UNIVERSITY OF LATVIA
INSTITUTE OF SOLID STATE PHYSICS

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PHASE TRANSITIONS AND PHYSICAL PROPERTIES OF $Na_{1/2}Bi_{1/2}TiO_3$-BASED SOLID SOLUTIONS

Summary of Doctoral Thesis

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Abstract

$Na_{1/2}Bi_{1/2}TiO_3$ (NBT) based solid solutions are interesting mainly due to possibility to develop lead-free compounds for practical applications. While attention is paid to improvement of electromechanical properties, other possible directions of applications and studies of physical nature of properties of these compounds are less developed. The aim of the doctoral thesis is synthesis and study of NBT-based compounds, which would widen the concept of possible applications, as well as nature of phase transitions and relaxor state, which is often observed in such compositions.

A new system of solid solutions NBT-$SrTiO_3$-$PbTiO_3$, in which relaxor properties change in a wider spectrum than in any other known solid solution systems of relaxor ferroelectrics, passing different stages of relaxor state stability, is discovered. Detailed study of dielectric properties is performed, paying attention to widely-used Vogel-Fulcher and power laws, as well as offering a new approach for description of the dielectric dispersion in the whole temperature range, where relaxor state exists, using one distribution function of relaxation times. For description of relaxor state, study of polarization, thermal expansion, electromechanical properties and electrocaloric effect is also used. Efforts were made to determine the Burns temperature. Dielectric nonlinearity was evaluated. Performing critical analysis of nowadays widely used thermodynamic equations, it was shown that, in spite of describing electrocaloric effect in ferroelectrics very well, they are not applicable in relaxor state. Influence of different substitution in perovskite ABO_3 A- and B-site on NBT-$SrTiO_3$-$PbTiO_3$ solid solutions is studied, showing that, besides distribution of different size/valence ions in equivalent sites of lattice, the weakening of ferroelectric state has an important role in development of relaxor properties. Study of NBT-$BaTiO_3$ and NBT-$CdTiO_3$ systems is done, clarifying phase diagrams and physical properties of these solid solutions. The obtained results also give the possibility to make important conclusions about phase transitions in pure NBT, which is an object of wide discussions.

For some of the studied compositions, high values of electrocaloric effect are observed, which make them interesting for new applications, based on this effect. All of the compounds are lead-free or with low lead content. Therefore there is obtained new information about possible substitution of lead-containing ferroelectric materials for various applications with the new materials.

Contents

Introduction

Motivation

Nowadays ferroelectric (FE) materials are of great practical importance. They are widely used in actuators, sensors, transducers, as well as in nonlinear and integral optics, in production of capacitors, memory elements, ultrasound converters etc.

At the moment compositions with high lead content, such as lead zirconate titanate (PZT) and its modifications with lanthanum (PLZT), solid solutions of lead magnesium niobate and lead zinc niobate with lead titanate (PMN-PT and PZN-PT), dominate in the world market of FE materials. However, in the result of production, application and waste recovery of these materials, lead-containing compounds, characterized by high toxicity, are excreted into environment. Therefore considerations, connected with protection of environment and health of the world's population, stimulate intensive research of new alternative FE materials, which would not contain lead or would contain it only in small concentration.

$Na_{1/2}Bi_{1/2}TiO_3$ (NBT), as well as NBT-based solid solutions, which show various properties, interesting for practical applications, are among the most perspective materials, from this point of view. As the largest part of the studies is devoted mostly to improvement of the electromechanical properties, till recent times other possible directions of applications and studies of physical nature of properties of these compositions are disregarded. Therefore it is very important to synthesize and perform physical studies of new NBT-based compounds, which would allow one to extend concept of application possibilities in a wide spectrum, starting with traditional applications, where piezoelectric effect is used, and ending with rather exotic ones, connected with use of electrocaloric effect, as well as of phase transitions and nature of relaxor state, which, for example, was stated in NBT-$SrTiO_3$-$PbTiO_3$ in the groundwork of this thesis.

Relaxor state is the second very important aspect in studies of NBT solid solutions, as nowadays this is one of the most urgent topics in physics of ferroelectrics. Despite the intensive research of relaxor ferroelectrics, know by now, their physical nature and origin are still an object of wide discussions. Therefore study of new families of relaxor ferroelectrics, like, for example, NBT-$SrTiO_3$-$PbTiO_3$, where gradual transfer from relaxor to classical FE properties depending on concentration of the solid solution components, passing sequent characteristic sub-states, is observed, could give significant contribution to physics of relaxor ferroelectrics.

Another relevant aspect of studies of NBT solid solutions is extending concept of pure NBT, where nature of phase transitions, despite the wide research, is not completely clear till this moment.

Aim and Objectives of the Work

The aim of the doctoral thesis is to obtain and study NBT-based solid solutions with intention to widen concept of phase transitions and properties not only in the studies groups of solid solutions, but also in pure NBT and get additional information about relaxor ferroelectrics, as well as appreciate potential applications of the studied materials.

There are established the following objectives:

- Perform measurements and analysis of structural, dielectric and polarization properties of new NBT-based solid solutions group NBT-$SrTiO_3$-$PbTiO_3$ (NBT-ST-PT);
- Clarify phase diagram and character of physical state in NBT-$BaTiO_3$ and NBT-$CdTiO_3$, basing on study of structural, dielectric and polarization properties;
- Study features and description, characteristic to relaxors in NBT-ST-PT solid solutions (Vogel-Fulcher law, power law, distribution of relaxation times, Burns temperature, dielectric nonlinearity);
- Study influence of different perovskite A- and B-site substitution (Li, K, Ag, Ca, $NaNbO_3$, $PbMg_{1/3}Nb_{2/3}O_3$) on NBT-ST-PT solid solutions;
- Perform study of electrocaloric effect and electromechanical properties in NBT-ST-PT;
- Interpret phase transitions in NBT.

Author's Contribution

Most of the studies were performed in the Institute of Solid State Physics, the University of Latvia (UL). The studied materials were prepared in the Laboratory of Synthesis and Processing of the Department of Ferroelectrics of the Institute of Solid State Physics, UL. Measurements of their structure were performed in the Laboratory of X-ray Diffraction Analysis of the Department of Ferroelectrics of the Institute of Solid State Physics, UL. The author has performed measurements, data processing and analysis of dielectric permittivity, polarization and electromechanical properties. She has processed and analyzed x-ray diffraction data, a part of which were obtained in the framework of bachelor's thesis of R. Ignatans, student of the Faculty of Physics and Mathematics, UL, as well as obtained microstructure images of the studies samples with scanning electron microscope.

Thermal expansion measurements were done in the University of Vienna in collaboration with Prof. A. Fuith. The author of the thesis took part in the experimental measurements, working in the University of Vienna for approximately one month, performed processing and analysis of all measurement data. Electrocaloric effect measurements were done in the University of Oulu in collaboration with Dr. tech. J. Hagberg and M. Sc. (tech.) J. Peräntie. The author has performed processing and analysis of the obtained measurement data. The author has also analyzed and used dielectric spectroscopy data in a wide frequency range, obtained in the Vilnius University in collaboration with Prof. J. Banys, M. Sc. M. Ivanov and M. Sc. Š. Svirskas.

The author had performed analysis of the study and made the conclusions, discussing the obtained results with her colleagues. The author had presented the results of the present work at local and international conferences, together with colleagues had prepared scientific manuscripts.

Scientific Novelty of the Work

New NBT-based materials were synthesized and studied, as well as concept of such compositions, previously mentioned in literature, was widened. A new family of solid solutions with relaxor properties (NBT-ST-PT) was obtained, in which stability of the FE state changes in a wider spectrum in comparison with other relaxor ferroelectrics known by now. A complex experimental approach in study of relaxor state was used in this work. The obtained results provide new information about relaxor ferroelectrics, as well as extend concept of application possibilities of the studied materials (including new applications, based on electrocaloric effect). For the first time, a common description of dielectric dispersion, using Frölich model, is offered for the whole temperature range, where relaxor properties exist. The studied materials are lead-free materials or materials with low lead content. Therefore new information about possible replacement of lead-containing FE materials with the new materials for traditional applications was obtained.

1. Literature Review

1.1. Facts and Hypotheses about NBT and Its Solid Solutions

Sodium bismuth titanate $Na_{1/2}Bi_{1/2}TiO_3$ (NBT), compound of perovskite structure ABO_3, which contains heterovalent ions in equivalent (A-site) positions, was discovered in 1961 [1]. At room temperature this material is in FE state, as it exhibits high remnant polarization (P_r = 38 μC/cm^2) and coercive field (E_c = 73 kV/cm) [1, 2]. This composition has specific temperature-frequency dependence of dielectric permittivity (Fig. 1.1). At rather high temperature T_m (approximately 320 °C) it has diffused maximum of dielectric permittivity, position of which does not depend on frequency. Whereas at lower temperatures (approximately 200 °C) frequency-dependent shoulder of dielectric permittivity appears [1, 3]. In the region of this shoulder, at depolarization temperature T_d polarization of previously poled samples disappears [4-7]. The main goal in studying NBT is modification of it to obtain good piezoelectric material for different applications and, first of all, to decrease E_c and increase T_d [5, 8].

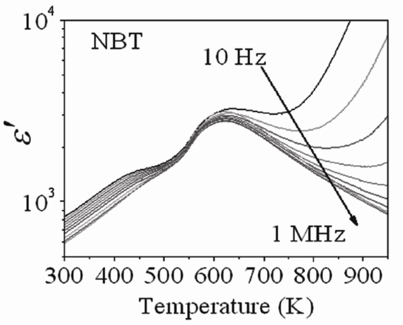

Figure 1.1. **Temperature dependences of the real part of dielectric permittivity at different frequencies [3]**

According to x-ray diffraction and neutron diffraction studies, there are two structural phase transitions in the phase diagram of NBT – between the high-temperature cubic phase and tetragonal phase with phase coexistance region from ~500 °C to ~540 °C and between the tetragonal phase and rhombohedral phase with phase coexistance region from ~255 °C to ~400 °C [4-11]. Moreover birefringence studies [10] indicate possibility that the tetragonal and the rhombohedral phases are incommensurate, in the result of which the phase transition can occur through some kind of an intermediate phase with cubic symmetry. As it is seen in Fig. 1.2, anomalies of physical properties correlate with structural changes at the phase transition between the tetragonal and the cubic phases. Whereas, at the phase transition between the rhombohedral and the tetragonal phases, such a correlation cannot be found [12]. The absence of correlation leads to contradictory concepts about nature of the phases and inconclusive phase diagrams.

