates in vacuum and by low energy ion irradiation.

The treatment of 0.5-mm-thick LiNbO$_3$ plates during 2–20 minutes by annealing in vacuum in temperature range from 650 to 850 °C and by Ar$^+$ ions irradiation with energy 2–5 keV have been used for increasing of the bulk conductivity due to lithium segregation and oxygen out-diffusion. It was shown experimentally that both treatments resulted in significant decreasing of external electric field in the treated volume thus leading to the domain growth in the crystal bulk. The obtained polarization reversal is characterized by formation of CDWs which position and aperture were defined by created inhomogeneity of the bulk conductivity [1]. The geometry of CDWs has been investigated by optical microscopy and confocal Raman microscopy. The significant difference of the domain geometry in vicinity of Z$^+$ and Z$^-$ polar surfaces has been revealed.

The study of formation and expansion of the CDWs allowed to separate the main stages of the domain evolution in the bulk. It was shown that kinetics of domain structure for the treated crystals represent two stages. First, nucleation on Z$^-$ polar surface with subsequent merging resulted in formation of CDWs in vicinity of Z$^-$ surface and in the bulk [2]. Second, the sideways domain wall motion with increasing of the CDWs area. The obtained effect can be used for producing of the periodical domain structure in the crystal bulk with controlled geometrical parameters which can be used for investigation of CDWs properties and for domain engineering in LiNbO$_3$ crystals.

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Electric-field control of inhomogeneous magnetic states

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The presence of inhomogeneous magnetic states dramatically modifies the magnetic, magneto-optical, and magnetic resonance properties of the sample compared to those in single domain state. Furthermore, the magnetic textures like domain walls, vortices, and skyrmions locally reduce the symmetry of the crystal and give rise to new properties such as electrical conductivity, magnetization of ferroelectric domain wall [1], and electric polarization of magnetic domain wall [2].

In this report the results of experimental studies and numerical simulations of electric-field induced micromagnetic structure transformation are presented. The voltage in the range of 500V-2kV was applied between the tip electrode and the substrate of iron garnet film. In the immediate vicinity of the tip the high electric field up to several MV/cm was generated. Micromagnetic structure transformation in this region was observed by conventional magneto-optical technique. In figure 1 the dependence of the stripe domain head displacement on the

Fig.1

DC voltage is shown. The application of AC electric field leads to the oscillation of the domain wall at the forcing frequency.
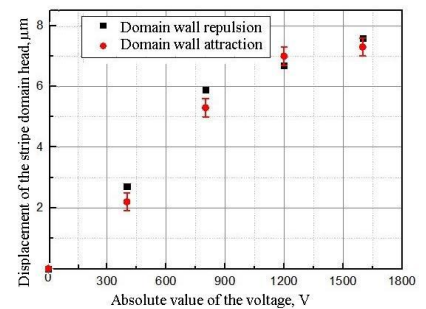
The application of the in-plane magnetic field enhance the effect of electric-field induced domain wall motion by an order of value as can be seen from figure 2.
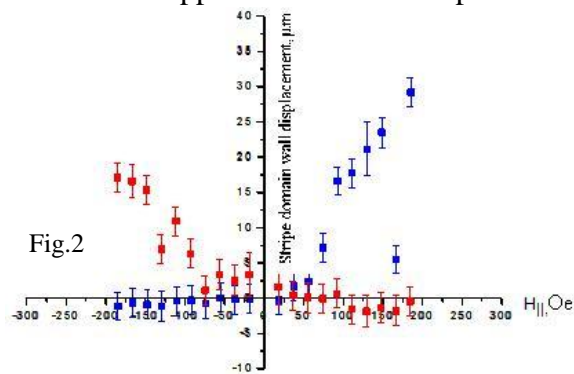
Fig.2

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Effect of twinning on magnetic properties of $Tb_{1-x}Ho_xAl_3(BO3)_4$

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In TbAl3(BO3)4 single crystal the magnetoelectric polarization has been observed for the first time with anomalous temperature dependence: electric polarization induced by in-plane magnetic field (P∥a; H⊥c-axis) which is small at low temperatures (4K) remarkably increases by almost an order of magnitude at high temperatures (15÷300K) [1]. A giant magnetoelectric polarization is found in the magnetically (nearly) isotropic $HoAl_3(BO_3)_4$. The polarization value in transverse field geometry at 90 kOe reaches 5400 $\mu C/m^2$ which is significantly higher than reported values for the field-induced polarization of linear magnetoelectric or even multiferroic compounds [2].

It is important for understanding of the mechanism of the magnetoelectric polarization formation to find out the mutual influence of holmium (Ho^{3+}) and terbium (Tb^{3+}) ions in the rare-earth subsystem. In this case, in terms of polarization, the $Tb_{1-x}Ho_xAl_3(BO_3)_4$ crystal can't be considered as the superposition of (3-x) $TbAl_3(BO_3)_4$ + x $HoAl_3(BO_3)_4$ with its own polarization vectors.

The main element of the crystal structure of rare-earth alumoborates (sp. gr. R32) is helical chains of edge-shared AlO_6 octahedra oriented along the c axis. The chains can rotate both to the left and to the right. We suggest that the polarization has the opposite signs for left and right twins, so the measured polarization value is determined by an uncompensated fraction of the left and right twins [3].

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Polarization reversal and domain kinetics in MgO doped lithium tantalate single crystals

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We present the study of polarization reversal process and domain kinetics in the novel representatives of the single crystals of the lithium tantalate family most important for high-power nonlinear optical applications: 1 mol.% MgO doped stoichiometric lithium tantalate (MgOSLT) and 8 mol.% MgO doped congruent lithium tantalate (MgOCLT) [1,2]. The polarization reversal has been studied by *in situ* visualization of domain kinetics and by analysis of the switching current using modification of the Kolmogorov-Avrami approach.

The studied MgOSLT and MgOCLT z-cut wafers were produced by Oxide corp. and Yamaju Ceramics, respectively. The hexagon domains with walls oriented along Y crystallographic directions was obtained in MgOSLT and triangle domains with walls oriented along X directions in MgOCTL. Two stages of domain structure evolution were revealed for both crystals: slow growth of the small isolated domains and motion of macroscopic domain walls by merging with isolated domains. The appearance of the residual domains resulted in qualitative change of domain kinetics scenarios in MgOCLT.

The switching current data measured during application of the rectangular field pulses were divided into three parts corresponding to the stages of domain kinetics revealed by *in situ* visualization. The analysis of the switching current was based on modified K-A approach taking into account the fast motion of the macroscopic domain walls. The characteristic times and the macroscopic domain wall velocity were extracted by fitting of the current data. The activation field dependence of the switching time has been revealed with activation fields equal to 3.2 kV/mm in MgOSLT and 4.9 kV/mm in MgOCLT. Dependence of the coercive field on the external field ramp rate dE_{ex}/dt was measured by application of the triangular field pulses. The lowest coercive field in MgOSLT (about 150 V/mm) and MgOCLT (about 1.2 kV/mm) was estimated in quasi-static limit (for dE_{ex}/dt approaching to zero). The main parameters of the switching process have been compared with other representatives of lithium tantalate family [3-5].

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Studies of Ferroelectric and Magnetic Phase Transitions in $PbFe_{0.5}B_{0.5}O_3$ (B-Nb, Ta, Sb) multiferroics and solid solutions on their base

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This presentation gives an overview of the recent results obtained in the laboratory of multiferroics of the Research Institute of Physics, Southern Federal University, in collaboration with other Russian and foreign laboratories, in studying complex multiferroic perovskites $PbFe_{0.5}B_{0.5}O_3$ (B-Nb, Ta, Sb) and some solid solutions on their base [1-16]. With the help of dielectric, piezoelectric, pyroelectric and magnetic measurements and Mössbauer spectroscopy ferroelectric and magnetic phase transitions were studied and x, T- phase diagrams of several $PbFe_{0.5}B_{0.5}O_3$ - based solid solutions were constructed. We discuss the coexistence of antiferromagnetic, spin-glass and superparamagnetic states in the systems under study, anomalies of structural and electrophysical parameters in the range of magnetic phase transitions, as well as the possibility to change the temperature of the magnetic phase transition in $PbFe_{0.5}B_{0.5}O_3$ by technological means.

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Dispersion of switching processes in ferroelectric ceramics

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A study is made of the polarization processes in ferroelectric lead zirconate-titanate ceramics (PZT) in AC electric fields with an amplitude of 840 V/mm in a frequency range of 50 to 1500 Hz. Dielectric hysteresis loops were measured by the Sawyer-Tower method simultaneously with distant temperatire control with the aid of thermal vision camera Testo–875-1. High voltage amplifier TREK 677B was exploited as a source of high AC voltage. The experimental results given below were obtained for a sample with a size of 5x5x1 mm.

On applying an AC electric field of fixed amplitude the sample initially demonstrates non-saturated minor hysteresis loops which become saturated with further exposure under field, i.e. the loop reshaping takes place. This reshaping is accompanied by a self-heating of the sample. Maximal temperature of the sample self-heating (T_{max}) was depending on the sample area.

Loop saturation was observed only for those frequency values (220 Hz and above) for which the sample heating temperature is larger than $90^{o}C$ (fig.1a). This temperature range corresponds to a sharp decrease of the coercive field of the PZT which may be observed by ordinary heating of the sample in an oven. The rate of self-heating increases with the increase of the frequency thus resulting in the shortening of the time of hysteresis loop reshaping.

The increase of the electric field frequency results in a decrease of the reversible polarization values (P_r) both for initial minor and reshaped loops (fig.1b). In the last case voltage drop at the sample is observed which is explained by the increase of the conductivity. This decrease obeys the exponential rule (fig.1c). Approximation of the experimental data making use of exponential regression with the aid of MathCad14 resulted in an analytical expression for the frequency dependence of the polarization value P:

$$P = P_s \cdot \exp(-f \cdot \tau) + P_{irr} = 0.279 \cdot \exp(-2.826 \cdot 10^{-3} \cdot f) + 0.032.$$

Here P_s is the maximal value of reversible polarization in C/m^2, P_{irr} is the irreversible component polarization, τ is the time constant in s, characterizing the exponential decay of polarization, and f is the frequency in Hz. The maximal experimentally observed P_r has a value of $0.6 \cdot P_s$. The time constant may be interpreted as $\tau = T/2 = 1/2f_{cr}$, where f_{cr} is the maximal frequency for which the full switching of the sample is possible in the given field.
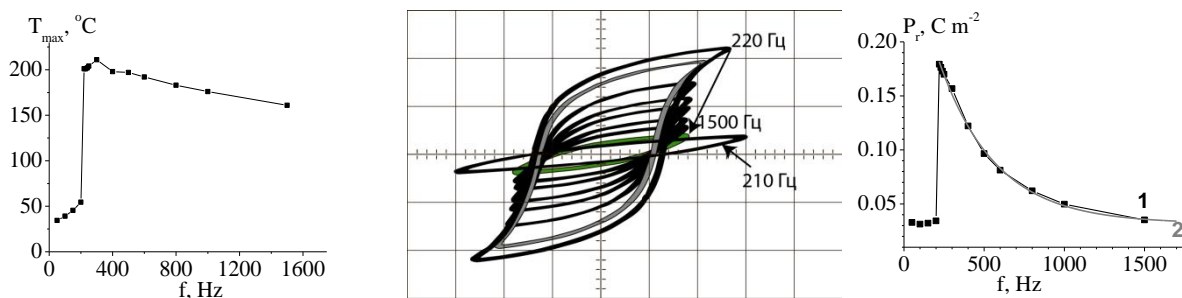
fig.1. Frequency dependence of (a) T_{max}; (b) reshaped dielectric hysteresis loops; (c) maximal reversible polarization (curve 1 – experiment, 2 – calculation). E_{amp} = 840 V·mm^{-1}

Heterogeneity of Lanthanum – Gallium Tantalate Crystals

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One of the main problems for the operation of a single crystal of $La_3Ga_{5,5}Ta_{0,5}O_{14}$ (LGT) is its heterogeneity. Optical transmission spectra and their transformations at electron irradiation and isothermal annealing have been investigated for LGT crystals nominally pure and grown in the different atmospheres (argon or argon – oxygen atmosphere with various concentrations of oxygen (2% and less 2%) and air). The crystals were grown by Czochralski method by the company Fomos-Materials.

Optical transmission, diffused reflection and scattering spectra were measured with spectrophotometer "Cary 5000 UV-VIS-NIR" in the wavelength range 250-3000 nm and attachment "DRA 2500" for diffused reflection and scattering measurements.

The polar cuts LGT samples were oriented at irradiation perpendicular to the electron beam and the irradiation doses were 10^{12} -$3 \cdot 10^{15}$ cm^{-2}. Quite different transmission spectra have been registered for the crystals after each electron dose irradiation. The electron influence was surprisingly different for crystals obtained in various atmospheres.

For the crystals grown in the argon atmosphere, the transmission spectra exhibit a weak absorption band in the range 290 nm. On the same wavelength range a wide absorption band for the crystals grown in air was observed too, but it is much stronger. The optical transmission spectra of the crystals grown in the argon with oxygen atmosphere significantly differ from the spectra of the crystals grown in argon and air. Strong absorption bands in the range 290 nm, 360 nm and 480 nm was also observed.

After electron irradiation ($1 \cdot 10^{13}$ cm^{-2}) the crystals grown in the argon atmosphere exhibit the strong absorption bands at 290 nm and 350 nm. The doses increase influences on the intensity of those bands for all investigated samples variously. As for crystals grown in the argon with 2% of oxygen the electron irradiation leads to the strong changes of the absorption band at 360 nm and 480 nm.

The crystals obtained in different atmospheres (the argon and in the argon with 2% of oxygen) were investigated by diffused scattering of X-rays before and after the irradiation. The results of research indicate the vacancy mechanism of color centers formation in these crystals. It may be explained by presence of oxygen and gallium vacancies.