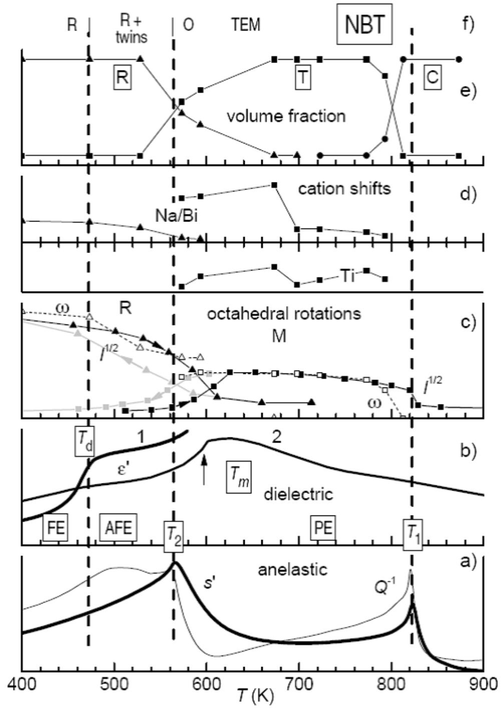

Figure 1.2. **Anomalies of different properties in NBT as a function of temperature: a) elastic properties; b) dielectric properties; c) octahedral rotations, obtained from neutron diffraction; d) cation shifts, obtained from neutron diffraction; e) volume fraction obtained from neutron scattering [12]**

There are also many other uncertainties regarding NBT. To great extent they are connected with the temperature region between T_m and T_d, where anomalies of different properties indicate a phase transition at certain temperatures [4, 6, 9], which do not correlate with structural phase transition. Also it is not completely clear, what is the structure at room temperature. There is evidence of polar clusters' existence in nonpolar matrix, presence of local monoclinic structure or rhombohedral blocks and orthorhombic layers etc. [7, 13, 14]. The complicated domain morphology and uncertainties regarding phase of the tetragonal structure above T_m a.o. are also of great importance [4, 9, 11]. In general, NBT is still an object of wide discussions, and studies that would help to understand its structure and physical properties, are still urgent and attract large interest.

For the purpose of improving properties of NBT for practical applications and developing new lead-free FE materials or FE materials with low lead content, which could compete with nowadays widely used lead-based FE materials, comprehensive studies of NBT solid solutions are done. Research of NBT solid solutions can also provide a possibility to better understand the processes ongoing in NBT, explain origin of different dielectric and other anomalies and give information about nature of the phase transitions, thus solving different contradictions, connected with interpretation of structural and physical properties of NBT.

There are well studied NBT binary solid solutions with $K_{1/2}Bi_{1/2}TiO_3$ (KBT), $BaTiO_3$ (BT), $SrTiO_3$ (ST), $Li_{1/2}Bi_{1/2}TiO_3$ (LBT), $Na_{1/2}La_{1/2}TiO_3$ (NLT), $NaNbO_3$ (NN) and $PbTiO_3$ (PT) as the second component, as well as influence of different additives on structure and properties of these solid solutions. There are done studies also of some ternary solid solutions, for example, NBT-KBT-BT, NBT-LBT-KBT etc. [15-18]. For many of these compositions, interesting properties were observed. Among them are relaxor properties, which nowadays attract a lot of interest.

1.2. Conception of Relaxor Ferroelectrics

As NBT solid solutions are often associated with relaxor ferroelectrics, the conception of this phenomenon is very important in their study.

Relaxor ferroelectrics can be defined as FE materials, which are characterized by diffused maximum of dielectric permittivity temperature dependence $\varepsilon'(T,f)$, shifting in direction of high temperatures, if measurement frequency is increased, (Fig. 1.3) without macroscopic symmetry change in the region of dielectric permittivity maximum temperature [19-22]. At high temperatures a deviation from the Curie-Weiss law, characterizing classical ferroelectrics, appears in these compositions [23]. While measurements of polarization as a function of electric field show so-called slim loops with negligible remnant polarization and coercive field [24].

It is considered that at high temperatures relaxor ferroelectrics are in paraelectric state [25, 26]. As temperatures decreases, at temperature T_B, which is usually called Burns temperature [27, 28], so-called polar nanoregions (PNRs), which most often are considered to be the origin of characteristic relaxor properties, start to appear. The dielectric permittivity maximum at temperature T_m is explained by rapid increase of interaction between PNRs [20, 29, 30]. In the temperature range between T_B and T_m, different empirical relations are used to describe ε'(T,f). One of the best-known is the power law [23].

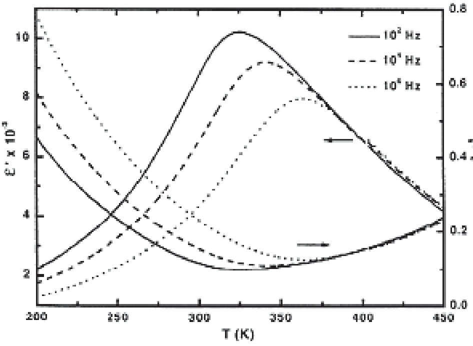

Figure 1.3. **Temperature and frequency dependences of the real part of dielectric permittivity ε'(T,f) [19]**

For some relaxor ferroelectrics, a spontaneous phase transition between relaxor and FE states occurs at temperature $T_t < T_m$, where a jump of ε'(T,f) is observed [31]. Besides it is considered that relaxor ferroelectrics have one more characteristic temperature T_f, where freezing of PNRs occurs [32, 33]. Usually it is assumed that this temperature coincides with the Vogel-Fulcher temperature, existence of which is postulated by the Vogel-Fulcher law, very frequently used for description of dielectric dispersion in the region of T_m and below T_m [32, 33].

Nowadays relaxor ferroelectrics are an object of wide discussions. For example, it is not clear, if the freezing really occurs at T_f, as no changes of structure or physical properties, which would testify to this, occur at this temperature. The relations often used to describe ε'(T,f) are empirical – they do not have strong physical basis. There are different opinions about structure of PNRs – the proposed models can be conditionally divided in two groups: 1) where they are considered as polar "islands" of nanometer size in a nonpolar cubic matrix; 2) where they are considered as polar domains of nanometer size, separated by wide nonpolar domain walls. Formation mechanism of PNRs is not clear. If PNRs are located in a nonpolar matrix, it is not clear, what is the role of this matrix, how PNRs interact with it etc. Therefore study of relaxor ferroelectrics is one of the most urgent topics in physics of ferroelectrics at the moment.

2. Experimental

2.1. Studied Samples

The studied ceramic samples of NBT solid solutions were prepared in the Laboratory of Synthesis and Processing of the Department of Ferroelectrics of the Institute of Solid State Physics, UL.

All samples were obtained by solid state reaction from chemical-grade (99.0-99.9%) oxides and carbonates, such as Na_2CO_3, Bi_2O_3, $SrCO_3$, PbO, TiO_2, Nb_2O_5, MgO, Ag_2O, K_2CO_3, Li_2CO_3, $BaCO_3$, $CaCO_3$ and CdO. Two-stage calcination was performed. The first calcination was done at 850-1000 °C 2 h, the second one – at 950-1070 °C 2-3 h, and sintering – at 1120-1410 °C 2-6 h (depending on composition).

The following solid solution systems were prepared:

- **$0.4Na_{1/2}Bi_{1/2}TiO_3$-$(0.6-x)SrTiO_3$-$xPbTiO_3$** *(x = 0.00...0.25);*
- **$(0.4-x)Na_{1/2}Bi_{1/2}TiO_3$-$0.6SrTiO_3$-$xPbTiO_3$** *(x = 0.00...0.30);*
- **$(1-x)(0.4Na_{1/2}Bi_{1/2}TiO_3$-$0.4SrTiO_3$-$0.4PbTiO_3)$-$xNaNbO_3$** *(x = 0.00...0.10);*
- **$(1-x)(0.4Na_{1/2}Bi_{1/2}TiO_3$-$0.4SrTiO_3$-$0.4PbTiO_3)$-$xPbMg_{1/3}Nb_{2/3}O_3$** *(x = 0.00...0.10);*
- **$0.4(Na_{1-x}Me_{1+x})_{1/2}Bi_{1/2}TiO_3$-$0.4SrTiO_3$-$0.4PbTiO_3$ (Me^{1+}: Li. K un Ag)** *(x = 0.00...0.375);*
- **$0.4Na_{1/2}Bi_{1/2}TiO_3$-$(0.4-x)SrTiO_3$-$0.2PbTiO_3$-$xCaTiO_3$** *(x = 0.00...0.40);*
- **$(1-x)Na_{1/2}Bi_{1/2}TiO_3$-$xBaTiO_3$** *(x = 0.10...1.00);*
- **$(1-x)Na_{1/2}Bi_{1/2}TiO_3$-$xCdTiO_3$** *(x = 0.00...1.00);*
- **$(1-x)Na_{1/2}Bi_{1/2}TiO_3$-$xCaTiO_3$** *(x = 0.03...0.40);*
- **$0.24Na_{1/2}Bi_{1/2}TiO_3$-$0.56Sr_{0.7}Bi_{0.2}TiO_3$-$0.2PbTiO_3$.**

The samples, obtained at optimal preparation regimes, were chosen for the measurements.

In addition, for comparison with the studied composition groups, there was paid attention to the well-known materials $(1-x)PbMg_{1/3}Nb_{2/3}O_3$-$xPbTiO_3$ ((1-x)PMN-xPT) with x = 0.1 and x = 0.08, also prepared by the conventional two-stage processing, and $Pb_{1-x}La_x(Zr_{0.65}Ti_{0.35})_{1-x/4}O_3$ (PLZT-x) with x = 0.09 and x = 0.0925, prepared using two-stage hot-pressing.

2.2. Methods of Study

A large variety of experimental methods was used to study NBT solid solution systems. Most of the measurements were done in the Institute of Solid State Physics, UL, but some – in cooperation with the University of Oulu, the University of Vienna and the Vilnius University.

Structure analysis was done, using x-ray diffractometer *PANalytical X'Pert PRO*. Rietveld method [34, 35] was used for more detailed structure studies. Microstructure was examined with scanning electron microscope *Zeiss EVO 50*.

Special attention was paid to study of dielectric properties. Temperature and frequency dependences of the real part of dielectric permittivity ε' and dielectric loss tangent were obtained in the range 100 Hz – 1 MHz, using LCR meter *HP4284A*. The measurements were done on heating and cooling with the rate of ≤ 2 °C/min. In cooperation with the Vilnius University dielectric properties were considered in a wider frequency range, using the coaxial line method (1 MHz – 3 GHz) and the waveguide method (8-40 GHz).

Polarization as a function of electric field (hysteresis loops) were obtained by Sawyer-Tower method (frequency 0.005 Hz).

In collaboration with the University of Oulu direct measurements of electrocaloric effect (ECE) were performed. A function generator *Agilent 33120A*, connected whit a high voltage amplifier *Radiant RT6000HVA* was used to produce rectangular (3,25 s) or triangular (20 s) electrical pulse. Whereas the thermocouple response was measured by a multimeter *Agilent 34420A*. Multimeter *Agilent 34411A* was used for simultaneous measurements of polarization. All measurements were performed under computer control in *ESPEC BTZ175E* or *Memmert UFP400* ovens.

Thermal expansion measurements were done in collaboration with the University of Vienna, using *Perkin Elmer* dynamic mechanical analyzer *DMA7e*. Measurements were performed on cooling with rate 2 °C/min.

Electromechanical properties were also studied. It was done by modified interferometry method, described in detail in [36], as well as resonance-antiresonance method, using impedance analyzer *HP4194A*.

3. Results and Discussion

3.1. NBT-ST-PT Solid Solutions

A new system of relaxor ferroelectrics NBT-ST-PT ($Na_{1/2}Bi_{1/2}TiO_3$-$SrTiO_3$-$PbTiO_3$), in which relaxor properties change in a wider spectrum than in other known solid solution systems of relaxor ferroelectrics, is discovered in the work [37, 38].

Two groups of solid solutions are considered: 0.4NBT-(0.6-x)ST-xPT and (0.4-x)NBT-0.6ST-xPT. X-ray diffraction results have shown that all studied compositions are 100% perovskites without a secondary phase. At room temperature, cubic symmetry is observed in both groups of solid solutions at low PT concentrations. With increasing of PT content, tetragonality appears and increases monotonously. Studies of microstructure have shown that all compositions are dense ceramics with well-developed grain structure (average grain size – 3-10 μm).

3.1.1. Dielectric and Polarization Properties of NBT-ST-PT

In 0.4NBT-(0.6-x)ST-xPT system, at low PT concentrations $0.00 \le x \le 0.05$ (Fig. 3.1 a), temperature-frequency dependence of dielectric permittivity ε'(T,f) has pronounced relaxor behaviour in the whole experimental temperature range below T_m [21, 22]. Only slim polarization hysteresis loops were observed in the whole studied temperature range, which indicates that it is not possible to induce transition to FE state by applying electric field in these compositions (see Subchapter 1.2).

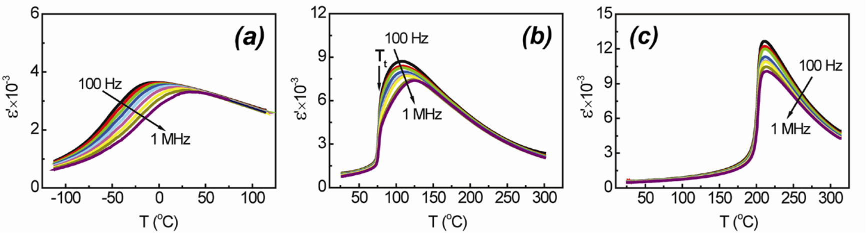

Figure 3.1. **Temperature dependences of dielectric permittivity ε' at several fixed frequencies for 0.4NBT-(0.6-x)ST-xPT solid solutions at PT concentrations x = 0.05 (a), x = 0.15 (b), x = 0.25 (c) (cooling curves)**

Compositions in the concentration range around x = 0.10 also have well-expressed relaxor behaviour (Fig. 3.1 b). However, in these compositions, it is possible to induce FE state by applying electric field, which is supported by observation of double polarization hysteresis loops in certain temperature range, as well as polarization hysteresis loops characteristic to FE state at lower temperatures (Fig. 3.2 a). Temperature dependences of critical electric fields E_{k1} and E_{k2}, at which first order phase transitions from relaxor to FE and from FE to relaxor state accordingly occur, were obtained from double polarization hysteresis loops. It was shown that dependence $E_{k2}(T)$ is quasilinear and there always exists temperature, at which $E_{k2} = 0$ (Fig. 3.2 b). At this temperature (T_{t1}) FE state is spontaneously destroyed at $E = 0$, which is observed also as ε'(T,f) jump on heating previously poled sample (Fig. 3.1 b).

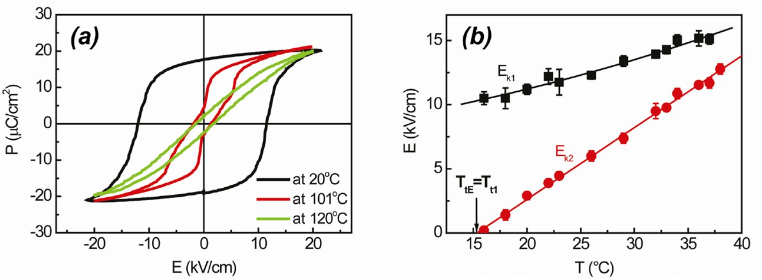

Figure 3.2. **a) Polarization hysteresis loops (P(E)) for composition 0.4NBT-0.45ST-0.15PT at several temperatures; b) temperature dependences of critical electric fields E_{k1} and E_{k2} for composition 0.4NBT-0.45ST-0.10PT**

Whereas dependence $E_{k1}(T)$ declines from $E_{k2}(T)$ on decreasing temperature (Fig. 3.2 b). The declining increases also on decreasing PT concentration, and at $x = 0.10$ $E_{k1}(T)$ obviously has a minimum $E_{k1min} > 0$. This means that in certain concentration range FE state can be induced only by applying electric field $E > E_{k1}(T)$. For $x = 0.15$ $E_{k1}(T)$ dependence reaches $E_{k1} = 0$ at certain temperature (T_{t2}), which means spontaneous phase transition from relaxor to FE state and is indicated also by jump in ε'(T,f) dependence, observed at this temperature on cooling (Fig. 3.1 b).

At high PT concentrations $0.20 \leq x \leq 0.25$ (Fig. 3.1 c), behaviour close to classical FE phase transition is observed. Dielectric permittivity curve has rather sharp maximum at T_m, which is frequency-independent. Dispersion of dielectric permittivity appears only in a narrow temperature range in vicinity of T_m. Phase transition temperatures T_{t1} and T_{t2} almost coincide with the maximum temperature.

Phase diagram for 0.4NBT-(0.6-x)ST-xPT system of solid solutions is shown in Fig. 3.3. Similar observations regarding dielectric and polarization properties were done also for (0.4-x)NBT-0.6ST-xPT system.

Dielectric properties were described with nowadays widely used power law [23], which describes ε'(T) above T_m, and Vogel-Fulcher law [32, 33], which together with flat distribution of relaxation times describes ε'(T,f) dispersion in the region of T_m. Parameters of these relations as functions of concentration

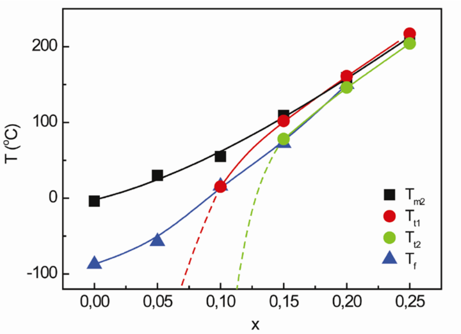

Figure 3.3. **Phase diagram of 0.4NBT-(0.6-x)ST-xPT system of solid solutions: concentration dependence of phase transition temperature T_t on heating (T_{t1}) and on cooling (T_{t2}) and dielectric permittivity maximum temperature T_m on cooling (T_{m2}) (at 1 kHz). At x = 0.10 temperature T_{t1} is observed only for previously poled sample**

were obtained. According to the obtained values of the power law parameters, diffusion of ε'(T) reaches maximums at x = 0.10 and only then decreases. Approximation with the Vogel-Fulcher law indicated that activation energy E_A decreases from 0.15 eV to almost 0 eV, frequency f_0 changes in the range from ~10^{12} Hz to ~10^9 Hz, while Vogel-Fulcher temperature T_f increases on increasing PT content.

3.1.2. Description of Relaxor State

Although the Vogel-Fulcher law is mostly used for description of dielectric dispersion in relaxor ferroelectrics, its use raises a question about interpretation of the dielectric dispersion below the freezing temperature T_f. Interpretation of the freezing process itself is not clear as well, as the relaxation time increases outside the real experimental time scale already at temperatures significantly above T_f. Attempts to relate T_f to the phase transition temperature T_{t1}, which is done in case of PMN [39], are also doubtful. Therefore in this doctoral thesis a different approach in description of the dielectric dispersion is considered.