Presence of point defects in structure and processes of recharge have an influence on color centers formation. It leads to generation of optical active localized states. Formation processes might be activated with additional postgrowth treatment particularly with annealing.

Isothermal annealing in the air was carried out at temperature 500 ^{0}C, 600 ^{0}C, 700 ^{0}C, 800 ^{0}C, 900 ^{0}C, 1000 ^{0}C, each sample was held within 4 hours at only one temperature. The experiment required using the polar cut samples 2 mm thickness. All samples were investigated with methods of optical spectroscopy, optical microscopy, atomic force microscopy, X-ray photoelectron spectroscopy before and after annealing. A strong effect of the annealing temperature on the state of defects in langatate structure and crystal surfaces has been revealed. It depends on the growth atmosphere.

In this study scattering spectra of LGT crystals grown in argon – oxygen atmosphere were also observed and investigated.

Increase and relaxation of abnormal conduction current in lithium niobate crystals with charged domain walls

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The time dependence of the conduction current (j_c) just after partial polarization reversal has been measured in temperature range 100-200 $^{\circ}$C in stoichiometric lithium niobate (SLN) single crystals. The obtained 10^3-10^4 times increase of j_c as compared with the single domain state has been attributed to appearance of conductive charged domain walls (CDW). The temperature dependence of characteristic times of increase and relaxation of CDW conduction current was measured [1].

It was demonstrated that the current, measured during polarization reversal, consisted of conventional switching current and the CDW conduction current. The temperature dependence of j_c increase rate resulted in negligible input of j_c for T < 150°C and domination of its contribution for T > 200 °C. The linear dependence of high-field CDW conductivity on the total switched area for the area less than 2 mm^2 and conductivity decrease for further switching was obtained. This fact was explained in the framework of the model based on the complex conduction current pathway along CDWs.

The visualization of the static domain structures on the Y cut after partial polarization reversal allowed to reveal that the domains nucleated at Z+ polar surface grew in the polar direction and stopped close to Z– surface while merged at Z+ surface, thus forming the large domain with spike-like charged domain wall (CDW area).

The CDWs border, which connected the opposite polar surfaces by the shortest path, gives the maximum contribution to bulk conductivity. The input of the inner part of CDWs is significantly reduced, due to its connection with Z+ polar surface through the complex pathway.

Two stages of the switching process have been separated for analysis of the current data in terms of the modified K-A model taking into account the input of CDW conductivity. At the first stage the lateral size of the CDW area is relatively small and the conduction current is proportional to the switched area. At the second stage only the boarder part of CDW area, which is situated closer to the electrode boundary and the inner perimeter of the domain structure provides the input to the conduction. The physically clear parameters have been extracted by fitting of the experimental data within this model [2].

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Cascade of phase transitions in a complex multi-sublattice magnetic oxide CuB_2O_4

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The copper metaborate CuB_2O_4 CuB_2O_4 has a complex crystal structure (SG $I\bar{4}2d$, $Z=12$). Magnetic Cu^{2+} ions ($S=1/2$) in the unit cell occupy two different crystallographic positions, *4b* and *8d*. The compound demonstrates a unique combination of magnetic, magnetoelectric, linear and nonlinear optical properties. To mention some of them, Cu(*4b*) and Cu(*8d*) magnetic sublattices order at different temperatures, 21 K and ~ 8 K, respectively. Multiple frustrated and nonfrustrated antisymmetric exchange interactions within and between the *4b* and *8d* magnetic sublattices result in a rich complex magnetic phase diagram. Narrow zero-phonon (ZP) exciton lines were observed for all transitions between the crystal-field-split *3d*-states.

In the Institute of Spectroscopy, we carry out high-resolution optical studies of CuB_2O_4 single crystals. We have found a large sublattice-sensitive optical linear dichroism (LD) on ZP Cu(*4b*) exciton lines which arises below the temperature of the antiferromagnetic ordering in the crystallographically isotropic (*xy*) plane of CuB_2O_4 [1]. We elucidate the nature of this LD attributing it to the magnetic Davydov splitting. Using the LD data we have discovered a splitting of the phase transition at ~ 8 K into two transitions and have found three additional magnetic phase transitions at the temperatures below 2.0 K. Moreover, we were able to specify arrangement of spins in different incommensurate phases of the copper metaborate.

As a result, we show that the discovered optical LD can be used as a new efficient method for revealing hidden features of magnetic phase transitions and magnetic structures in complex multi-sublattice magnetic oxides.

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Anomaly of dielectric, piezoelectric properties and conductivity of strongly doped LiNbO₃:Zn crystals

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$LiNbO_3$ crystal interests experts in integral and nonlinear optics, acousto-electronics, quantum electronics, solid state physics. Especial interest towards crystals doped by "threshold" concentration of Zn ($\sim 4.5 \div 5.0$ mol. %) is caused by high optical damage resistance and perspective of application in planar technology of optical converters based on periodically poled structures.

Polar clusters formed by antisite defects localized along the polar axis appear in strongly doped crystals, such as $LiNbO_3$:Zn. In originally $LiNbO_3$:Zn poly-domain crystals doped by "threshold" concentration (~ 4.5 mol. %) essential spontaneous unipolarity appears after high-temperature measurements and high-temperature shorted annealing ($T = 850 - 1000°C$). Perhaps, this effect is caused by two factors: instability of polydomain state in doped crystals at high temperature and conductivity, and collapse of the structure clusters that stabilize domain walls. This state of the crystals could be close to the single-domain one due to the static piezoelectric effect, thus it is meta-stable. Rise of unipolarity is accompanied by sharp jump anomalies of $\sigma(T)$ and $\varepsilon(T)$ dependences. The same jumps are observed for $LiNbO_3$:Zn crystals subjected to forced monodomainization. This means that the crystals contained "not switched" residual or "stubborn" domains that do not disappear at polarization switching. These domains are wedge-shaped domains with non-through charged slanting walls [1]. The monodomenization process does not lead to absolute unipolarity. It is possible that even after monodomainization crystals contain domains of the opposite sign. Turning crystals to single domain state is cooling of crystals from temperatures higher than Curie temperatures T_{Curie} at constant current. At high ion conductivity on lithium this means solid-phase electrolysis of the crystal. In the conditions of not completely reversible on lithium electrodes this leads to appearance of components concentrations gradients. This will rise concentration of structure defects that stabilize "stubborn" domain structure. In strongly doped crystals polar clusters that are formed by defects localized along the polar axis appear [2].

Anomalies on the temperature dependences of conductivity and dielectric constant occur at temperatures $\sim 800 \pm 10$K both for originally poly-domain and monodomainized $LiNbO_3$:Zn crystals.The domain structure evolution in the $LiNbO_3$:Zn crystals starts by thermal collapse of charged clusters that stabilize charged domain walls. The piezomodulus d_{333} of monodomainized crystal rises a bit less that piezomodulus of originally poly-domain crystals. It is connected with the higher unipolarity of of monodomainized crystals and much less amount of domains that are able to evolve at high temperature shorted annealing.

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Phase separation and magnetoelectric properties in manganites

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Possibility of the ferroelectricity and multiferroic behaviour [1] due to charge ordering were recently discussed [2]. The complicated interplay among charge, spin and lattice degrees of freedom in doped manganites lead to the unexpected phenomena such as phase separation with charge segregation [3]. The problem of spatially inhomogeneous states in the charged systems frustrated by the Coulomb interactions is constantly under debate for different systems. We consider the possibility of polar states and multiferroic-like behaviour due to magnetic phase separation with charge segregation phenomenon in pre-percolation regime in manganites. It is expected that pronounced changes of the electric properties might occur if the concentration of doped carriers is locally varied in a controllable way. The colossal magnetocapacitance effect at $La_{1-x}Sr_xMnO_3$ single crystals [4] was discussed in framework of that approach. The Coulomb interaction determines charge distributions and characteristic length of the phase separated states. The phase separation with charge segregation becomes possible because large dielectric constant and small density of extra charge in the range of charge localization. Localized charged states and phase segregation are described in the framework of the phenomenological theory of phase transitions. The energy gain of the phase separated states is estimated. The role of the Coulomb interaction is elucidated. The influence of magnetic field on that states is investigated in the pre-percolation regime and the possibility of polar states induced by external electric field. The dynamic of induced states is investigated and the sizes and the expansion kinetic of induced areas are determined. The influence of the external magnetic field on the writing of electric-field-induced polar states is considered. These phenomena are discussed in the framework of the model, which supposes the phase separation with charge segregation. Thus the properties of the local states induced by electric field in $La_{0.9}Sr_{0.1}MnO_3$ and $La_{0.89}Sr_{0.11}MnO_3$ single crystals [5,6] can be associated with this phenomenon.

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Domain Structures and Local Switching in Sr-doped Potassium Sodium Niobate Lead-free Piezoelectric Ceramics

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Search for lead-free materials with the electromechanical properties comparable to lead-zirconium titanate (PZT) is driven by the increased demands of environmental protection from lead. [1] The strontium doped sodium-potassium niobate (KNN) ceramics are considered among the promising piezoelectrics for the replacement of PZT. [2]

In this work we studied the influence of Sr^{2+} doping on the domain structure of KNN ceramics doped with Sr. [3] Ceramics with the compositionы $(K_{0.5}Na_{0.5})_{1-2x}Sr_xNbO_3$, where x = 0, 0.005, 0.02 and 0.08 have been produced by solid state synthesis. The sample surface has been polished carefully. Piezoresponse Force Microscopy (PFM) has been used for visualization of the domain structure and surface topography. Revealing of the grain structure by topography analysis was hampered by revealing of the initial domains structure during polishing. The scanning electron microscopy in low voltage regime allowed us to obtain the contrast between individual grains and reveal the grain boundaries. The complicated quasi-periodic domain structures have been revealed by PFM.

The obtained experimental results are discussed in terms of ceramics processing and influence of the domain walls on piezoelectric performance.

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Electromechanical Properties of $K_{1-x}(NH_4)_xH_2PO_4$ Type Single Crystals

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In the last decades the focus of interests of researchers of solid state physics is shifted to disordered and partially disordered materials. The mixed ferro-antiferroelectric (FE - AFE) crystals of $K_{1-x}(NH_4)_xH_2PO_4$ type are good examples of such materials. The crystals of this system undergoes transition to ferroelectric (FE), antiferroelectric (AFE), relaxor (RF) or dipole glass (DG) states in dependence on concentration x. Their dielectric properties, structure, lattice dynamic etc. are studied now. However the electromechanical and acoustic properties of these mixed crystals are not discussed practically, in spite of the fact that they possess piezoelectric effect in both the tetragonal paraelectric high temperature phase and in the low temperature phases.

The purpose of present work to discuss electromechanical, dielectric and elastic properties of $K_{1-x}(NH_4)_xH_2PO_4$ type of single crystals in the vicinity of transition to low-temperature phases.

The main attention we concentrated on analysis of temperature dependencies elastic compliance S_{66}, piezoelectric constant d_{36} and dielectric constant ε_{33}, which are interconnected and pass through maxima in the vicinity of transition temperature.

It was found in particular.

1. Temperature dependences of ε_{33}, elastic compliance difference $[S^E_{66} - S^D_{66}]$ and d_{36} are obeyed to Curie – Weiss law in PE phase within wide temperature range. (S^D_{66} is compliance of electrical clamped crystal.)

2. The shapes of corresponding $\varepsilon_{33}(T)$ and $S^E_{66}(T)$ dependences near the phase transition temperature for FE, RF and DG compounds are similar. It is an evidence of considerable contribution of strain component x_6 to polarization P_3 in paraelectric phase due to piezoelectric effect.

3. A smearing of the both dielectric (ε_{33}) and elastic (S^E_{66}) anomalies in the vicinity of FE phase transition is increased with increasing of inhomogeneity $x(1-x)$ is observed.

4. The shapes and positions of ε_{33} and S^E_{66} anomalies for AFE single crystals in the vicinity of phase transition temperature are different. It was revealed a weaker contribution of strain component x_6 to polarization P_3 in comparison with contributions of other polarization mechanisms.

5. Analysis of $S^E_{66}(T)$ dependences shape for AFE single crystals speaks in favor that AFE phase transition is inproper ferroelastic transition too.

6. Obtained temperature dependences of nonlinear permittivity and elastic compliance for relaxor compounds can be explained qualitatively in the framework of Random Field model proposed in Ref. [1].

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Intrinsic vs impurity-induced features of SrTiO$_3$:Mn as probed by EPR

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Strontium titanate SrTiO$_3$ (STO) is the top model of the family of strongly-polarizable ABO$_3$ perovskite structure oxides revealing a variety of unusual phenomena. Recent interest to Mn-doped STO is related to the so-called "magnetoelectric multiglass" state that was reported in STO:Mn ceramics and considered as an intrinsic effect associated with presence of 12-fold coordinated Mn^{2+} off-centers [1]. Later, e.g., in [2] this effect was treated as an extrinsic one due to observed precipitates of the ferrimagnetic Mn$_3$O$_4$ [2]. At the same time, dielectric anomalies were found in Mn-doped STO single crystals, too [3]. So, the microscopic origin of Mn-impurity induced dielectric anomalies in STO is still an open question.

We report on extensive EPR study of a series of high-quality Verneuil-grown STO:Mn crystals from Furuuchi Corp. (Tokyo, Japan). It was found that the development of the dielectric anomalies correlates well with the concentration of the Mn^{2+} impurity centers. EPR spectra of these cubic symmetry centers at T > 100 K experience drastic broadening on cooling from 500 K to ~ 60 K. This behavior originates from the slowing down of the Mn^{2+}-center dynamics with characteristic activation energy of ~ 34 meV. Interestingly, this dynamic at high temperature Mn^{2+} center gives rise to two types of static centers at T < 10 K. The higher symmetry one is oriented along the quasi-cubic [110]-direction revealing C$_2$ orthorhombic point symmetry. Another one is monoclinic C$_s$, whose principal axis is slanted by ~12 degrees from <100> towards [110]-type axes. In general, the EPR spectra of all the STO:Mn samples reveal presence of both centers with the sample-dependent concentrations. We found that most likely the Mn^{2+} center of C$_s$-symmetry are formed in perturbed metastable regions of the sample while centers possessing the C$_2$-symmetry – in the relaxed ones. This follows from the observed transformation of the EPR spectrum on a weeks-long timescale at room temperature. To our mind, this situation reveals presence of the two energetically near-degenerate microscopic structures of the Mn^{2+} impurity centers in STO.