We have shown that the dielectric dispersion can be described in the framework of one relaxation mechanism in the whole temperature range, where it is observed. The Frölich model for distribution of potential barriers G(H) was used. Distribution of relaxation times τ can be derived from this model:

$$g(\ln\tau) = \begin{cases} C = \text{const}, & \tau_{min} < \tau < \tau_{max} \\ 0, & \tau < \tau_{cmin} \text{ vai } \tau > \tau_{max} \end{cases} \tag{3.1}$$

If measuring frequencies fit the range $\tau_{min} << 1/\omega << \tau_{max}$ ($\omega = 2\pi f$ – cyclic frequency), where τ_{min} and τ_{max} are the lower and the upper limits of the relaxation time distribution, it follows from this distribution that:

$$\begin{aligned}\varepsilon'(\omega,T) &= A(T) - B(T)\cdot \ln \omega \\ \varepsilon''(\omega,T) &= \mathrm{const}\end{aligned} \tag{3.2}$$

As τ_{max} increases, if temperature is decreased, but remains finite in the whole temperature range, then, at low enough temperatures, for any experimentally available frequency ω, $1/\omega << \tau_{max}$, Eq. (3.2) will be valid in all measured frequency range, where $1/\omega >> \tau_{min}$ is fulfilled. The coefficients A(T) and B(T) can be expressed via G(H) parameters and difference between the dielectric permittivity below and above the dispersion region (ε_s-ε_∞):

$$B(T) = (\varepsilon_s - \varepsilon_\infty)\cdot \frac{k\cdot T}{\nu_0} \tag{3.3}$$

$$A(T) = \varepsilon_\infty - B(T)\cdot \ln \tau_{min} \tag{3.4}$$

$$\varepsilon'' = \frac{\pi}{2}\cdot B \tag{3.5}$$

where ν_0 – width of G(H) distribution.

We have shown that such a simple approach can be extended in the whole temperature range of the dielectric dispersion, where distribution function of relaxation times can be regarded as wide, respectively, on conditions that $\tau_{max} >> \tau_{min}$. First of all this assumption is based on the often observed ε''(T,ω). As we have stated for composition 0.4NBT-0.5ST-0.1PT (Fig. 3.4 a) and as it can be seen also from the results published by other authors [33, 40], in the range of low temperatures, relaxor ferroelectrics have a so-called ε''(T,ω) master curve, that is characterized by frequency-independent ε''(T) in the frequency range, which increases in direction of low frequencies, if temperature is decreased. At low temperatures this range is wide enough to contain all experimentally used frequencies.

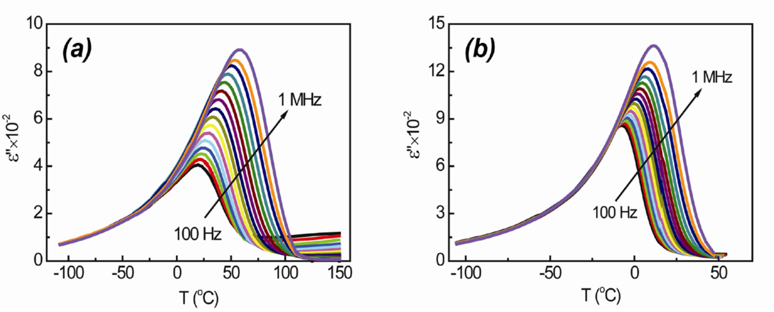

Figure 3.4. **ε''(T,ω) cooling curves for compositions a) 0.4NBT-0.5ST-0.1PT and b) 0.9PMN-0.1PT**

The corresponding behaviour of ε' is schematically shown in Fig. 3.5 a. This dependence qualitatively corresponds to the experimentally observed $\varepsilon'(\ln\omega)$ dependence, assuming that the boundary between $\varepsilon'(\ln\omega) \sim \ln(\omega)$ and $\varepsilon'(\ln\omega) = \text{const}$ is smooth (Fig. 3.5 b). It is important to take into account that the proposed description cannot be combined with freezing ($\tau \to \infty$), to avoid unlimited increase of ε_s with increasing τ. Of course, as it follows from the previously made assumptions, the description, which contains relations (3.1) and (3.2), can be used in the temperature and frequency range, where the condition $\tau_{\min} < 1/\omega < \tau_{\max}$ is satisfied.

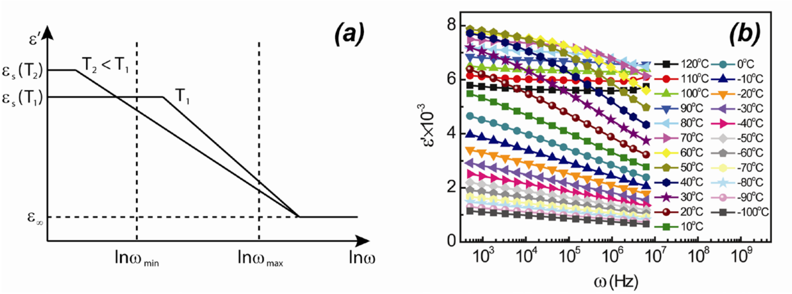

Figure 3.5. **a) schematical representation of $\varepsilon'(\omega)$, which illustrates the main features of dielectric dispersion; b) $\varepsilon'(\omega)$ for composition 0.4NBT-0.5ST-0.1PT**

Besides 0.4NBT-(0.6-x)ST-xPT we have evaluated the above mentioned approach also for 0.9PMN-0.1PT (Fig. 3.4 b) and PLZT-0.09, to extend our conclusions outside one particular system of relaxor ferroelectrics, and obtained similar results. Even if the above described behaviour of $\varepsilon''(T,\omega)$ does not fit all known experimental results, obtained for relaxor ferroelectrics, it seems us quite typical and shows a way how to apply the same description of relaxation in both sides of the formally extrapolated T_f. Moreover, it can be assumed that other $\varepsilon''(\ln(\omega))$ experimental results, which contain a diffused maximum, can be related to the same description, and maximum of $g(\ln\tau)$ has only marginal role.

3.1.3. Dielectric Nonlinearity

Like dielectric dispersion, dielectric nonlinearity as a function of static electric field is also studied for 0.4NBT-(0.6-x)ST-xPT solid solutions in comparison with widely-known relaxor ferroelectrics 0.92PMN-0.08PT and PLZT-0.0925.

Nonlinearity of either real or imaginary part of dielectric permittivity was measured. For 0.4NBT-0.5ST-0.1PT, pronounced dependence of dielectric permittivity from electric field $\varepsilon(E)$, similar to the one observed in 0.92PMN-0.08PT, is stated. It corresponds to the electric field dependence of polarization – $P(E)$ has a characteristic quasilinear part at low E values and well-expressed declining (saturation) at higher E values, which indicates transition into a state, where all

PNRs are oriented in direction of the field. The nonlinearity of P(E) at high E values increases with decreasing temperature.

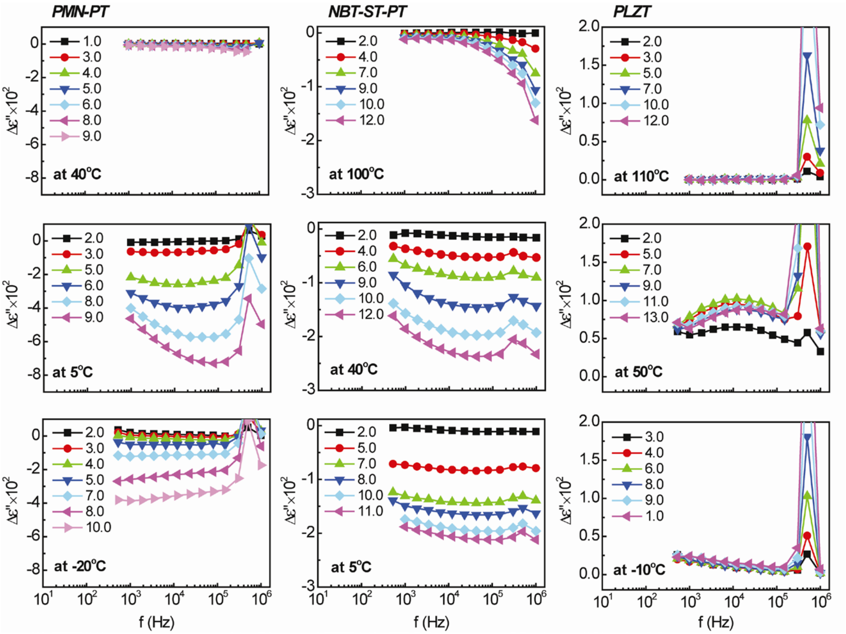

Figure 3.6. **Difference between ε'', measured at different values of bias field $E_= \neq 0$, and ε'', measured at $E_= = 0$, as a function of frequency for compositions 0.92PMN-0.08PT, 0.4NBT-0.5ST-0.1PT and PLZT 9,25/65/35 at three different temperatures: above T_m, in the region of T_m and below T_m (values of electric field in the labels are given in kV/cm)**

Frequency dependence of the imaginary part of dielectric permittivity ε''(lnf) (Fig. 3.6) is more suitable for study of electric field influence on distribution of relaxation times, as it directly characterizes the form of the distribution function in the framework of the description, proposed for dielectric dispersion in Subchapter 3.1.2. At temperatures, which are significantly higher than T_m, the values of ε'' and correspondingly the influence of electric field in 0.4NBT-0.5ST-0.1PT and 0.92PMN-0.08PT is negligible. In the vicinity of T_m, absolute value of the change Δε''(lnf) = ε''(E,lnf)–ε''(E = 0,lnf) in these compositions significantly increases and is more expressed in a high frequency region (the pronounced anomaly in a narrow frequency range above 100 kHz could be related to electromechanical resonance, caused by electric field). In the temperature region below T_m, Δε''(lnf) significantly decreases and is weakly frequency-dependant. Such behaviour of dielectric nonlinearity does not correspond to the one, which follows form the superparaelectric model [42], according to which the most significant changes should occur in the part of the spectrum with higher relaxation times, which corresponds to the low frequency range.

For PLZT-0.0925 the character of nonlinearity is significantly different, comparing to 0.4NBT-0.5ST-0.1PT and 0.92PMN-0.08PT, which can be explained by presence of large internal fields in this composition [42].

3.1.4. Thermal Expansion and Electromechanical Properties

Measurements of temperature dependences of thermal expansion $dl/l = (l(T)-l_0)/l_0$, where l_0 is linear dimension of a sample in the beginning of the measurement, were done for 0.4NBT-(0.6-x)ST-xPT (Fig. 3.7 a) in order to find the Burns temperature [27, 28] in this system of solid solutions.