Regarding the origin of the long-lived perturbation in STO, it follows from the EPR studies of the Mn^{4+}-ion centers that one of the possible sources is a residual stress. It looks that the structure of STO has a pronounced tendency towards tetragonal distortion in the (100)-oriented platelets and [100]-needles with the sign and a value of a distortion depending on the samples size and shape. At last, a huge irreversible quadratic electric-field effect on the EPR spectrum of the Mn^{4+} ions in STO in the cubic phase (T > 105 K) was observed. So, SrTiO$_3$:Mn single crystals are complex objects providing researchers a lot of a new information and revealing a strong interplay of the intrinsic and extrinsic properties of STO and peculiar features of Mn-impurities.

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Spin dynamics of the system with honeycomb structure probed by local methods

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Nontrivial topology, strong electronic, spin and orbital correlations in planar honeycomb lattice yield a rich variety of ground states. We present nuclear magnetic and quadrupole resonance studies addressing to the ground states of the quasi-two-dimensional honeycomb lattice compound $InCu_{2/3}V_{1/3}O_3$.

In the quantum spin-1/2 lattice long-range order is prohibited due to the presence of quantum fluctuations. This effect depends on the spin coordination number z (the number of neighbors). The long-range order is possible at T=0 in the 2D case in Heisenberg square lattice model with z=4, while the magnetic ions in the honeycomb lattice have coordination number z=3. Thus quantum fluctuations are weaker than in the 1D case but stronger than in the 2D square lattice and the AFM order for the honeycomb lattice is fragile.

In the $InCu_{2/3}V_{1/3}O_3$ quasi Heisenberg 2D magnetic system is realized by copper magnetic ions with spin S=1/2. Uncorrelated finite size structural domains occurring in the planes are expected to inhibit the long range magnetic order. Surprisingly, our experimental data show the development of two collinear antiferromagnetic sublattices in $InCu_{2/3}V_{1/3}O_3$ below 35K. We have investigated the mechanism of setting the antiferromagnetic order with several methods focused on NQR and NMR results. In order to describe the experimental results some models of magnetic sublattices were considered and the most successful model was chosen.

From lead zirconate to PZT: evolution of structure

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Antiferroelectrics and antiferroelectric-based functional materials are known for more than 60 years. $(PbZrO_3)_{1-x}(PbTiO_3)_x$ (PZT) solid solution attract special attention due to their practical importance. Despite of the long history the microscopic origin of their exceptional dielectric and electromechanical properties is not completely understood. A lack of adequate description to large extent is related to the limited possibility of the study of the structural transformations and critical phenomena in the ceramic samples. In recent years the revival of the interest to the physics of PZT solid solution is observed. To large extent this revival is related to the developments in the single crystal growth and to the new experimental possibilities in studying the extremely small single crystals using high-flux synchrotron radiation sources. Particular interesting are the concentration regions in the vicinity of the pure $PbZrO_3$ and so-called Morphotropic Phase Boundary (MPB), separating the regions of rhombohedral and tetragonal symmetry.

In a last few years we performed systematic study of the structural transformations in the PZT solid solutions [1-5]. A number of complementary experimental techniques (predominantly scattering) were used to determine the details of the phase diagram and formation of the nanodomain states in the low-x and MPB regions. Critical dynamics in different points of the Brillouin zone was studied, providing the ideas about the microscopic origin of the structural instabilities in the PZT crystals. Phenomenological theory describing the sequence of the phase transitions in the pure $PbZrO_3$.

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Ferroelectric nanocomposites on basis of magnetic porous glasses

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This contribution is devoted to studies of physical properties of ferroelectric nanocomposites (NCM) on basis of porous magnetic alkali borosilicate glasses. Magnetic glasses were produced by induction melting [1] and conventional melting in a platinum crucible [2]. After special heat treatment and chemical etching the micro- (PGMIP) and macroporous (PGMAP) matrices with average pore diameter 5 and 50 nm have been prepared. The crystal structure of glasses has been studied by X-rays diffraction and it is shown that magnetite nanoparticles exist inside of these matrices skeletons. We have studied the magnetic properties of these glasses. At the next step the porous space has been filled by ferroelectrics $NaNO_2$ and KH_2PO_4 and a new type of NCM with spatially separated magnetic and ferroelectric orderings has been produced. In Fig.1 and Fig. 2 the dependencies $\varepsilon(T)$ at 1 kHz at B=0 T and B=10 T
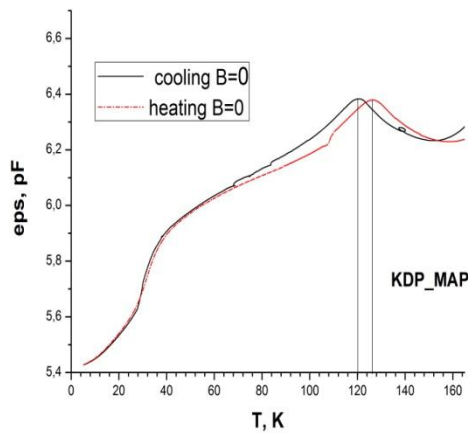
Fig.1 Dependencies $\varepsilon(T)$ for NCM PGMAP+KH_2PO_4 at cooling and heating in zero applied field
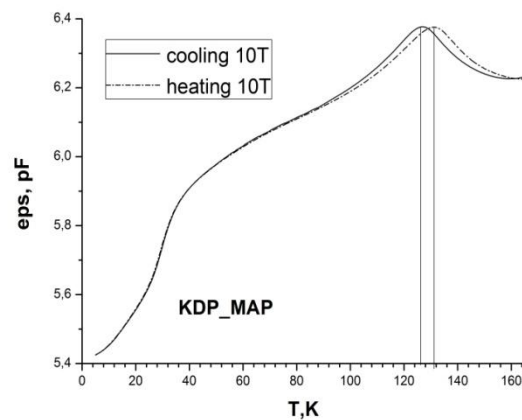
Fig.2 Dependencies $\varepsilon(T)$ for NCM PGMAP+KH_2PO_4 at cooling and heating in applied field B=10 T.

are presented for NCM PGMAP+KH_2PO_4 . It is easy to see that application of magnetic field B=10 T results to a shift of ferroelectric phase transition on ~6 K to the side of high temperatures. This shift appears due to magnetostriction [3] in magnetic porous glasses.

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Modeling of coexisting low-temperature long-range and short-range magnetic structures in multi-sublattice strontium - lanthanide oxides

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We report on experimental and theoretical studies of spectral and magnetic properties of dilute and concentrated quasi-one-dimensional lanthanide oxides SrR_2O_4, $SrY_2O_4:R^{3+}$ (R=Yb, Er) which contain two different types of zig-zag chains formed by deformed oxygen octahedrons with the trivalent lanthanide ions at the center. In particular, the unusual magnetic structures revealed earlier in the neutron scattering investigations of $SrEr_2O_4$ [1] and $SrYb_2O_4$ [2] are interpreted within the self-consistent four-particle cluster model.

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POSTER SECTION

Magnetic, structural and electrical investigations of the CuCrS2

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The article contains new data of the $CuCrS_2$ (the rhombohedral unit cell, space group R3m) that relates to multiferroics [1]. The samples used in the study were: the powder, ceramics and single crystals. The samples were investigated by XRD, the scanning electron microscope JEOL JSM-7001F, neutron scattering (triple axis spectrometer IN3), magnetic, resonance and electrical methods. It is found that the powder and ceramic samples $CuCrS_2$ are antiferromagnetic semiconductors. The propagation vector k=(−0.493, −0.087, 1.25) r.l.u. describes a three-dimensional helical arrangement of magnetic moments of Cr^{3+} ions below the Neel temperature 37.5 K [2]. The magnetic, resonance, electrical and transport properties of the real single crystals depend on the detailed technology of synthesis and the microstructure and elemental composition. Single crystals $CuCrS_2$ synthesized by chemical
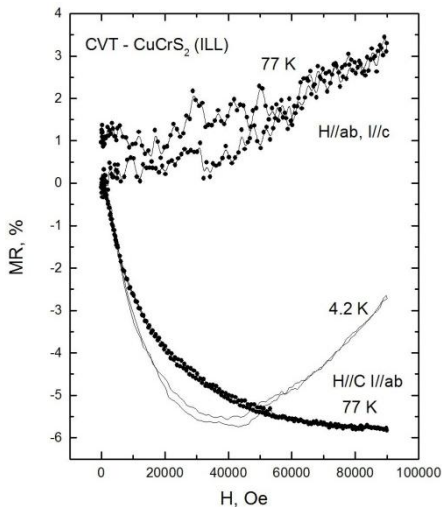
vapour transport (CVT) from pure elements Cu, Cr, S are of particular interest because of their microstructural and physical properties. It is found that these crystals can be considered as layered heterostructures consisting of alternating layers of single-crystals of disulfide $CuCrS_2$ and spinel $CuCr_2S_4$. The thickness of spinel layers ranges from 20 nm up to 1 micron. The current-voltage characteristic is non-linear, and the resistance depends also on the measuring carrent. The resistance and magnetoresistance (MR, Fig. 1) are anisotropic. The resistance of a single crystal in the plane perpendicular to the C axis is two orders of magnitude less than that along C axis. Moreover, the type of conductivity is anisotropic in the single crystal: it is metallic in ab-plane (below 150 K) and semiconducting along c-axis. The figure shows the field dependences of the magnetoresistance for the CVT single crystal $CuCrS_2$ with 15% of $CuCr_2S_4$ phase.

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Local study of phase transition during intercalation in zero-strain anode material LTO

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Here we discussed microscopic studies of spatial heterogeneity of phase transition of spinel $Li_4Ti_5O_{12}$ into rock-salt-type $Li_7Ti_5O_{12}$ during lithiation.

Lithium titanate oxide $Li_4Ti_5O_{12}$ (LTO) is one of the commercially available anode materials with low price, excellent safety issues and outstanding structural stability during cycling. Electrochemical Li^+ intercalation in spinel-type $Li_4Ti_5O_{12}$ and formation of $Li_7Ti_5O_{12}$ can be described as follows:

$$^{8a}Li\ ^{16d}[Li_{1/3}Ti_{5/3}]\ ^{32e}O_4 + Li^+ + e \rightarrow ^{16c}Li_2\ ^{16d}[Li_{1/3}Ti_{5/3}]\ ^{32e}O_4 \tag{1}$$
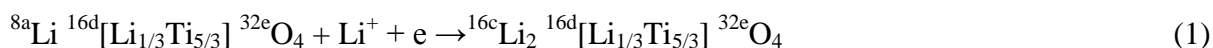
Despite the fact that LTO is rather well-studied material, there is no clear understanding of peculiarities of phase transition and even the symmetry of $Li_7Ti_5O_{12}$ phase. While Julien et al [1] claims that phase transition (1) is accompanied by lowering the crystal symmetry from cubic Fd3m to tetragonal $I4_1/amd$, Mukai at el [2] argued with it standing for cubic rock-salt type of $Li_7Ti_5O_{12}$.

Here we present results of heterophase structure study using different microscopic techniques with micro- and sub-micro spatial resolution thus bridging gap between integral macroscopic and local nano-scale TEM studies of LTO. We demonstrated notable heterogeneity of partially lithiated $Li_{4+x}Ti_5O_{12}$ using Micro-Raman spectroscopy and attributing phase transition with Raman Spectra band shifts. For the first time we studied local heterogeneity using Electrochemical Strain Microscopy [3]. Unique compact samples without binder and conductive additives allowed us combine Micro-Raman with optical microscopy. Phase transition in LTO during lithiation is discussed in terms of fractal geometry [4].

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Preparation, dielectric and piezoelectric studies of the BI_3TINbO_9 and $CaBi_2Nb_2O_9$ ceramic samples with additions of different atoms

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The bismuth layer-structured ferroelectrics (BLSF) materials are of technical interest in the field of electronic industry and information technology for their potential use in high temperature piezoelectric devices and nonvolatile ferroelectric random access memories due to their high Curie points (T_c), low aging and excellent fatigue endurance property. However the piezoelectricity of these materials is limited because of their relatively high conductivity, whose influence is enhanced with porosity of ceramics. Therefore the researches devoted to the solution of these problems are important now. The purpose of the present work was the preparation of the dense ceramics of the BSLF phases by hot pressing and the studies of the influence of the additions of different atoms on its dielectric, transport and piezoelectric properties.

The ceramic samples of BLSF phases Bi_3TiNbO_9 - I, $Bi_2CaNb_2O_9$ – II and $Na_{0,5}Bi_{2,5}Nb_2O_9$ – III with additions of 1-5 at.% different atoms (W, Ta, Sc, Ce в for I, Li, Nd, Sc, W, Mo for II and Bi,Sc – for III) were synthesized by the hot pressing technique. The values of the measured density of the received ceramics were 99% of theoretical values. By the X-Ray diffraction studies it was established that ceramics possess a pure BLSF phase and no second phases were found. The unit cell sizes of the contained in samples BLFC phases were determined.

In the temperature range of 290 – 1250 K and the frequencies range of 25 - 10^6 Hz the peculiarities of temperature- frequency dependencies of the dielectric permittivity $\varepsilon(T)$ and losses tgδ(T), and also electric resistance $\rho(T)$ were studied. The temperature dependences of piezoelectric and pyroelectric effects were studied by the alternating mechanical load and quasistatic method respectively in the temperature range of 290 – 1000 K. The ferroelectric P–E hysteresis loops were measured at 295 K by Sawyer-Tower technique.