Usually temperature-independent thermal expansion coefficient α, which corresponds to linear temperature dependence of thermal expansion, or weakly temperature-dependent α is expected in paraelectric state [43, 44]. The Burns temperature is identified as temperature, where remarkable deviation from such behaviour starts in direction of low temperatures, and is interpreted as contribution of local electrostriction due to formation of PNRs [43, 45].

Careful study of temperature dependences of thermal expansion and thermal expansion coefficient in 0.4NBT-(0.6-x)ST-xPT does not reveal a temperature region which could be distinguished as pure paraelectric state, although temperature dependence of thermal expansion coefficient becomes less expressed with increasing temperature (Fig. 3.7). At the same time, if α(T) is compared for samples with various concentrations of PT, the following features can be extracted:

- α is weakly concentration-dependent at high temperatures,
- significant differences in concentration dependence of α start to appear in temperature region of T_B = 400 °C,
- the higher is concentration of PT in the composition, the more expressed is the decreasing of α(T) in direction of low temperatures.

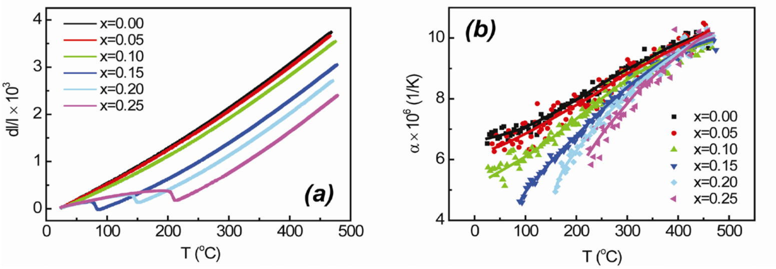

Figure 3.7. **Temperature dependences of thermal expansion (a) and thermal expansion coefficient (b) for NBT-ST-PT compositions with various PT concentrations x**

In this case, paraelectric behaviour could be related to the temperature region with weakly concentration-dependent thermal expansion coefficient α. Assuming that thus determined T_B could be identified with the Burns temperature, lack of the expected paraelectric behaviour could be related to the fact that T_B is rather close to the upper limit of the measurement temperature range. As thermal expansion is proportional to concentration of PNRs n and square of dipole moment μ_{loc}^2 of PNRs, and taking into account that n decreases with increasing PT content, due to approaching normal ferroelectric phase transition, the more expressed deviation from the high-temperature behaviour at higher PT concentrations x indicates increasing of μ_{loc}.

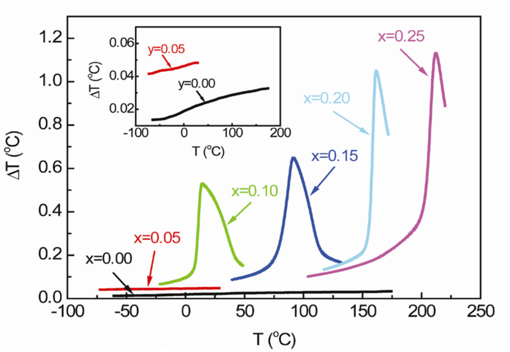

Figure 3.8. **ECE temperature change ΔT as a function of temperature at E = 20 kV/cm for 0.4NBT-(0.6-x)ST-xPT compositions with various PT concentrations x**

The study of electromechanical properties showed that character of longitudinal deformation $u_{11}(E)$ at room temperature depends on location of particular composition in the phase diagram. At $x \leq 0.10$, respectively, for compositions, which are in relaxor state at room temperature, u_{11} is proportional to the square of polarization. Whereas for compositions with higher PT content butterfly-type $u_{11}(E)$ dependence, characteristic to FE state, is observed. For compositions with $x \geq 0.15$ high $u_{11}(E)$ maximal values, reaching 0.06%, are observed.

3.1.5. Electrocaloric Effect

Pronounced electrocaloric effect (ECE) is observed in 0.4NBT-(0.6-x)ST-xPT compositions. Values and nature of ECE is very different depending on concentration range of PT (Fig. 3.8, 3.9). In the range of low concentrations, values of ECE are extremely low, ΔT(T) continuously increases with increasing temperature in all studied temperature range. Approaching PT concentration range, where electric field-induced phase transition from relaxor to FE state is observed, a maximum appears in the ΔT(T) dependence in the region of T_{t1} (Fig. 3.8).

Differences appear also in ΔT(E) dependences (Fig. 3.9). At low concentrations of PT ΔT(E) is roughly proportional to E^2 (Fig. 3.9. a). While at higher concentrations such dependence is observed in the whole electric field range only at $T \gg T_t$, but, when approaching T_{t1}, – only in the small electric field range. At higher electric fields, ΔT(E) dependence becomes more expressed, and a diffused jump appears, as electric field E reaches critical field E_{k1} (Fig. 3.9 b).

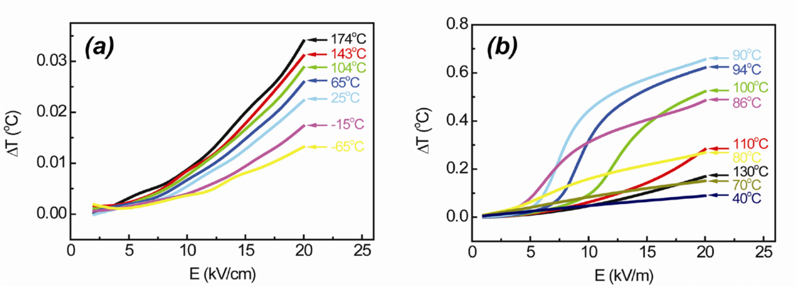

Figure 3.9. **ECE temperature change ΔT as a function of electric field ΔT(E) at different temperatures for compositions 0.4NBT-0.6ST (a) and 0.4NBT-0.45ST-0.15PT (b) (measurements are done for electric field change from 0 to different values)**

Below Tt_1, where FE state remains stable after removing field, the jump at ΔT(E) dependence becomes irreversible, appearing only when field is applied to thermally depoled sample. For composition 0.4NBT-0.5ST-0.1PT, where FE state, like in $PbMg_{1/3}Nb_{2/3}O_3$, can be caused only by electric field, a well-expressed jump of ΔT(E) is observed for depoled samples during the first application of electric field and maintained in all temperature range from T_{t1} region in direction of low temperatures. While for compositions with higher concentration of PT, this jump vanishes if temperature is lowered below T_{t2}, reflecting spontaneous transition to FE state even without applying electric field (Fig. 3.10). The highest values of ECE are reached for 0.4NBT-0.4ST-0.2PT and 0.4NBT-0.35ST-0.25PT, reaching ~1.1 °C at 160 °C and 210 °C correspondingly. In the electric field range, where the FE state is stable, ΔT(E) is close to linear.

Taking into account wide use of thermodynamic relations in evaluation of ECE in ferroelectrics, it is examined to what extent they are valid for the studied system of solid solutions and, perhaps, for relaxor ferroelectrics in general. It is shown that entropy values calculated by the Clausius–Clapeyron relation [46] for a phase transition from FE to relaxor state are twice as large as the experimentally determined ones. Such a difference can be explained, taking into account that the Clausius–Clapeyron relation describes a phase transition from homogenous FE to homogenous nonpolar phase, but in reality a part of FE phase – PNRs – do not transfer into nonpolar phase.

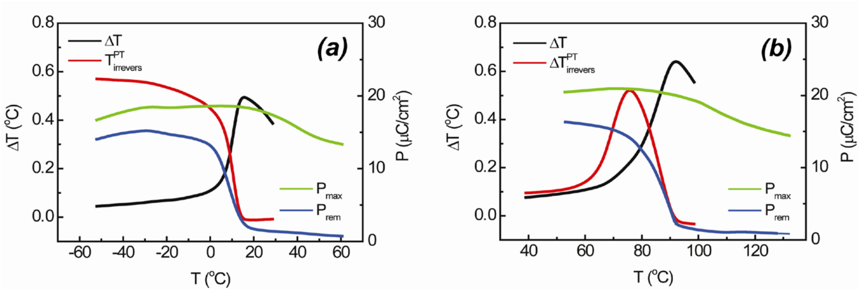

Figure 3.10. **Reversible ΔT and irreversible $\Delta T^{PT}_{irrevers}$ temperature changes (measured at the first applied electric field for thermally depoled sample, corrected for the hysteresis heat), as well as maximal P_{max} (at 20 kV/cm) and remnant P_{rem} polarizations as functions of temperature for compositions 0.4NBT-0.5ST-0.1PT (a) and 0.4NBT-0.45ST-0.15PT (b)**

According to Ginzburg-Devonshire phenomenological description, electric field-induced polarization, particularly its square (P^2), is a measure of ΔT. Concentration dependences of both experimentally obtained properties allow us to examine this trend. It is shown that ECE maximal value $\Delta T_{max}(x)$ changes much more rapidly than $P_{max}{}^2(x)$. This indicates a large part of the total P(E) (~8 μC/cm², if evaluated from 0.4NBT-0.6ST) does not give contribution to entropy. Obviously this is the part, which is connected with reorientation of PNRs under electric field.

3.2. Modified NBT-ST-PT Solid Solutions

NBT-ST-PT form solid solutions with large variety of other components. In the work, quadruple solid solutions of 0.4NBT-0.4ST-0.2PT with $NaNbO_3$ (NN), $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) and $CaTiO_3$, as well as compositions, in which Na is partly substituted by Li, K and Ag, were studied.

Studies of dielectric permittivity indicate that NN and PMN favour development of relaxor properties in 0.4NBT-(0.6-x)ST-xPT, passing the same stages as in case, if PT content is increased in 0.4NBT-(0.6-x)ST-xPT, but in the opposite direction. It is well seen in Fig. 3.11, where temperature-frequency dependences are shown for the compositions with NN. Similar tendency was observed for the compositions with PMN. $T_m(x)$ decreases and difference $T_m–T_t$ increases, if either NN or PMN concentration increases. The development of relaxor state with increasing of NN or PMN content is indicated also by study of polarization hysteresis loops.

Previously it was shown that addition of NN to $A^{2+}B^{4+}O_3$ type of ferroelectrics shifts a phase transition in direction of lower temperatures and significantly suppresses FE properties [47]. Considering influence of components of solid

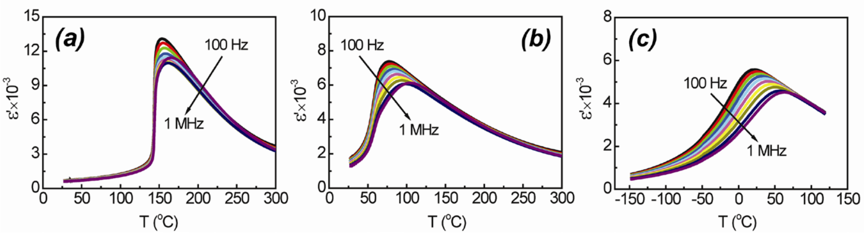

Figure 3.11. **Temperature dependences of dielectric permittivity at several fixed frequencies for (1-x)(0.4NBT-0.4ST-0.2PT)-xNN solid solutions with NN concentrations x = 0.00 (a), x = 0.04 (b) and x = 0.10 (c) (cooling curves)**

solutions on the relaxor properties, besides the ion disorder, which influences mostly the local surrounding, obviously their influence on macroscopic properties, characterizing the FE state, like spontaneous polarization P_s, spontaneous deformation u_s and FE phase transition temperature T_c, should also be taken into account. This is supported by T_c, P_s and u_s as functions of component concentrations of such relaxor ferroelectrics as $Pb_{1-x}La_x(Zr_{1-y}Ti_y)O_3$ (PLZT), $Ba(Ti_{1-x}Zr_x)O_3$ (BTZ) and $Ba(Ti_{1-x}Sn_x)O_3$ (BTS).

The change of the nature of the phase transition in 0.4NBT-(0.6-x)ST-xPT system depending on Sr/Pb concentration ratio also confirms such a point of view regarding development of relaxor properties.

When studying quadruple system of solid solutions 0.4NBT-(0.4-x)ST-0.2PT-x$CaTiO_3$, x-ray diffraction results showed that volume of the unit cell V(x) monotonously decreases on increasing Ca concentration at room temperature. Taking into account the sizes of the ions, this indicates that Ca in ABO_3 perovskite replaces ions in the A-site. At the same time, tetragonality is independent of $CaTiO_3$ concentration till x = 0.15 (Fig. 3.12).

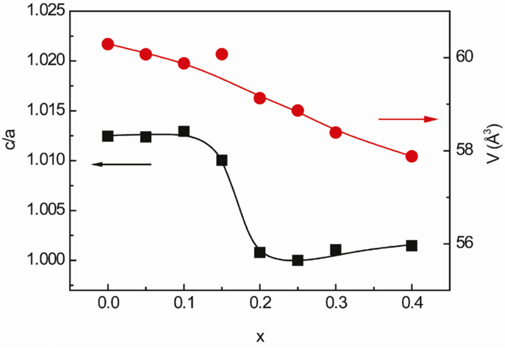

Figure 3.12. **Concentration dependences of unit cell volume and tetragonality for 0.4NBT-(0.4-x)ST-0.2PT-x$CaTiO_3$ solid solutions**

Temperature dependences of dielectric permittivity ε'(T) at fixed frequencies, reveal strong decreasing of maximal value of dielectric permittivity ε'_{max}, if concentration of Ca is increased (Fig. 3.13 a). Whereas temperature of ε'(T) maximum $T_m(x)$ (T_{m1} – on heating, T_{m2} – on cooling) and phase transition temperature $T_t(x)$ (T_{t1} – on heating, T_{t2} – on cooling) decrease very weakly until Ca concentration x = 0.25 and x = 0.10 respectively (Fig. 3.13 b).

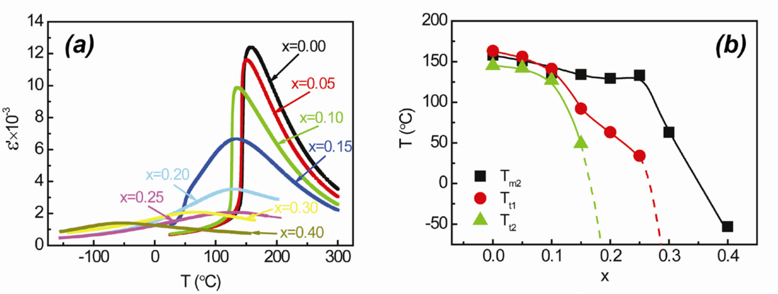

Figure 3.13. **a) Temperature dependences of dielectric permittivity ε'(T) for 0.4NBT-(0.4-x)ST-0.2PT-x$CaTiO_3$ compositions (obtained on cooling at 1 kHz), b) Phase diagram of 0.4NBT-(0.4-x)ST-0.2PT-x$CaTiO_3$: phase transition temperatures T_{t1}, T_{t2} and temperature of ε'(T,f) maximum T_{m2} as functions of concentration x (at 1 kHz). In compositions with $CaTiO_3$ concentrations x = 0.20 and x = 0.25, temperature T_{t1} is observed only for previously poled sample**

Measurements of polarization hysteresis loops P(E) indicated that remnant and maximal polarizations P_{rem} and P_{max} do not depend on Ca concentration at room temperature till x = 0.30, at higher concentrations they decrease rapidly.

Study of temperature dependences of the critical electric fields E_{k1} and E_{k2} in composition with $CaTiO_3$ concentration x = 0.25 has shown that $E_{k1}(T)$ depends on prehistory of the sample, and in case, if the sample is thermally depoled, it has higher values and is even less temperature-dependent comparing to the measurements without thermal depolarizing between the measurement temperatures. The difference can be explained by different mesoscopic structure in both cases, as the sample does not retrieve the initial state after removing electric field.

The steep decreasing of dielectric permittivity values, on the one hand, and the stability of temperatures T_m, T_{t1}, T_{t2} and polarization, if concentration of Ca in 0.4NBT-(0.4-x)ST-0.2PT-x$CaTiO_3$ is increased (till certain concentration limit), on the other hand, allows us to suggest that they are related to different physical mechanisms. Usually it supposed that the mechanism, giving the largest contribution to the values of dielectric permittivity, is related to PNRs. The obtained results can be explained, assuming that the regions, containing Ca^{2+} ions, are energetically more favourable for development of PNRs. Therefore, in the region of low $CaTiO_3$ concentrations, Ca^{2+} ions are located mostly inside PNRs, not influencing the surrounding matrix.

For 0.4NBT-0.4ST-0.2PT solid solutions, where Na is gradually replaced by one of the monovalent metals – Li, K or Ag – ($0.4(Na_{1-x}Me_{1+x})_{1/2}Bi_{1/2}TiO_3$-0.4ST-0.4PT ($Me^{1+}$: Li, K and Ag)), it is shown that such a substitution till 37.5 mol% influences properties (structure, dielectric permittivity, polarization) of the obtained compositions less in comparison with similar substitution in pure NBT. Study of dielectric properties indicated opposite $T_m(x)$ tendencies for Li and Ag, which correlates with the atomic masses of these elements.

3.3. NBT Solid Solutions with BT and Other Compositions

(1-x)NBT-xBT solid solutions are widely studied nowadays, mostly focusing on the concentration region around the morphotropic phase boundary ($x \approx 0.06$). In this work, studies of (1-x)NBT-xBT are done in a wide concentration range above the morphotropic phase boundary ($0.10 \leq x \leq 0.97$).

X-ray diffraction measurements indicate that all studied (1-x)NBT-xBT have a tetragonal structure at room temperature. The maximal tetragonality $c/a \approx 1{,}020$ is observed at BT concentration approximately $x = 0.2$ and is much larger than in pure BT ceramics, where $c/a \approx 1{,}010$ [25]. On further increasing of BT content ($x > 0.3$) the tetragonality decreases, although exactly BT could be regarded as responsible for stabilization of the tetragonal state. Temperature dependence of the diffraction pattern points to a phase transition between phases with tetragonal and cubic symmetry. Besides, a phase coexistence is observed in certain concentration range. The Rietveld method was also applied for treatment of the diffraction pattern, which indicated that the phase coexistence is present even in wider temperature range.

For compositions with low BT content, dielectric spectroscopy indicates dielectric properties similar to pure NBT, respectively, the frequency-independent maximum of dielectric permittivity and the shoulder in the temperature dependence (Fig. 3.14 a, b). The well-expressed jump of $\varepsilon'(T)$, located in the low temperature part of the shoulder is frequency-independent and has expressed thermal hysteresis. While the weakly temperature-dependent part in direction of higher temperatures has various degree of frequency-dependence, which is more expressed when $\varepsilon'(T,\omega)$ measurement is performed on cooling. The jump of $\varepsilon'(T)$ together with the thermal hysteresis indicate the first order phase transition between FE and some kind of non-FE phase.

For composition 0.9NBT-0.1BT the frequency-independent jump is observed only on heating, while on cooling the shoulder is smeared and has relaxor behaviour in the whole temperature range in direction of low temperatures. The x-ray diffraction measurements, showing high concentration of cubic phase immediately after cooling till room temperature, as well as ageing of dielectric permittivity indicate that continuous growing of PNRs occurs during cooling and smooth transition to FE state takes place depending on temperature or even depending on time due to slow relaxation into FE state.