It was established that samples show ferroelectric properties with a temperature of a Curie point varying with compositions from 1030 K to 1295 K. High-frequency (f $\geq$ 100 kHz) ε and tgδ show the expressed maximum and a minimum respectively at the temperature near to T_c. The maxima, plateau-like areas and/or breaks were also found on the temperature dependences of $\varepsilon(T)$, tgδ(T) which positions were displaced with a frequency towards high temperatures. The conclusion was made about relation of these dielectric features with the relaxation processes caused by the existence in structures of the phases of oxygen vacancies. It was established that additions of some atoms significantly increase the electric resistance of the samples and that at temperatures lying higher than 600 K the temperature dependencies $\rho(T)$ submits to Arrhenius's law $\rho = \rho_o \exp(-E_a/kT)$ with of activation energies E_a equal to 1,0 or 1,6 eV for the samples of different compositions. These values correspond to thermally activated oxygen vacancies diffusion. It was found that the polarized samples show piezoelectric and pyroelectric effects. The value of piezoelectric module d_{33} of samples at 295 K varies with their composition within 10 – 20 pC/cm^2, these values remain under heating to 1000 K. The conclusion was made that the synthesized and studied samples are perspective for creation of high-temperature piezomaterials. The ways of introduction of the addition atoms to crystal structure of BLSF phases and mechanisms of their influence on electrical and ferroelectric properties are discussed.

Unexpected influence of Mn-doping on structural and multiferroic properties of $PbFe_{2/3}W_{1/3}O_3$ ceramics

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A new multiferroic perovskite solid solution system of $Pb(Fe_{1-x}Mn_x)_{2/3}W_{1/3}O_3$ ($0<x<1$) has been prepared by conventional solid-state reaction under different sintering conditions (air, vacuum or Ar environments). Structure, phase composition, thermal, magnetic and dielectric properties of prepared compounds have been systematically investigated and clean perovskite phase was established at room temperature for compositions with $0<x<0.4$. The gradual incorporation of manganese is accompanied by a complex evolution of the lattice parameter and of the magnetic and dielectric properties. Combined X-ray and neutron powder diffraction, EDS, iodic titration and Mössbauer data allowed determination of chemical, phase composition, valence state, site assignment and occupancies of all perovskite sublattices. It was found that the ordering degree of the Fe and W/Mn cations strongly depends on the amount of Mn substitution. As was derived from the Rietveld refinement of X-ray and neutron powder diffraction patterns, the compounds crystallize in space group Pm3m ($0<x<0.8$) or Fm3m ($0.8<x<1$). The substitution of Mn^{3+} cation for Fe^{3+} one suppresses spin and dipole states obviously, leading to a gradual reduction of both antiferromagnetic and relaxor ferroelectric phase transition temperatures. While the antiferromagnetic order of the undoped compound is rapidly suppressed by the doping, a relaxor ferroelectric behavior similar to that of the pure phase is observed up to relatively large Mn contents. In contrast, an additional spin-glasslike behavior which appears around 20 K is essentially unaffected until $x=0.1$. It was established that multiferroic properties of perovskite $Pb(Fe_{1-x}Mn_x)_{2/3}W_{1/3}O_3$ disappear completely for $x>0.4$. For heavier Mn doping the prepared samples were not single phase with several impurity phases.

Antiferromagnetic G-type order with propagation vector $\mathbf{k} = (1/2,1/2,1/2)$ was derived from neutron powder diffraction data registered for the samples with $x<0.4$ below and above T_N. This type of magnetic structure does not change with the amount of Mn^{3+} cation but the value of magnetic moment on the B-site decreases with increasing of doping concentration. The origin of spin and dipole ordering of $Pb(Fe_{1-x}Mn_x)_{2/3}W_{1/3}O_3$ are explained in terms of the super exchange interactions via anions and local distortions of the crystal structure owing to special polarized lone electron pair of Pb^{2+} captions.

Effect of the Mn doping in different Pb-based perovskites are compared and discussed in details and possible reasons for the observed difference are described.

Magnetic Field Control of Local Domain Growth in Manganites

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The materials include, first of all, complex oxide compounds where due to the strong electronic correlations unique spin and transport properties, pronounced smearing of the dielectric transition, charge and magnetic order (low-doped lanthanum strontium manganite) are observed. The search for the materials with the magnetocapacitive properties is mainly focused on the weakly conducting multiferroics [1, 2]. Possibility exists to achieve analogous results by means of acting on the charge inhomogeneities possessing the magnetic properties. The distinct contrast of the electric field induced polar states was observed in $La_{0.89}Sr_{0.11}MnO_3$ single crystals [3]. Here we report the results of the dynamic of the induced states in the different condition of writing and relaxation and influence of magnetic field on this behavior. Local charged states have been induced at the surface of lanthanum strontium manganite single crystals as result of the local bias application by a conducting scanning force microscope tip. Charge and size of the created structures increase significantly if the induction occurs in a magnetic field. It indicates the tendency of manganites toward charge segregation stimulated by the magnetic ordering. The polar nanoscale areas are formed at room temperature by applying electric field via the tip of scanning probe microscope to the surface of the $La_{1-x}Sr_xMnO_3$ (x=0.1, 0.11) single crystals. Local properties of the induced states are verified with techniques of the piezoresponse force microscopy (PFM) and of the Kelvin probe force microscopy (KFM). The piezoelectric contrast is observed in these states pointing to the existence of a local polar state. It is amazing that the induced charged states relax with characteristic time constant of about 50-100 hours at room temperature. These results are complemented by the measurements of surface potential hysteresis loops in standard pulse *dc* mode. The electric-field-induced contrast is observed in Kelvin mode confirming local modification of the surface electric properties of manganites. We investigate the dynamic of induced states and determine the sizes of induced areas. These results show the dependence of the surface potential of induced area on the writing time a similar as for ferroelectrics. The influence of the external magnetic field on the writing process of electric-field-induced polar states is found out.

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Thermal and dielectric properties of the multilayer capacitor based on BaTiO3

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Electrocaloric effect (ECE) in dielectric materials has a great potential in realizing of solid-state cooling devices with compact size and high efficiency what is highly desirable for a wide range of applications such as on-chip cooling and temperature controlling for sensors, electronic devices, and medical instruments. This effect is the change of the temperature or entropy connected with electric field variation under isothermal and adiabatic conditions, respectively. Rather large EC effect can be obtained in ferroelectric materials near phase transition point under large electric field (E>300 kV/cm). However, the breakdown field for bulk materials is typically no more than 60 kV/cm. On the other hand, thin ferroelectric films can support higher breakdown fields, namely at about 1000–2000 kV/cm, due to small thickness and low voltage. This is the reason that gigantic intensive ECE ($\Delta T_{AD} \approx 14$ K) was observed in such kind of ferroelectric materials [1]. Unfortunately, monolayer thin films have small thermal mass which brings about small electrocaloric heat. Multilayer ceramic capacitors (MLCCs) have been suggested [2, 3] as an alternative design for electrocaloric coolers as they combine high breakdown field due to thin layers (typically > 5 µm) as well as large thermal mass and, therefore, high cooling power.

In this work, we present the experimental data concerning ECE studied under isothermal and adiabatic conditions, permittivity depending on frequency and electric field, hysteresis loops, pyroelectric current, heat capacity and thermal expansion in MLCC based on $BaTiO_3$ widely used at the moment in ceramic capacitors due to high values of permittivity near room temperature. A commercially available MLCC (C4532Y5V1A107Z, TDK Corporation, 100 µF) consisting of 200 interdigitated layers of doped $BaTiO_3$ and Ni was used. The nominal thickness per layer is 6.5 µm for $BaTiO_3$ and 2.0 µm for Ni.

The results obtained are discussed in relation to transformation of physical properties ECE associated with phase transitions in multilayer thin films of barium titanate compared to bulk material with experimental data of the other authors. The effect of nonequilibrium conditions as well as frequency of external electric field on dielectric and thermal properties is considered. It was found that cooling power can be scaled using intensive and extensive ECE's in the set of MLCC.

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Effects of dielectric ageing in lead-free ceramics of the niobate family

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The aim of this work was an investigation of the dielectric ageing processes and subsequent "rejuvenation" at different levels of the field and temperature impact on the material under study – ferroelectric ceramics of $(K_{0,5}Na_{0,5})(Nb_{1x}Sb_x)O_3$+0.5mol.% MnO_2 (KNN-x) with x = 0.05 (KNN-5).

Dielectric studies at low and infra-low frequencies were performed with Sawyer-Tower method which supposes the measurements of the polarization loops after various durations of the constant amplitude sinusoidal field E application.

In Figure 1(a) an evolution of the polarization loop is shown after different durations of the E = 8 kV/cm at 1 Hz application to the KNN-5 ceramics sample preliminary kept for 24 h at 61°C. In Figure 1(b) the time dependence of the effective dielectric permeability $\varepsilon'_{eff}(t)$ is presented that was obtained from the polarization loops with the given value of E. This value of E ensured the measurements of the so-called partial (non-saturated) loop cycles. This allowed to follow the development of the polarization P of a sample with the described "training" of the preliminary aged KNN-5 sample. Moreover, the choice of the low E values (less than the coercive field E_c) practically excluded either the sample heating with such a field "annealing" or the field degradation of the sample (field fatigue). It has been found that an increase of the effective dielectric permeability is well described by the power law $\varepsilon'_{eff} = \varepsilon'_{st} + B\, t^c$ (solid line in Figure 1(b)), where ε'_{st} is the initial value of ε'_{eff}, B – an amplitude c – an exponent that can be extracted from the fit of the data.

The obtained results are analyzed within the approaches with interaction of the domain walls with defects [1,2].

a   b
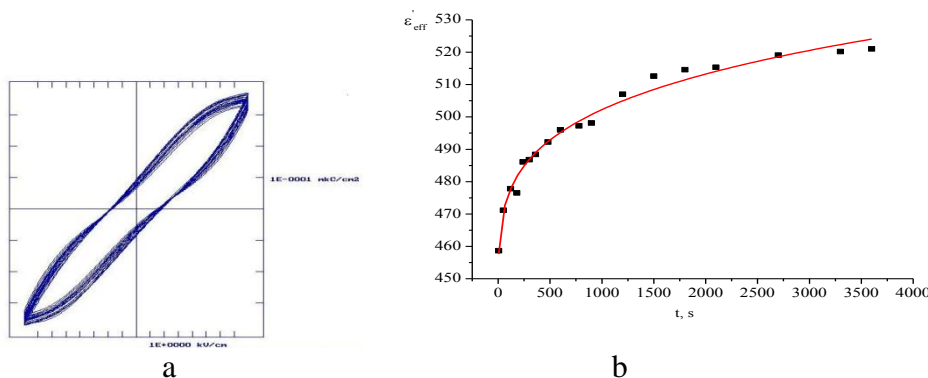
Figure 1.

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Study of domain structure formation by beam of charged particles in MgO doped lithium niobate

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The formation of ferroelectric domains by irradiation of polar surfaces by focused electron beam has been studied in MgO doped congruent lithium niobate crystals (MgOLN) both experimentally and by computer simulation. The periodical domain patterns have been produced and effective second harmonic generation (SHG) has been demonstrated.

The irradiation of polar surfaces was performed by scanning electron microscope (Auriga Crossbeam workstation, Carl Zeiss) with electron-beam lithography system (Elphy Multibeam, Raith) using dot, line and stripe exposure regimes. The opposite surface was covered by solid Ta electrodes and grounded. The irradiated Z^--surface was coated by resist. The domain patterns revealed by chemical etching were visualized by several microscopic methods: optical (OM), piezoresponse force (PFM), scanning electron (SEM) and confocal Raman (CRM) microscopies.

Dot exposure of Z^+ surface led to formation of the stable needle-like domains with lateral size about 2 μm and length above 200 μm at 100-nm-distance from the surface. For linear exposure the domain geometry changed with the increase of the dose from the chain of isolated domains with average size about 200 nm and period about 800 nm to comb-like structure as a result of domain merging. The main stages of domain structure evolution have been revealed. The mechanism of domain appearing and growth under the field produced by space charge was proposed and explained in terms of kinetic approach [1]. The domain forward domain growth has been attributed to electrostatic interaction of the elementary steps existing at the charged domain wall of needle-like domain [2].

The domain formation on Z^- surface for MgOLN crystals coated by resist was investigated experimentally and by computer simulation [3,4]. It was shown that the pattern quality depends on the resist thickness and electron energy. The measured dependencies of domain size on dose were revealed and used for optimization of the poling process. SHG of green light was demonstrated for the domain structure with period of 6.89 μm. The high homogeneity of the periodical poling was confirmed by achieved efficiency of SHG, which was significantly higher than for conventional electric-field poling.

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Domain structure in lithium tantalate during polarization reversal in highly non-equilibrium switching conditions

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The formation of domain structures during polarization reversal was studied in single crystals of MgO doped lithium tantalate (MgOSLT) and near congruent lithium tantalate (NCLT).

The kinetics of phase transitions in highly non-equilibrium systems is related to the investigation of self-assembling of nanoscale structures, which are considered as one of the main trends in nanotechnology. The domain structure evolution in single crystals of uniaxial ferroelectrics can be considered as a model for investigation of phase transformation in highly non-equilibrium conditions. Moreover the self-assembled ferroelectric domain structures with submicron periods can be used for production of nonlinear-optical devices with new types of nonlinear-optical interactions. In this work the highly non-equilibrium switching conditions were obtained by polarization reversal of MgOSLT with metal electrodes and NCLT covered by photoresist layer.