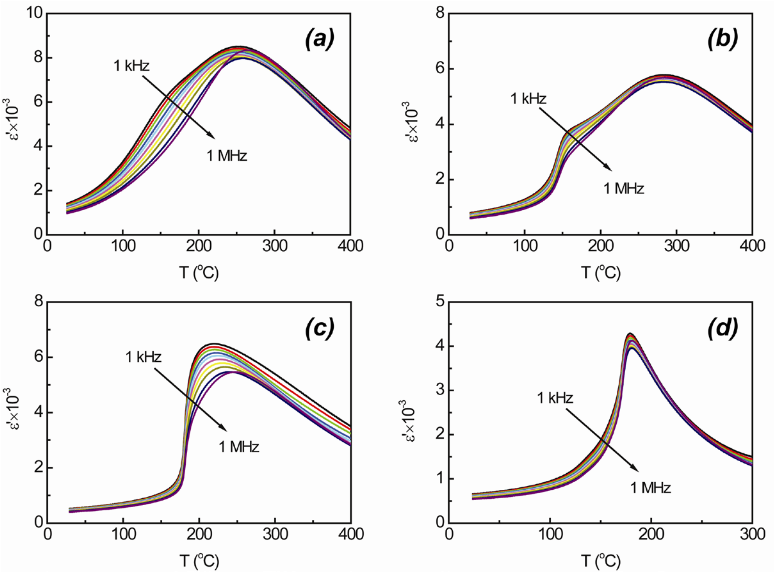

Figure 3.14. **Temperature-frequency dependences of dielectric permittivity, obtained on cooling, for (1-x)NBT-xBT compositions with BT concentrations a) x = 0.1, b) x = 0.2, c) x = 0.4, d) x = 0.9**

For compositions in the concentration range $0.3 \leq x \leq 0.8$ (Fig. 3.14 c) behaviour, typical for relaxor ferroelectrics, is observed. In compositions with high BT content ($x = 0.9$) the FE-paraelectric phase transition nature, which is characteristic to pure BT ceramics, is approached (Fig. 3.14 d).

Concentration dependences of the dielectric permittivity maximum temperature T_m (T_{m1} – on heating, T_{m2} – on cooling) and the phase transition temperature T_t (T_{t1} – on heating, T_{t2} – on cooling) are shown in Fig. 3.15 b. Most probably the dielectric permittivity maximum, observed at the low BT concentration range ($x \leq 0.25$), cannot be identified with the relaxing maximum of compositions with higher BT content. The height of this frequency-independent maximum decreases, and it most probably disappears with increasing BT concentration (Fig. 3.15 a).

Starting from concentration region, where maximum of dielectric permittivity exhibits relaxor behaviour ($x = 0.30$), T_m decreases on increasing BT content, whereas T_{t1} and especially T_{t2} remains approximately the same in a wide BT concentration range (Fig. 3.15 b). Moreover, T_{t1} corresponds to the phase coexistence region, determined from x-ray diffraction measurements (on heating).

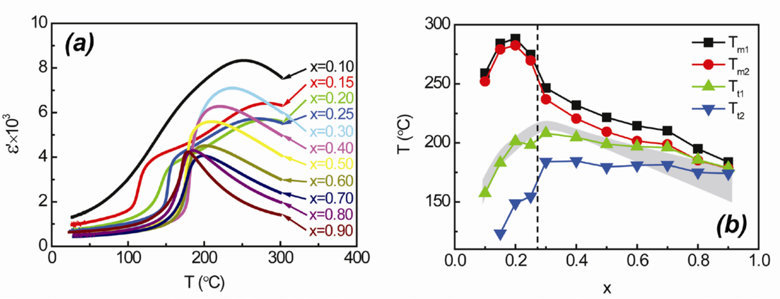

Figure 3.15. **a) Temperature dependences of dielectric permittivity for (1-x)NBT-xBT with various BT concentrations (cooling curves at 1 kHz); b) ε'(T,f) maximum and phase transition temperatures T_m (T_{m1}, T_{m2}) and T_t (T_{t1}, T_{t2}) as functions of concentration, obtained at 1 kHz, for (1-x)NBT-xBT (the phase coexistance region, determined from x-ray diffraction heating measurements, is highlighted)**

Approximations of ε'(T) with the power law [23] for compositions with $0.1 \leq x \leq 0.25$ indicates significantly higher values of the parameter γ than for compositions with the ε'(T,f) maximum of relaxing nature. It supports the assumption that the maximum of ε'(T), which appears in this concentration range, cannot be identified with the relaxing maximum, observed at higher concentrations.

For all solid solutions rather high remnant P_{rem} and maximal P_{max} polarization (at 90 kV/cm) values were observed. The highest values of P_{rem} (above 30 μC/cm²) and P_{max} (above 40 μC/cm²) were observed for compositions in the concentration range x = 0.15-0.25, what corresponds to the maximum in the concentration dependence of tetragonality. Whereas the highest coercive field E_c values were found in the concentration range x = 0.3-0.6.

Interesting results were obtained also regarding the binary NBT solid solutions with $CdTiO_3$. It is shown that these compositions have three morphotropic phase boundaries, which separate rhomohedral, cubic, tetragonal and rhombohedral phases. The highest values of maximal polarization, remnant polarization and electromechanical properties are observed in the tetragonal phase in the vicinity cubic-tetragonal morphotropic phase boundary.

3.4. Interpretation of Phase Transitions in Pure NBT and NBT with Small Concentration of Modifiers

The obtained results regarding NBT-based solid solutions give a possibility to make considerations about phase transitions in pure NBT and NBT with small concentration of modifiers. As it was already mentioned in the literature review (see Subchapter 1.1), NBT depolarization temperature T_d is traditionally identified with a phase transition between the rhomohedral and unknown, probably antiferroelectric phases. The relaxing shoulder in the region of T_d (Fig. 1.1 in Subchapter 1.1) usually is also related to this phase transition. Whereas the phase transition temperature T_m is often supposed to be a phase transition temperature between the unknown, probably, antiferroelectric and tetragonal FE phases.

In this work it was shown that the frequency-dependent ε'(T,f) shoulder, which is observed below the dielectric permittivity maximum temperature T_m in pure NBT, can be transformed into a jump-like ε'(T) change at temperature T_d, where pronounced dielectric dispersion persists only in the temperature range $T_d \leq T < T_m$. Such a transformation is stated by ageing at $T < T_d$ for solid solution 0.9NBT-0.1BT. It is observed also for poled samples, as described by other authors [48, 49]. The relaxor properties of the shoulder can be present not only in rhombohedral phase, as it is for pure NBT, but also in tetragonal phase, which is indicated by the results obtained for 0.9NBT-0.1BT.

By studying NBT solid solutions with $CaTiO_3$ we have shown that the upper limit of the NBT rhombohedral phase region corresponds to the rapid change of ε'(T) and its thermal hysteresis – to ε'(T) thermal hysteresis. Whereas for NBT solid solutions with $Sr_{0.7}Bi_{0.2}TiO_3$ (SBT) and PT we have observed that the shoulder, which has remarkable frequency dispersion in low temperature side, has characteristic thermal hysteresis in the temperature range, where it is frequency-independent ($T < T_m$).

The frequency-independent maximum of ε'(T), which is observed in the concentration range of tetragonal phase in pure NBT, exists also in the temperature region, which is cubic according to x-ray diffraction measurements, as we have observed it, for example, in composition 0.8NBT-0.2BT.

The mentioned observations testify that the relaxor properties in pure NBT and NBT with small content of modifiers appear together with the polar state, although they do not depend on symmetry of the particular polar state. The relaxor state, corresponding to the ε'(T) shoulder, tends to be unstable, gradually transforming into FE state in time. The FE state destroys the dielectric dispersion, characteristic to the ε'(T) shoulder. Besides, decay of polarization at T_d in pure NBT and NBT with small concentration of modifiers (which looks like a sharp jump in the low temperature part of the ε'(T) shoulder) is similar to the one in relaxor ferroelectrics at T_t. This explains the preservation of the macroscopic symmetry, observed at $T < T_d$, for unpoled sample in the temperature range above the dispersion region, respectively, above the ε'(T) shoulder. In general, the difference from classical relaxor ferroelectrics is that the considered dispersion mechanism is observed on the frequency-independent ε'(T) background with the maximum at T_m, characteristic to NBT and coexists with various crystallographic symmetry groups.

Conclusions

A new solid solution system of relaxor ferroelectrics NBT-ST-PT, in which relaxor properties, passing different stability levels of relaxor state depending on PT concentration, change in a wider spectrum than for other known systems of relaxor ferroelectrics, is obtained and studied. Phase diagram is constructed for this system of solid solutions.

The Burns temperature, as well as parameters of the Vogel-Fulcher law and the power law, traditionally used for description of relaxor state, is determined in NBT-ST-PT solid solutions. It is shown that dielectric dispersion in relaxor ferroelectrics can be described with one relaxation mechanism in the whole temperature range, where it is observed, without postulating freezing of PNRs. Analysis of dielectric nonlinearity in NBT-ST-PT did not show trend of $\varepsilon''(\ln\omega)$ as a function of bias field that would correspond to the superparaelectric model.

Compositions with small region of relaxor state stability, characterized by difference between temperature of dielectric permittivity maximum and phase transition temperature $T_m - T_t$, have high ECE values, which are above 1 °C and are connected with electric field-induced phase transition between relaxor and FE states. Concentration dependences of field-induced polarization and ECE in NBT-ST-PT indicate contributions from different polarization mechanisms. For compositions with PT concentration till $x = 0.05$, electric field-induced reorientation of PNRs dominates in polarization.

In NBT-ST-PT solid solutions, modified with Ca, dielectric permittivity maximum and phase transition temperatures do not depend on Ca concentration at low Ca content, while value of the dielectric permittivity maximum significantly decreases in the whole concentration range. It can be interpreted, assuming that Ca concentrates mainly inside PNRs, stabilizing them.

Modifying NBT-ST-PT solid solutions with NN and PMN favours stabilization of relaxor state. Whereas substitution of Na with monovalent metals (Li, K and Ag) in NBT-ST-PT weakly influences physical properties in comparison with similar substitution in pure NBT. Besides distribution of ions with different valences/sizes in equivalent sites of ABO_3 perovskite, weakening of FE state in the result of ionic substitution has an important role in stabilization of relaxor state.

There is clarified phase diagram for NBT-BT system of solid solutions above the morphotropic phase boundary. It is shown that a change of the polar state occurs around T_m in BT concentration range $0.2 \leq x \leq 0.3$, and $\varepsilon'(T,f)$ behaviour, characteristic to relaxors, is observed on increasing BT content in a wide concentration range. Tetragonality reaches the maximal value on changing of the polar state nature.

It follows from the performed studies that, in contrast to classical relaxor ferroelectrics, in case of NBT, the relaxor dispersion mechanism acts on the frequency-independent $\varepsilon'(T)$ background with maximum at T_m.