It was shown, that polarization reversal in MgOSLT with metal electrodes leads to formation of dense quasi-regular submicron-size domain structures at Z- polar surface revealed by deep chemical etching. The hexagonal domains with walls orientation mostly along Y crystallographic directions have been visualized on Z+ polar surface. This fact can be attributed to domain growth from Z+ surface and formation of the charged domain walls with the domains tips situated close of Z- surface. The self-organized formation of the quasi-regular structures is governed by electrostatic interaction between the elementary steps propagating along the domain walls [1,2]. The obtained independence of the domain structure period (about 1 μm) on Z- polar surface on the electric field indicated the self-organized nature of the domain formation.

In situ visualization of the domain kinetics during polarization reversal of NCLT crystals covered by photoresist film allowed to separate two stages of domain structure evolution: (1) formation of maze domain structure; (2) motion of macroscopic domain walls. Visualization of static domain structures with high spatial resolution by atomic force microscope has revealed the chains of isolated nanodomains oriented along Y directions appeared in front of the macroscopic domain wall [3].

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Crystal and magnetic structures, phase transitions in quasi-one-dimensional pyroxenes $Na_{0.5}Li_{0.5}FeGe_2O_6$

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The possibility of cation substitution in pyroxenes allows the investigation the gradual change of structural and magnetic properties under doping. $Na_{0.5}Li_{0.5}FeGe_2O_6$ was prepared by the standard solid-phase reaction method and has been investigated using X-ray and neutron powder diffraction, and further characterized by magnetic and calorimetric measurements. The crystal structure of $Na_{0.5}Li_{0.5}FeGe_2O_6$ at 300 K is monoclinic $C2/c$. Calorimetric investigations indicate a displacive first order phase transition at T = 271±1 K which is accompanied by the appearance of superstructure reflections in the X-ray patterns. At this transition $Na_{0.5}Li_{0.5}FeGe_2O_6$ undergoes a space group change from $C2/c$ to $P2_1/c$) (fig. 1).
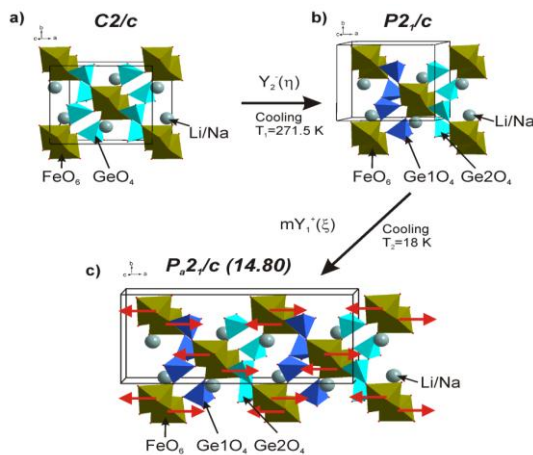
Fig. 1. Crystal structures of a) G_0 phase ($C2/c$); b) G_1 phase ($P2_1/c$); c) G_2 phase (P_a2_1/c) where red arrows show the magnetic moment of Fe ions. Big black arrows show phase transitions under cooling. Critical modes which distort the crystal structure at phase transitions are indicated near the arrows.

Magnetic order has been found below the Néel temperature $T_N \approx 18$ K and has been refined from neutron diffraction. The quasi-low-dimensional magnetic spin system $Na_{0.5}Li_{0.5}FeGe_2O_6$ exhibits a collinear antiferromagnetic structure with the space group P_a2_1/c and the doubling of the unit cell along the crystallographic a-axis of the pyroxene crystal (propagation vector k = (1/2, 0, 0)) (fig. 1). The critical modes which are responsible for the phase transitions have been determined.

Verwey Phase Transition in Biogenic Magnetite

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Magnetite (Fe_3O_4) nanoparticles play important role in living organisms. Presently there are some experimental facts of observation of electron magnetic resonance (EMR) signals of magnetite in biological systems. The wide anisotropic signals were detected in different biological systems: cultures of dividing cells, magnetotactic bacteria, organs of navigation and magnetoreception in insects, birds and fish, in mammal and human tissues (nerve, brain, heart, liver, placenta, blood etc.) in cancer cell cultures, in tumours.

At room temperatures (T=300K) magnetite is ferrimagnetic material with inverse spinel structure, but in the vicinity of 124 K, Verwey Transition temperature [1], it is transformed into monoclinic structure. At Verwey transition, T_v, there are anomalies in most of the controlling magnetic energies, most notably in magnetocrystalline anisotropy energy, where there is a very large increase in its magnitude. EPR-technique allows us to detect and investigate changes of magnetic parameters of magnetite nanocrystals. The present report concerns the characteristics of magnetite nanocrystals that we detected investigating different biologic tissues by EPR technique (human cancer tumors [2], brain of snails, pathologic spinal cord, heart and lung of rats). The temperature and angular dependencies of EMR signals were investigated. When studying the temperature behavior of EMR signal the characteristic non-monotonic temperature dependencies of resonance field (H_{res}), linewidth (ΔH) and integral intensity (I) К were observed within the temperature interval 5-300. MR parameters of EMR spectra demonstrated the following behavior:

1. In the vicinity of Verwey Transition temperature of bulk magnetite a maximum for H_{res}, I and local minimum for ΔH were observed. In different samples some dispersion of Verwey temperature values was detected within interval about 110-125 К, as it is known about the dependence of T_v on the stoichiometry of magnetite.

2. High correlations (more than 0.95) between the temperature dependence of the $H_{res}(T)$ and $\Delta H(T)$ and temperature dependence of magnetite magnetocrystalline constant K_1 are detected in high temperature phase.

3. EMR signals of biogenic magnetite are characterized by anisotropic behavior of H_{res}, in a wide interval of temperatures 100-300 K. The resonance field of EMR line is successfully described by the expression:

$$H_{res}(\theta) = \frac{\omega}{\gamma} - H_{ax}P_2(cos\theta) - H_{cub}\left[1 - \frac{5}{4}sin^2(2\theta) - \frac{5}{4}sin^4\theta sin^2(2\varphi)\right].$$

The values of axial and cubic contributions depended on temperature and changed when going through the phase transition temperature.

4. At about 130K anisotropic point (T_k) was detected, at which the anisotropy disappears.

All listed peculiarities allow to suppose, that there are oriented magnetite nanoparticles in all studied tissues. The coincidence of referred anomalies temperature with Verwey temperature in bulk magnetite single crystals and the fact of observed anisotropy of EMR signals indicate high degree of order of magnetite nanoparticles in biological tissues.

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EPR studies of Mn^{4+} impurity center anisotropy in SrTiO$_3$ single crystals

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Strontium titanate SrTiO$_3$ (STO) is a very popular and thoroughly studied compound that is representative of the family of highly-polarizable ABO$_3$ oxides. At room temperature it adopts the cubic O$_h^1$ perovskite structure. At $T_{af} = 105$ K it undergoes a second order antiferrodistorsive cubic-to-tetragonal O$_h^1$- D$_{4h}^{18}$ structural transition.

Relatively recently STO doped with manganese have attracted significant attention of the researchers due to the observation in STO:Mn ceramics of the so-called "magnetoelectric multiglass phase" [1]. In spite of rather intense studies there is still much of the controversy on the mechanism of the ordering effects as well as symmetry and properties of Mn centers in STO (see, e.g.,, [2-4] and refs. therein). One of the most powerful experimental approaches that allow studying Mn impurities is the electron paramagnetic resonance (EPR).

We report on detailed EPR study of the small tetragonal distortions of the octahedral Mn^{4+} impurity centers detected in the cubic phase of high-quality Verneuil grown STO:Mn single crystals (Furuuchi Chemical Corp., Tokyo). Presence of such Mn^{4+} center distortions in STO above the T_{af} have been reported by Müller [5] and was related to the off-center shift of the octahedral Mn^{4+} ion along the [001] crystallographic direction. However, presence of such center was not confirmed by any further research.

We have detected the obvious distortion of the ideal cubic structure of octahedral Mn^{4+} centers in EPR spectra of (001)-oriented platelet-shaped STO:Mn crystals. It turned out that this observation is not consistent with the simple assumption on the off-center Mn^{4+} ion position. Instead, Mn^{4+} spectra clearly reveal almost homogeneous macroscopic symmetry lowering from cubic to tetragonal structure. Moreover, it was found that the distortion in the case of [001] oriented platelet is inversely proportional to its thickness and even changes sign on going from the platelet shape to the rod one revealing the sensitivity of the Mn^{4+} centers symmetry on the macroscopic symmetry of specimen under study. We found also that the anisotropy value decreases slightly, by ~10% for samples annealed at 1000°C for 10 hours in air. This indicates that the observed anisotropy is only partially related to the residual stress/structural disorder in the sample. Possible origins of the observed phenomenon are discussed taking into account surface energy size and shape effect in highly polarizable samples.

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Synthesis and electrochemical modification of sodium cobaltates Na_xCoO_2 single crystals

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Sodium cobalt oxides attract attention due to enhanced thermoelectric power, superconductivity and existence of magnetically ordered phases [1]. Sodium content in Na_xCoO_2 may be changed reversibly in wide range and immensely influence to physical properties. However phases with specific sodium content can be obtained, which correspond to some Na orderings as observed by diffraction techniques. Phases of Na_xCoO_2 with x=0.5, 0.66, 0.77 show sodium ordering commensurate to cobalt oxide lattice and therefore are in the focus of many studies. But most of them have been done on polycrystalline samples. This work devoted to synthesis of Na_xCoO_2 single crystals with x=0.5, 0.66, 0.77.

Single crystals of sodium cobalt oxide $Na_{0.8}CoO_2$ were grown by the optical floating zone technique in an image furnace (Crystal Systems Corp., Japan) acquired in Kazan Federal University [2]. One of the as-grown crystals is presented at fig. 1a. In such ingots the *c*-axis is always perpendicular to the growth direction and the crystal is relatively easy to cleave along the *ab* plane (fig. 1b). The growth of phases with lower Na content was unstable, thus electrochemical de-intercalation of sodium ions was used to obtain phases with lower sodium content [2]. A home built analogue potentiostat was used to control potentials and current in the electrochemical cell. X-ray diffraction (XRD) allows to measure the sodium content in the crystals as the c-axis parameter sensitive to sodium content [1]. In fig. 1c the positions of 008 diffraction peak in the XRD patterns of single crystal after subsequent treatments are shown. The positions of the peaks correspond to phases have been mentioned before.
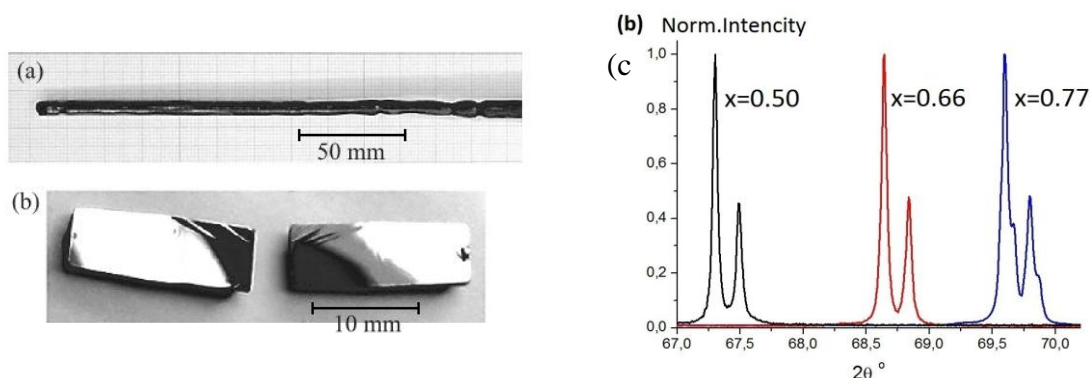
Fig.1 a) Sodium cobalt oxide $Na_{0.8}CoO_2$ as-grown crystal;
b) $Na_{0.8}CoO_2$ crystal freshly cleaved along *ab* plane;
c) XRD pattern of electrochemically treated Na_xCoO_2 crystals, peak 008 is only shown;

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Synthesis of nanocomposite multiferroics by implantation of Co^+ and Fe^+ ions into $BaTiO_3$ thin films

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Thin films of barium titanate ($BaTiO_3$) were deposited on silicon substrate using ion beam assisted deposition (IBAD). Then 40 keV Fe and Co ions were implanted into $BaTiO_3$ films with high fluences $(0.5-1.5) \times 10^{17}$ ion/cm^2 to synthesize nanocomposite multiferroic materials. In addition, the implanted films were annealed at 500ºC in vacuum to stimulate precipitation of dopant in the form of magnetic nanoparticles. The samples were characterized by using X-ray diffraction, scanning electron microscopy and Mössbauer spectroscopy. Magnetic and magnetoelectric properties were studied using coil magnetometry and magnetic resonance technique.

EDX element microanalysis of Co- or Fe-implanted $BaTiO_3$ shows that the films consist only "host" elements (Ba, Ti, O) and cobalt or iron dopant. Cross-section images of $BaTiO_3$ films before and after ion implantation allow to calculate sputtering yield ($S= 1.7$ atom/ion) and depth profiles of metal dopant concentration. XRD study shows that both as-deposited and subsequent implanted $BaTiO_3$ thin films have polycrystalline structure, and the peaks corresponding to tetragonal ferroelectric phase of $BaTiO_3$. Mössbauer spectra of Fe-implanted $BaTiO_3$ film display the doublet with isomeric shift for charge states of Fe^{3+} ions in $BaTiO_3$ lattice. Non-annealed $BaTiO_3$ films implanted with Fe ions at fluence of 0.75×10^{17} ion/cm^2 have no magnetic signal, while films implanted at fluence of 1.5×10^{17} ion/cm^2 show weak ferromagnetic signal. After annealing in vacuum Fe-implanted films reveal superparamagnetic response for low-fluence film and ferromagnetic signal for high-fluence sample. On the contrary, the films implanted with cobalt exhibit a pronounced ferromagnetism with magnetic hysteresis loop at room temperature. However Co- or Fe-implanted $BaTiO_3$ thin films don't reveal any magnetoelectric effects, although ones were early observed [1, 2] in the single crystals of $BaTiO_3$ implanted with Co or Fe to the same fluences. We assume that iron or cobalt nanoparticles form into the pores of polycrystalline film. This leads to weakening of mechanical coupling between magnetic nanoparticles and ferroelectric matrix of $BaTiO_3$. Therefore magnetoelectric effects in our samples weaken considerably.

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Investigation of the ferroelectric properties of BST 80/20 thin films via piezoresponse force microscopy

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Previous and today's dynamic random access memories (DRAMs) have been advanced by mainly focusing on how to make memory cells small to realize high density DRAMs. The most critical challenges in gigabit density DRAMs are yield loss due to large die size and small feature size, standby current failure caused by large chip size and small data retention times owing to reduced charge packet in the memory cell. In the recent years thin film perovskite materials with high dielectric constant such as PZT, $SrTiO_3$ and $(Ba,Sr)TiO_3$ (BST) have been investigated as dielectric materials for future DRAMs.

In this work, we report a voltage-induced domain growth kinetics in ferroelectric BST 80/20 films fabricated by RF magnetron sputtering measured via piezoresponse force microscopy (PFM). The experimental setup for the PFM measurements included Ntegra Prima (NT-MDT, Russia) atomic probe microscope, conductive tips NSG30/Pt with apex radius of 30 nm and function generator for applying DC voltage to the tip. A RF magnetron sputter system was used to deposit BST 80/20 thin films (thickness 150÷400 nm) on (100)-oriented Si substrate. The surface of the sample shows small grains which diameter ranges from 50 nm to 75 nm and roughness is less than 5 nm. Nanoscale studies revealed the existence of a self-polarization effect in the studied BST 80/20 thin films. Using the piezoresponse mode of the SPM to detect the out-of-plane polarization, the domain sizes were measured as a function of the applied writing voltage and the pulse time. The dynamics of domain growth is analyzed experimentally taking into account the strong inhomogeneity of the external electric field in the film. In addition, we investigated the thickness dependence of the induced polarization state in BST films. The experiments shown, that the value of induced polarization state increases with thickness of the BST films. In order to evaluate the stability of piezoresponse, we characterized the microscopic retention behavior of BST film. No obvious back switching can be observed when the piezoresponse read out again after 18 h.

Formation of micro- and nanodomain structure as a result of spontaneous backswitching in relaxor $Sr_xBa_{1-x}Nb_2O_6$ single crystals

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The process of spontaneous backswitching ("flip-back") after abrupt removing of the applied field has been studied in relaxor ferroelectric $Sr_xBa_{1-x}Nb_2O_6$ (SBN) single crystals in terms of analysis of the switching current and formation of micro- and nanodomain structures.

The studied samples represent the 0.5-mm-thick plates cut perpendicular to polar axis. The initial single domain state was created by sample cooling in dc field. The polarization reversal under application of the single rectangular field pulse with varied duration was realized using liquid electrodes. The switching current data and kinetic of the domain structure visualized by optical microscopy have been recorded simultaneously. The final static domain structures were visualized by piezoresponse force microscopy (PFM) (Fig. 1).

The dependence of the backswitched charge on the pulse duration has been measured. The switching current data have been analyzed using modified Kolmogorov-Avrami approach [1]. The main stages of the domain evolution during backswitching have been revealed. The appearance and growth of isolated nanodomains and sideways motion of the domain walls of residual domains have been separated.

It was demonstrated that the typical square-like shape of micro-domains (Fig. 1 a) correlates with the crystal symmetry (C_{4v}) [2]. The formation of rough domain boundaries (Fig. 1 b) was attributed to formation of isolated nanodomains in front of the moving domain wall due to correlated nucleation effect [3,4].
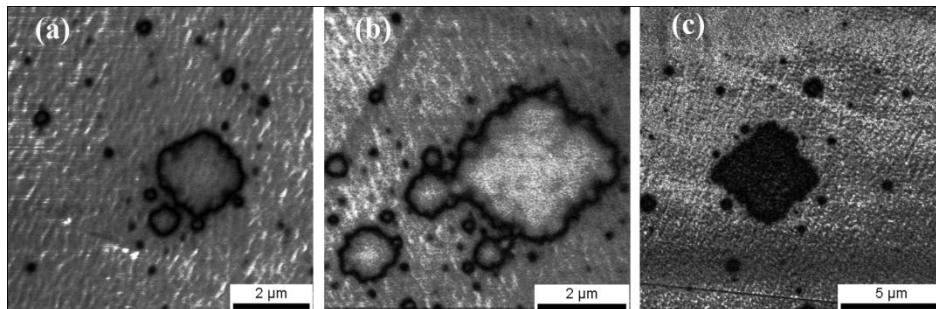
Fig. 1. Micro- and nanodomains appeared as a result spontaneous backswitching in SBN.

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Raman scattering investigation of temperature structural changes in relaxor ferroelectric BBN

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$BaBi_2Nb_2O_9$ (BBN) belongs to the Aurivillius family of Bi-layered perovskite-like oxides. The extensive class of perovskite-like compounds are actively investigated by specialists in solid state physics. The most important feature of perovskites—the presence of frameworks, layers, or networks of octahedra BX_6, pyramids BX_5, and squares BX_4 linked at their vertices. Bismuth layer structured ferroelectrics (BLSF) were synthesized and described for the first time by Aurivillius [1]. The general chemical formula of the Aurivillius compounds is $(A_2O_2)^{2+}(A'_{n-1}BnX_{3n+1})^{2-}$, where n is an integer between 1 and 5 indicating the number of the perovskite-like blocks between two adjacent $(A_2O_2)^{2+}$ layers, A and A/= Bi, Ba, Ln, Sr, Ca, Na, where B = W, Ta, Nb, Ti, Fe, Ga, and X= O, F, Br [1,2]. The Aurivillius compounds attracted considerable attention because of their potential application in ferroelectric random access memories, multilayer ceramic capacitors, electro-optic devices, ultrasonic and medical imagining devices. Macquart R. et al. have shown the presence of a diffused crystallographic phase transition near room temperature in $BaBi_2Nb_2O_9$ [3]. Authors believe this is from the paraelectric I4/mmm structure to the ferroelectric I4mm structure.

To understand the temperature phase transitions mechanisms in the $BaBi_2Nb_2O_9$ ceramics the Raman spectra were studied at temperature range from 8 to 550 K. The spectra in the 180 geometry were recorded on a Horiba Jobin Yvon T64000 spectrometer. The temperature studies were performed using an ARS CS204 X1.SS closed cycle helium cryostat. Raman spectra assignments have been performed. Detailed analysis of the line positions changes has been performed. The significant changes with temperature have been observed in the low wavenumber part of the spectrum. This part of the spectrum dues to vibrations of lattice and bismuth. The lattice vibration spectra in I4/mmm and I4mm phases were calculated. Comparative analysis of experimental and calculated spectra was made.

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Conditions of growth and physic-chemical properties of strongly doped optically nonlinear LiNbO₃:Zn crystals

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$LiNbO_3$ crystal interests experts in integral and nonlinear optics, acousto-electronics, quantum electronics, solid state physics. Especial interest towards crystals doped by "threshold" concentration of Zn ($\sim$ 4.5÷5.0 mol. %) is caused by high optical damage resistance and perspective of application in planar technology of optical converters based on periodically poled structures [1 – 4].

The system melt-crystal $LiNbO_3$:Zn in impurity concentration range $4 \leq C_m \leq 9$ mol.% was searched with small concentration step. This allowed us to determine more accurate values of the concentration thresholds in the melt as $\sim$ 5.4 and 6.8 mol. %. Three concentration areas were revealed. Significant change of physico-chemical melt properties occurs in each area. Thus $LiNbO_3$:Zn crystals grown from each concentration area have different characteristics. Favorable conditions for growth of optically and compositionally homogeneous defect-free $LiNbO_3$:Zn crystals are achieved in $5.4 \leq C_m \leq 6.8$ mol. % concentration of impurity in the melt. At $C_m > 6.8$ mol. % significant change of physico-chemical properties and thus structure of the melt occurs. Thermodynamical properties of the melt in this impurity concentration range are the following: obtaining of single-phase defect-free $LiNbO_3$:Zn crystals is possible only if less than 20 wt. % of the melt crystallizes into a boule. At crystallization of more than 20 wt. % of the melt the grown crystals contain two phases, $Li_6ZnNb_4O_{14}$ and $LiNbO_3$. In this concentration range impurity distribution coefficient of $LiNbO_3$:Zn crystals is much less than unity. impurity distribution is classical in this case: concentration rises from the cone to the bottom part of the boule. Crystals grown from this concentration area contain great amount of defects and have a high tendency to crack due to compound inhomogeneity of the crystals.

Due to significant change of physico-chemical properties of the melts from different concentration areas it is quite possible to obtain $LiNbO_3$:Zn crystals with different intrinsic structure, but the same impurity concentration. The searched $LiNbO_3$:Zn system is sensitive towards the zinc concentration in the melt. And this is why this system is completely different from system $LiNbO_3$:Mg. So the proximity of ionic radii of Zn^{2+} and Mg^{2+} cations is not a significant factor for making of conclusions that melt-crystal system would behave alike.

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Orientation phase transition in hematite

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The study of magnetoacoustic resonance is assotiated whis the possibility of the influence of both the magnetic field on the acoustic properties of the material and the external mechanical stress on its high-frequency magnetic properties. Magnetoacoustic resonance is determind as a common point in the spectra of sound (phonon) and spin compound α-Fe_2O_3 (hematite) is an easy-plane antiferromagnet in the temperature range from the Morin point T_M = 262 K to the Neel temperature T_N = 950 K. Interest expressed in (magnon) waves at which the frequencies and wave vectors **k** of this waves coinside respectively with each other. The interaction of the spin and elastic degrees of freedom (magnetoelastic interaction) splits these two interesting branches of the spectrum into two magnetoelastic branches that have no common points. In this work we investigated the branch of magnetoelastic waves, which is usually called the quasi-magnon or quasi-sound branch.

The experiments were performed on a hematite sample in the form of a parallelepiped, the faces were oriented with respect to the crystallographic axes of hematite within one degree. The acoustic measurements were performed in the transmission mode. Acoustic shear vibrations at frequencies of 5 – 50 MHz were excited by x-cut $LiNbO_3$ piezoelectric transducers, the sound propagation direction (**k**) was parallel to the threefold symmetry and the plane of polarization of acoustic vibrations was perpendicular to the basal plane of hematite and contained the chosen twofold symmetry axes. This scheme provided excitation of the magnetically dependent mode of the vibrations. Changes in the quasi-sound velocity (ΔV) were detected by measuring the phase shift. In the experiments directed compression (**P**) up to 180 MPa and magnetic field (H) up to 6 kOe was applied.

Our experiments results of measurements of the quasi-sound velocity V near the orientation phase transitions with variation in the parameters **H** and **P** (dependences V (H) at P = const and dependences V (P) at H = const. The most interesting features, in our opinion are as follows.
1. Dependences V (H) have minima for all the chosen values of **P.** The values of fields H = H_{min} at the minima of the dependences V(H) at **P** = const increase with an increase in the pressure **P**.
2. With an increase in the pressure **P**, the width of these minima also increases.
3. The minima are also present in the dependences V (P) at H = const.

A comparison of these results with the conclusions of the existing theory of magnetoacoustic phenomena performed.

Properties of NH_4HSO_4 ferroelectric embedded in nanoporous glasses

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The research of the physical properties of materials in a restricted geometry is one of the very interesting problems of modern solid state physics and is not only of fundamental interest but also of practical importance. In recent years, a considerable attention was focused on studies of ferroelectric porous glass nanocomposites. The properties of confined materials and in particular various types of phase transitions in some ferroelectrics have been extensively studied by different experimental methods. It was shown that the physical properties of nano- and micro- materials are significantly different from those of bulk ferroelectrics [1]. The main reason of a porous matrix usage is an ability to produce a controlled pore matrix with a large range of characteristic pore sizes and various geometries.

In this paper, we present the results of study of the phase transitions in the well-known ferroelectric NH_4HSO_4 embedded from the melt into porous glasses with pore size of about 46 nm. Bulk ammonium hydrosulfate undergoes two phase transitions at T_1=271.7 K and T_2=160 K [2]. However, despite that fact that it widely studied some questions at least regarding the phase transition at T_2 remain open, since at this temperature there is very sudden and significant change in the volume [2]. It was shown also that gigantic barocaloric effect is characteristic for this transformation [3].

The structural characterization of nanocomposite using electron microscope and X-ray powder diffractometer has shown that pores of glass matrix are filled with single crystals of pure ammonium hydrosulfate. The information on heat capacity, thermal dilatation, permittivity and susceptibility to hydrostatic pressure of ferroelectric component in confined conditions was obtained by the study of the same physical properties above of nanocomposite and empty glass. The influence of the pores on the ferroelectric phase transitions in NH_4HSO_4 nanocrystals embedded into the porous matrix was determined. The results obtained are discussed in comparison with the data for bulk NH_4HSO_4 investigated in [2,3,4]. The temperatures of phase transitions were found to be rather lowered. *T–p* phase diagram showed that ferroelectric phase in nanocomposite exists in more wider range of pressure.

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Formation of broad domain boundary in congruent lithium niobate modified by proton exchange

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The dependence of the domain kinetics on the applied field and the thickness of the proton exchange (PE) surface layers have been studied systematically in congruent lithium niobate (CLN) single crystals with various thicknesses of the modified layer.

The obtained formation of the nanodomains in front of the moving domain wall and self-assembled structures consisting of isolated domains – broad domain boundaries (BDB) [1] have been attributed to realization of highly non-equilibrium switching conditions caused by retardation of the bulk screening of depolarization field [2].

The samples under investigation were modified by PE parts of 0.5-mm-thick Z-cut CLN wafer. PE was carried out in sealed ampule with benzoic acid at the temperature of 300°C [3]. Variation of time of procedure results in formation of the non-ferroelectric layers with different thickness at both polar surfaces: 3.4 μm during 100 min and 4.6 μm during 230 min.
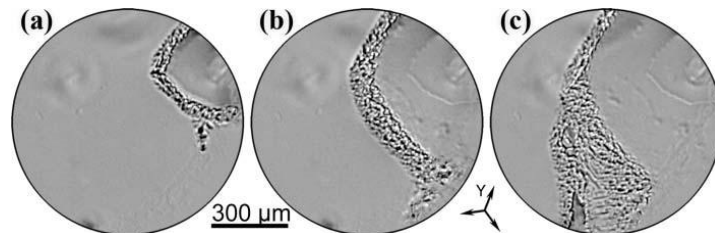
Fig.1 Formation and growth of BDB for CLN with 3.4 μm PE-layer. E_{ex}=1.7 kV/mm.

It was shown that the domain kinetics strongly depends on the excess of the applied field over the threshold value $E_{ex} = E_s - E_{th}$. Three types of the domain evolution were observed in studied field range in the sample with 3.4 μm PE-layer: (1) appearance and continuous growth of hexagonal domains for $E_{ex}{\approx}0$; (2) growth of domain rays for $E_{ex}=1.2\ kV/mm$; (3) formation and anisotropic growth of BDB for $E_{ex}=1.7\ kV/mm$. The domain kinetics changed qualitatively for 4.6 mm-thick layer: (1) growth of domain rays for $E_{ex}=1.4\ kV/mm$, (2) denser and less ordered web-like domain structure formed for $E_{ex}=2.4\ kV/mm$.

The field dependence of the wall motion velocity has been be attributed to activation wall motion mechanism taken into account existence of the bias fields

$$v(E) = v_{\infty}exp[-E_{ac}/(E-E_b)] \tag{1}$$

where E_{ac} is the activation field, E_b is the bias field, v_{∞} is the limiting value of the wall motion velocity. For 3.4 μm PE-layer: E_{ac} = 3.2 kV/mm, E_b = 20.3 kV/mm.

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Dielectric properties of relaxor $Pb(Fe_{1/2}Ta_{1/2})O_3$ ceramics sintered from mechanochemichally synthesized powders

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Both single crystals and ceramics of ternary perovskite $PbFe_{1/2}Ta_{1/2}O_3$ (PFT) exhibit relaxor-like dielectric behavior. However in contrast to classical relaxors such as $PbMg_{1/3}Nb_{2/3}O_3$ or $PbSc_{1/2}Ta_{1/2}O_3$ the dielectric permittivity maximum in PFT is located not in the cubic phase but within the temperature range of tetragonal phase [1,2]. Surprisingly, it was found out recently, that PFT ceramics obtained by sintering the mechanochemically synthesized powders does not show the relaxor-like behavior [3[.

In the present work we carried out comparative dielectric studies of highly-resistive Li-doped PFT ceramics obtained i) by sintering the mixture of nonactivated oxides and ii) ceramics obtained from mechanically activated powders.

Mechanical activation was carried out in the planetary-centrifugal mill AGO-2 (Russia). The formation of nanodispersed structure with the particle size 15 - 20 nm as a result of mechanical activation for 15 min at room temperature was demonstrated by X-ray diffraction and TEM. The sintering process was investigated by means of X-ray powder diffraction. The lattice parameters, the sizes of X-ray coherent scattering blocks and their distortion, as well as the density depending on annealing conditions were determined. Our studies have shown that due to mechanical activation dense PFT ceramics can be obtained at sintering temperature as low as 900 °C.

Both types of PFT ceramics exhibited a very large dielectric response (maximum permittivity values about 20000 at 1 kHz). However the relaxor-like behavior was observed only for PFT ceramics obtained from the nonactivated mixture of oxides.

It is supposed that in contrast to PMN, the relaxor-like behavior of PFT seems to be due to coexistence of tetragonal and cubic phases in a wide temperature range.

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Effect of lead excess on electrical response under IR irradiation in thin PZT films

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Thin ferroelectric films are attractable for a set of microelectronic applications such as random excess memories, microactuators, electromechanical and infrared sensors, magnoelectrics, microwave electronics, and so on [1]. In the last decade, experiments on interaction of infrared (IR) irradiation with thin PZT films have revealed not only pyroelectric response but photovoltaic one, too. According to [2,3] a photovoltaic effect observed in the films may bes caused by inclusions of semiconductive lead oxide in dielectric PZT perovskite matrix.

In the work, thin-film PZT-PbO heterostructures were deposited on platinized silicon substrate using RF magnetron sputtering and then annealed at high temperatures in the air. Variations of electrical response on IR irradiation of PZT-PbO heterostructure were studied depending on temperature of perovskite crystallization (T_{ann}). All the films under study showed different degrees of unipolarity. It was shown that polarity and waveform of the IR response is associated with a strong change of lead oxide content with T_{ann} variation (fig.1).
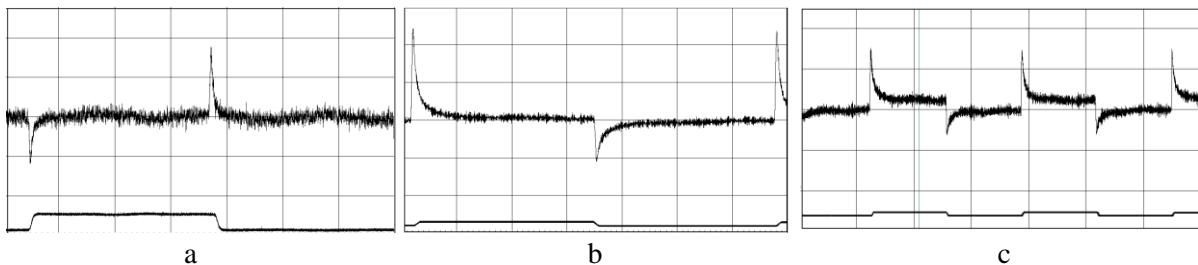
Fig.1. Different types of electrical response of PZT-PbO composite versus temperature annealing T_{ann}: a) 570 ^{o}C, b) 565 ^{o}C c) 560 ^{o}C

An analysis of the results obtained has shown at least two distinct mechanisms of electrical response. The first oscillogram (fig.1,a) reflects a classical pyroelectric signal, and other two oscillograms (fig.1,b and 1,c) – different kinds of photoelectric response in the vicinity of arrangements of lead oxides inclusions in thin-film perovskite matrix The possibilities of the optical information reading in such heterostructures are discussed.

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Changes in the composition of yttria-stabilized zirconia in a memristor structure due to electroforming and resistive switching process

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Considerable attention has been paid recently to the development of nonvolatile resistive memory devices (memristors) based on metal–insulator–metal (MIM) structures, in particular by using insulators in the form of oxides with high mobility of oxygen vacancies [1]. A number of physical models has been proposed to describe the electroforming and resistive switching processes in memory cells that includes the formation of conducting pathways (filaments) composed of metal atoms in oxide matrix and induced by the presence and electric-field-driven migration of oxygen vacancies or mobile oxygen ions in nonstoichiometric oxides [1–4]. The nature and morphology of conducting filaments are still a subject of debates and depend strongly on the composition and heterogeneity of oxide material.

The present report is focused on the results of cross-section transmission electron microscopy (XTEM) study of capacitor-like MIM structures based on a single insulating layer of yttria-stabilized zirconia (YSZ) containing 12 mol.% Y_2O_3 demonstrating the reproducible resistive switching after electroforming. The MIM structures with top Au electrode were fabricated by the method of magnetron sputtering on commercial $TiN/Ti/SiO_2/Si$ substrates. The structure and chemical composition of either the as-deposited thin-film structures or the structures subjected to electroforming and switching were analyzed by using the JEOL JEM-2100F high-resolution electron microscope operating at 200 keV and equipped by the X-Max energy-dispersive spectrometer (EDS).

The as-deposited YSZ film has a polycrystalline columnar structure typical of magnetron-deposited materials. Certain changes occur in the microscopic contrast after electroforming and repeatable resistive switching that correlates with the grain interfaces in oxide film. In particular, the EDS-measurements of chemical composition at the various depths in a direction parallel to the surface of YSZ film show the existence of metalized areas (100% of Zr, Y) in the memristor structures after electroforming compared to the quite uniform metal distribution in the as-deposited structures. The lateral size of these metalized areas is found to be about a few nanometers. A number of these areas increases while the O/Zr concentration ratio decreases with the increase in the insulator film depth, that corresponds to the polarity of voltage applied during the electroforming process.

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Effect of composition on the surface structure of piezoelectric ceramics based on lead zirconate titanate

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We investigated the structure of PZT-19 and DTN-19M ceramics with different stoichiometry of the composition. Investigations of the surface topography of the polar cut were performed using an atomic force microscope (AFM). To identify the structure of the grains on the AFM sample surface was polished and then etched in a solution of HCl with the addition of HF for 10 seconds. No considerable difference in grain size in the ceramics of different compositions was found. At the same time in the composition of the PZT-19M observed occurrence of grains conglomerates, while the PZT-19 composition has a more compact grain structure (fig. 1).
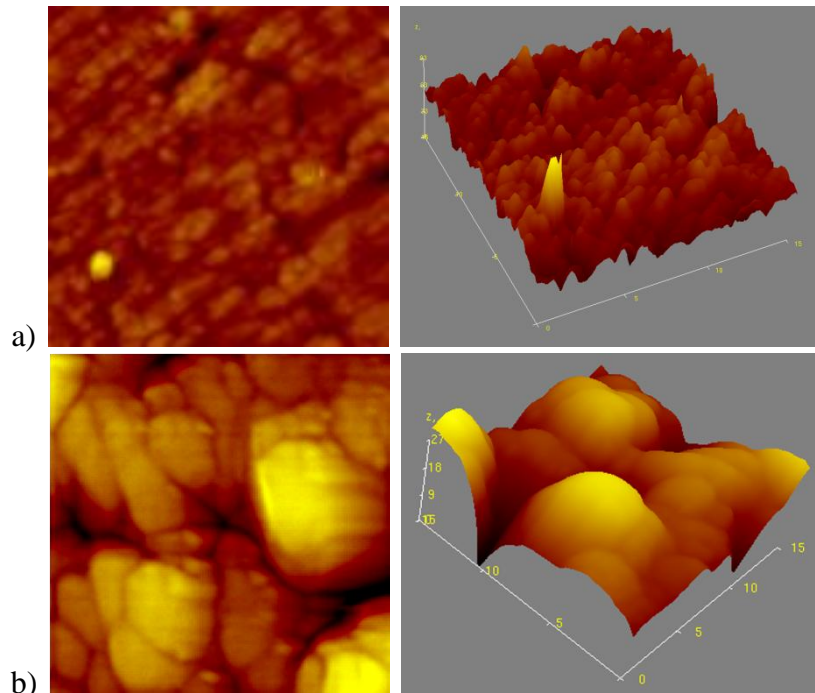
fig. 1. AFM image of the surface corresponding to the negative end of the spontaneous polarization vector of PZT-19 (a) and PZT-19M (b) ceramics. The image area is 15x15 μm, height: 90 nm (a), 30 nm (b)

The difference in the structure was observed on the sides corresponding to the positive ($+P_s$) and negative ($-P_s$) end of the spontaneous polarization vector. This is related to a different etching rate for $+P_s$ and $-P_s$ areas.

Dielectric properties of the single crystals of the ferroelectric solid solutions $(Pb_{1-x}Ba_x)_5Ge_3O_{11}$

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The X-ray diffraction and dielectric studies were performed on the single crystals of the ferroelectric solid solutions $(Pb_{1-x}Ba_x)_5Ge_3O_{11}$ with $0 \leq x < 0,12$ obtained by flux method in the conditions of slow cooling of the melts. It was established that the substitution of the Pb atoms by the Ba atoms causes the monotonic increases in the sizes of trigonal unit cell of crystals. The peculiarities of the dielectric properties and conductivity of the crystals were investigated in the ranges of temperatures of 4,2 - 800 K and the frequencies of 0,1 - 200 kHz. It was found that the increase of the concentration of Ba in crystals causes rather sharp degradation of the ferroelectric properties: temperature of Curie point T_c drop from 450 K to 120 K, the values of the peaks of dielectric permittivity ε_m and losses of $tg\delta_m$ in the vicinity of T_c reduce and broaden. In addition to anomalies in the range near of T_c, dielectric properties show anomalies of relaxation character in the temperature ranges 220 - 260 K and 30 - 170 K (see fig.). Dielectric characteristics of crystals with $x = 0,06 - 0,08$ noticeably depend on their thermal prehistory, in this concentration range the decreasing of ε_m with increasing of Ba concentration is replaced by growth. Observed peculiarities of the temperature and concentration dependencies of the dielectric properties of the solid solutions are related with dynamics of the thermolocalization of charge carriers on the defective levels with activation energies $U_{a1} \approx 0,65$ and $U_{a2} \approx 0,2$ eV, occurring in the temperature ranges 240 – 280 and 110 - 150 K respectively and with shift of T_c to temperature range of the charge localization on the U_{a1} level with a increasing of the Ba concentration.
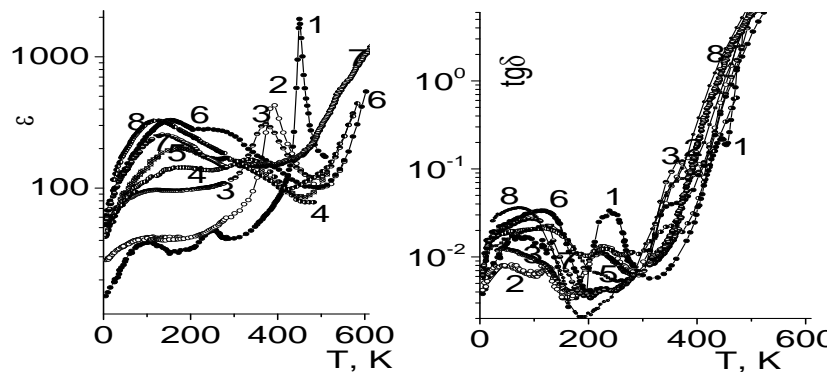
Fig. Temperature dependencies of $\varepsilon(T)$ and $tg\delta(T)$ of the crystals $(Pb_{1-x}Ba_x)_5Ge_3O_{11}$ with $x = 0$ (curves 1), 0,02 (2), 0,04 (3), 0,06 (4), 0,07 (5), 0,08 (6), 0,09 (7) and 0,10 (8), measured along a trigonal axis *c* of crystals on 1 kHz.

Microwave absorption study of the $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+y}$ single crystals in the superconducting transition region

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Microwave absorption (MWA) recorded on an electron spin resonance (ESR) spectrometer in the type II superconductors is due to the dissipative vortex motion [1]. Upon the transition from the superconducting state to the normal one such absorption has to disappear. However, if there are superconducting fluctuations with the Cooper pair lifetime larger than the microwave field period at temperatures higher than the critical one T_c, they can be revealed in the MWA measurements. This work is devoted to searching for MWA in $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+y}$ single crystals at $T>T_c$ and to studying the vortex liquid state with its help.

We investigated single crystals of the Bi-2212 compound with the yttrium dopant $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+y}$. The Y dopant concentration controls the hole doping level and the critical temperature. When the Y concentration is low ($x = 0 \div 0.1$), the hole-doping level is close to the optimum (OP) and the critical temperature is high (>90K). In the crystals with $x = 0.3$ the hole density is low (underdoped samples) and $T_c= 37K$. The microwave absorption is measured on an ESR spectrometer BER-418s Bruker with the frequency of 9.3 GHz.

The study revealed MWA in samples at temperatures both lower and higher than that of the superconducting transition. In underdoped samples MWA is found at temperature at 89K and below. It is by 40K higher than T_c. The MWA signal hysteresis is observed at $T<65K$ in this sample. Its shape looks like the hysteresis loop in the case of the vortex pinning by the surface [2]. At $T<T_c$ the hysteresis loop changes and takes the shape characteristic for the volume pinning. In the OP samples the temperature of the MWA appearance is higher than T_c by only several degrees of Kelvin.

The observation and behavior of MWA above critical temperature can be explained by using the hypothesis of the phase fluctuations of the superconducting order parameter and the existence of the vortex phase at $T>T_c$ [3]. Assuming that the vortex liquid is formed in the regions with the uncorrelated Cooper pairs, the vortex pinning should be of the surface type here because of the inefficiency of bulk pinning and the developed surface.

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Synthesis and dielectric properties of $(1-x)KTaO_3$-$xBiScO$ system

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Nowadays a search of lead-free ceramic materials is actual theme for investigations in materials science. One of prospect directions of such kind of search is synthesis of solid solutions based on $BiScO_3$. It was found that a lot of $BiScO_3$-based solutions have extreme values of physical properties near morphotropic phase boundary (for instance, $BaTiO_3$-$BiScO_3$ [1], $BiScO_3$-$PbTiO_3$ [2]). $KTaO_3$-$BiScO_3$ system is a new system among lead-free ceramic materials containing $BiScO_3$ as one of end members. $KTaO_3$ in this system is a virtual ferroelectric having at room temperature a cubic symmetry.

The aim of this report is to prepare and examine dielectric properties of $(1-x)KTaO_3$-$xBiScO_3$ ceramic material in order to find any anomalies of ferroelectric nature.

The samples with (x=0.05, 0.1, 0.2, 0.3, 0.4 and 0.5 were synthesized using a conventional solid state reaction method.

A set of dielectric anomalies at high temperatures were found for the samples under study. Temperature positions of these anomalies are x-dependent. For instance, two ε' (T) maxima centered on $T_{m1} \approx 680$ K and $T_{m2} \approx 980$ K are clearly observed for the sample with $x = 0.5$ (Figure 1). These maxima can be well taken into account as diffuse ferroelectric phase transitions.
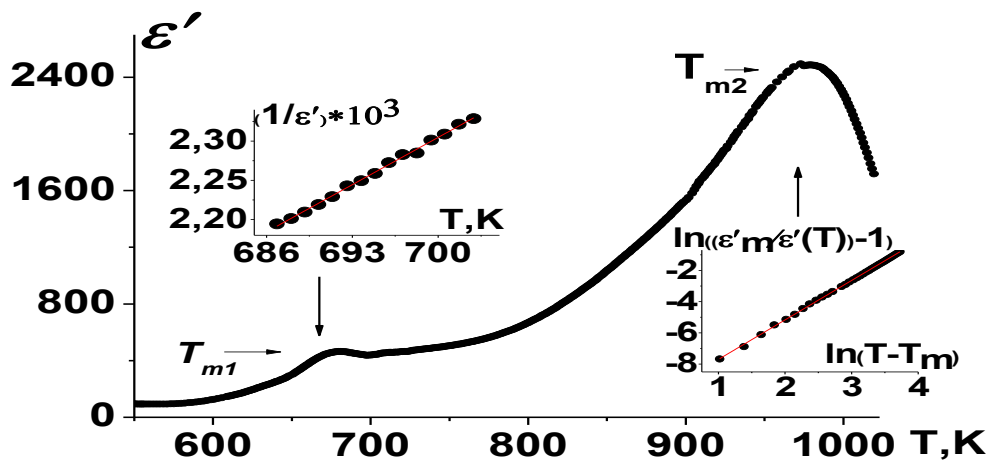
Figure 1. Temperature dependence of ε' for the sample with x=0.5

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Ordered state of the intrinsic two-component magnetoelectric material Li$_2$ZrCuO$_4$ stuied by ^{7}Li NMR

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Li$_2$ZrCuO$_4$ is as an intrinsic magnetoelectric two-component material where a frustrated quasi-1D S = 1/2 quantum spin magnetic Cu^{2+} sublattice is coupled with a frustrated 3D pseudospin-1/2 quantum Ising-glasslike electric Li$_I^+$ sublattice. [1]. Here we present the results of experimental and theoretical study of the low-temperature ^{7}Li NMR line shapes in a axis oriented polycrystalline samples. The onset of an incommensurate spin-spiral-like order below T$_N$ ≈ 6 K leads to a dramatic change of the ^{7}Li NMR spectrum. The proposed model of interacting incommensurate spin and glassy ordered electrical pseudospin sublattices enables a consistent description of the ^{7}Li NMR line shapes[2]. We show that the peculiar NMR line shapes are determined by the specific, sample dependent, distribution of the Li$_I$ ions in the glassy ordered electric sublattice. The spin-flop transition occurs at 3.5T that leads to the spectrum transformation. That allows making the preposition concerning to the spin structure in the spin-flop phase.

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Temperature dependence of the magnetization in GdMnO$_3$/SrTiO$_3$:Nb

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We studied the magnetic properties of GdMnO$_3$ thin films deposited onto Nb doped SrTiO$_3$ substrate. We performed the measurements of the magnetization in the temperature range 1.9-300K under different values of the external magnetic field using the zero magnetic field cooling (ZFC) and the magnetic field cooling (FC) regime (Fig.1).
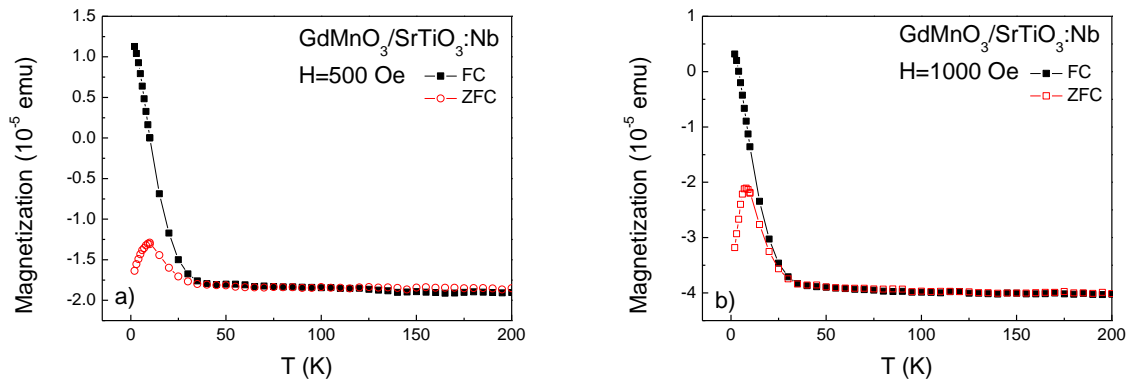
Fig.1. Temperature dependence of the magnetization of GdMnO$_3$/SrTiO$_3$:Nb thin films at different values of the external magnetic field H=500 Oe –a) and H=1000 Oe – b).

The splitting of the FC and ZFC magnetization of the GdMnO$_3$/SrTiO$_3$:Nb heterostructure starts from the temperature T=40K (Fig.1.a), that corresponds to the ordering temperature in the sample [1]. In addition, the zero-field cool run shows a cusp at ~10 K under H=500 Oe (Fig.1 a). If the measurement is repeated under a higher field H=1 kOe (Fig. 1 b), both the splitting temperature and the cusp shift to lower temperatures. From these features the presence of competing ferromagnetic/antiferromagnetic interactions leading to a glassy behavior can be suggested.

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EPR Characterisation of iron oxide nanoparticles embedded in hyperbranched polimers

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Synthesis and research of metals' and metal compounds' nanoparticles with magnetic properties is associated with advanced technologies of magnetic fluid use in biomedical applications. Ability of magnetic fluids' movements contactless control allows to use them into the organism under the action of an external magnetic field as targeted drug delivery, to conduct tumors' hyperthermia by heating of the magnetic particles in an alternating magnetic field, to contrast NMR-tomographic images, and in transfection of cells by means of a magnetic field. Iron oxide nanoparticles that are used as the dispersed phase in magnetic fluids, can be used as targeted products in biological objects due to their low toxicity. Selection of nontoxic synthetic nanoparticles' stabilizers with biosimilar structure and properties is an urgent task. Especially promising for this purposes are non-toxic hyperbranched polyesterpolyols (GBPP). Branched structure with the presence of terminal functional fragments combined with the presence of cavities in the structure of macromolecules allows to control of magnetic nanoparticles' stabilization mechanism, to adjust their size and dispersion. The degradation and biodegradation of polyesterpolyols and their derivatives allow unhindered utilize the magnetic fluid's components from the human body.

In this research composite nanoparticles Fe_2O_3/H20, where H20 – hyperbranched polyesterpolyol (Boltorn H20), that are based on 2,2-bishydroximethylpropanoic acid, were synthesized and measured by EPR. Concentrated samples in the form of brown powder and a frozen solution were investigated.

EPR measurements of powder sample at room temperature (300 K) detected the Lorentz shaped line with the linewidth $\Delta H \sim 500$ G and g-value about 2.015.

Sediment fraction and over sediment fraction were also studied. Over sediment fraction didn't demonstrate any EPR spectra. In sediment sample there was a complicated wide and a multicomponent EPR spectrum with super hyperfine splitting due to a few (three or four) nitrogen nuclei.

To determine magnetic characteristics of nanoparticles the temperature dependence of EPR spectra of synthesized polymer samples with nanoparticles of Fe_2O_3/H20 was investigated. Temperature behavior of the signal corresponding to iron oxide nanoparticles was the following. When decreasing the temperature within the interval 300K – 100K, the EPR line was slowly moved into the low fields, and the linewidth was gradually growing. But lower the temperature 100 K the more large displacement of line into low fields and its strong widening were observed. Temperature behavior of parameters was analyzed by Nagata-Ishikhara dependence. As it was determined the temperature behavior of nanoparticles was close to superparamagnetic. This fact is agreed with the detected size of the particles (5-10 nm). At low temperatures (<100K) the superparamagnetism was frozen.

Electric Field Deposition Behavior on Self-Polarization Effect in LiNbO$_3$ Thin Films

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Ferroelectric thin film integration with Si and other integrated device substrates has the potential to enable new modes of photonics integration as well as a new class of high work/volume piezoelectric devices for MEMS integration. Thin films of Lithium Niobate (LiNbO$_3$) posses a number of advantages over bulk material including the possibilities of producing step index profiles, selectively introducing dopants, and the fabrication of multilayer structures. The prospect of producing high quality (oriented and possessing low optical loss) thin films of LiNbO$_3$ on silicon substrates is particularly attractive because the silicon provides a rigid and flat substrate ideal for large area processing of devices by lithographic techniques and it allows for the integration of lithium niobate electro-optic and silicon integrated circuit technology. The studied LiNbO3films were deposited by applying the electric field during radio-frequencies magnetron sputtering of the single-crystalline target in Ar/O=1 atmosphere (0.6 Pa) on Si(110) substrate at 550 ºC. Atomic force microscopy measurements indicate that the surface roughness of the LiNbO$_3$ thin films was 4-10 nm, which meets the demands for practical waveguiding devices. The ferroelectric properties have been studied by visualization of the as-growth domain structure, recording induced ferroelectric states by piezoresponse force microscopy (PFM) using Scanning probe laboratory NTEGRA-Prima (NT-MDT, Russia). The asymmetry of the distribution of vertical PFM (VPFM) signal is a manifestation of the so-called self-polarization effect. The maximum of the VPFM histogram of this distribution is shifted toward negative (or positive) values of the piezoelectric response, which implies that the polarization vector in most grains is directed toward the upper (or lower) interface. In work discusses the possible mechanisms of the origin a self-polarization in LiNbO$_3$ thin films.

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