Thesis

- A new system of solid solutions 0.4NBT-(0.6-x)ST-xPT, in which relaxor properties, passing different levels of relaxor state stability, changes in a wider spectrum than in other known solid solution systems of relaxor ferroelectrics, is discovered. Besides distribution of ions with different valences/sizes in equivalent sites of lattice, weakening of FE state has an important role in stabilization of relaxor state.
- Dielectric dispersion in relaxor ferroelectrics can be described in the framework of one relaxation mechanism in the whole temperature range, without postulating freezing temperature, at which the edge of distribution of relaxation times $\tau_{max} \rightarrow \infty$. Such an approach prevents problems, which appear when the Vogel-Fulcher law is used for description of relaxor state.
- Corrections are done to (1-x)NBT-xBT phase diagram. Nature of phase transition and dielectric properties change in the concentration region x = 0.20-0.30, as transformation from dependences, characteristic to NBT, to properties, characteristic to relaxor ferroelectrics occurs. Tetragonality and polarization reach high values in this concentration region.
- In 0.4NBT-(0.6-x)ST-xPT system of solid solutions, nature of ECE depends on location of particular composition in the phase diagram. Compositions with $0.20 \leq x \leq 0.25$ have high ECE values (reaching ~1 °C at 20 kV/cm) in the relaxor-ferroelectric phase transition region. Traditional thermodynamic concepts are not applicable for description of ECE in relaxor ferroelectrics.

References

1. G. A. Smolensky, V. A. Isupov, A. I. Agranovskaya, N. N. Krainik, "New ferroelectrics of complex composition," *Phys. Solid State*, 1961, vol. 5, pp. 2651-2654.
2. B. J. Chu, D. R. Chen, G. R. Li, Q. R. Yin, "Electrical properties of $Na_{1/2}Bi_{1/2}TiO_3$-$BaTiO_3$ ceramics," *J. Eur. Ceram. Soc.*, 2002, vol. 22, pp. 2115-2121.
3. Y. Hidaka, S. Tsukada, S. Kojima, "Aging of dielectric properties in $Na_{0.5}Bi_{0.5}TiO_3$ ceramics," *Ferroelectrics*, 2008, vol. 376, pp. 134-139.
4. G. O. Jones, P. A. Thomas, "The tetragonal phase of $Na_{0.5}Bi_{0.5}TiO_3$ – a new variant of perovskite structure," *Acta Crystallogr. B*, 2000, vol. 56, pp. 426-430.
5. Y. Watanabe, Y. Hiruma, H. Nagata, T. Takenaka, "Electrical properties and phase transition temperatures of lanthanoid substituted $(Bi_{1/2}Na_{1/2})TiO_3$ ceramics," *Ferroelectrics*, 2007, vol. 358, pp. 139-145.
6. J. Y. Yi, K. S. Hong, "dependence of incommensurate phase formation on vacancy type in La-doped $(Na_{1/2}Bi_{1/2})TiO_3$," *J. Appl. Phys.*, 2004, vol. 96, pp. 1174-1177.
7. V. Dorcet, G. Trolliard, P. Boullay, "The structural origin of the antiferroelectric properties and relaxor behaviour of $Na_{0.5}Bi_{0.5}TiO_3$," *J. Magn. Magn. Mater.*, 2009, vol. 321, pp. 1758-1761.
8. Y. Hiruma, T. Watanabe, H. Nagata, T. Takenaka, "Piezoelectric properties of $(Bi_{1/2}Na_{1/2})TiO_3$-based solid solution for lead-free high-power applications," *Jpn. J. Appl. Phys.*, 2008, vol. 47, pp. 7659-7663.
9. G. O. Jones, J. Kreisel, V. Jennings, M. A. Geday, P. A. Thomas, A. M. Glazer, "Investigation of peculiar relaxor ferroelectric: $Na_{0.5}Bi_{0.5}TiO_3$," *Ferroelectrics*, 2002, vol. 270, pp. 191-196.
10. M. Geday, J. Kreisel, A. M. Glazer, K. Roleder, "Birefringence imaging of phase transitions: application to $Na_{0.5}Bi_{0.5}TiO_3$," *J. Appl. Crystallogr*, 2000, vol. 33, pp. 909-914.
11. J. Yao, W. Ge, L. Luo, J. Li, D. Viehland, H. Luo, "Hierarchical domains in $Na_{1/2}Bi_{1/2}TiO_3$ single crystals: Ferroelectric phase transformations within the geometrical restrictions of a ferroelectric inheritance," *Appl. Phys. Lett.*, 2010, vol. 96, pp. 222905 (3).
12. F. Cordero, F. Craciun, F. Trequattrini, E. Mercadelli, C. Galassi, "Phase transitions and phase diagram of the ferroelectric perovskite $(Na_{0.5}Bi_{0.5})_{1-x}Ba_xTiO_3$ by anelastic and dielectric measurements," *Phys. Rev. B,* 2010, vol. 81, pp. 144124 (10).
13. I. P. Aleksandrova, A. A. Sukhovskii, Yu. N. Ivanov, Yu. E. Yablonskaya, S. B. Vakhrushev, "^{23}Na NMR study of the local order in the $Na_{1/2}Bi_{1/2}TiO_3$ structure in a weak magnetic field," *Phys. Solid State*, 2008, vol. 50, pp. 496-501.
14. J. Kreisel, P. Bouvier, B. Dkhil, P. A. Thomas, A. M. Glazer, T. R. Welberry, B. Chaabane, M. Mezouar, "High-pressure x-ray scattering of oxides with a nanoscale local structure: application to $Na_{1/2}Bi_{1/2}TiO_3$," *Phys. Rev. B*, 2003, vol. 68, pp. 141131-141137.
15. J.-R.Gomah-Pettry, S. Said, P. Marchet, J.-P. Mercurio, "Sodium-bismuth titanate based lead-free ferroelectric materials," *J. Eu. Ceram. Soc.*, 2004, vol. 24, pp. 1165-1169.
16. J. K. Lee, K. S. Hong, Ch. K. Kim, S. E. Park, "Phase transitions and dielectric properties in A-site ion substituted $(Na_{1/2}Bi_{1/2})TiO_3$ ceramics (A = Pb and Sr)," *J. Appl. Phys.*, 2002, vol. 91, pp. 4538-4542.

17. V. V. Shvartsman, D. C. Lupascu, "Lead-free relaxor ferroelectrics," *J. Amer. Ceram. Soc.*, 2012, vol. 95, pp. 1-26.
18. Y. Hiruma, K. Yoshii, H. Nagata, T. Takenaka, "Phase transition temperature and electrical properties of $(Bi_{1/2}Na_{1/2})TiO_3$-$(Bi_{1/2}A_{1/2})TiO_3$ (A = Li and K) lead-free ferroelectric ceramics. *J. Appl. Phys.*, 2008, vol. 103, pp. 084121 (7).
19. G. A. Samara "The relaxational properties of compositionally disordered ABO_3 perovskites" *J. Phys.: Condens. Mat.*, 2003, vol. 15, pp. R367-R411.
20. A. A. Bokov, Z.-G. Ye, "Recent progress in relaxor ferroelectrics with perovskite structure," *J. Mater. Sci.*, 2006, vol. 41, pp. 31-52.
21. G. Calvarin, E. Husson, Z. G. Ye, "X-ray study of the electric field-induced phase transition in single crystal $Pb(Mg_{1/3}Nb_{2/3})O_3$," *Ferroelectrics*, 1995, vol. 165, pp. 349-358.
22. Y. Hiruma, K. Yoshii, H. Nagata, T. Takenaka, "Phase transition temperature and electrical properties of $(Bi_{1/2}Na_{1/2})TiO_3$-$(Bi_{1/2}A_{1/2})TiO_3$ (A = Li and K) lead-free ferroelectric ceramics. *J. Appl. Phys.*, 2008, vol. 103, pp. 084121 (7).
23. R. L. Moreira, R. Lobo, "Phenomenological study of diffuse phase transitions," *J. Phys. Soc. Jpn.*, 1992, vol. 61, pp. 1992-1995.
24. V. Koval, C. Alemany, J. Brianc, H. Brunckova, K. Saksl, "Effect of PMN modification on structure and electrical response of xPMN–(1-x)PZT ceramic systems," *J. Eur. Ceram. Soc.*, 2003, vol. 23, pp. 1157-1166.
25. F. Jona, G. Shirane, "Ferroelectric crystals," Oxford-London-New York-Paris: Pergamon press, 1962.
26. C. Lei, A. A. Bokov, Z.-G. Ye, "Ferroelectric to relaxor crossover and dielectric phase diagram in the $BaTiO_3$-$BaSnO_3$ system," *J. Appl. Phys.*, 2007, vol. 101, pp. 084105 (9).
27. G. Burns, F. H. Dacol, "Glassy polarization behavior in ferroelectric compounds $Pb(Mg_{1/3}Nb_{2/3})O_3$ and $Pb(Zn_{1/3}Nb_{2/3})O_3$," *Solid State Commun.*, 1983, vol. 48, pp. 853.
28. P. M. Gehring, H. Hiraka, C. Stock, S.-H. Lee, W. Chen, Z.-G. Ye, S. B. Vakhrushev, Z. Chowdhuri, "Reassessment of the Burns temperature and its relationship to the diffuse scattering, lattice dynamics, and thermal expansion in relaxor $Pb(Mg_{1/3}Nb_{2/3})O_3$," *Phys. Rev. B*, 2009, vol. 79, 224109 (14).
29. D. Viehland, S. J. Jang, L. E. Cross, M. Wuttig, "Freezing of the polarization fluctuations in lead magnesium niobate relaxors," *J. Appl. Phys.*, 1990, vol. 68, pp. 2916 (6).
30. A. A. Bokov, M. Maglione, A. Simon, Z.-G. Ye, "Dielectric behavior of $Ba(Ti_{1-x}Zr_x)O_3$ solid solution," *Ferroelectrics*, 2006, vol. 337, pp. 169-178.
31. Z.-G. Ye, M. Dong, "Morphotropic domain structures and phase transitions in relaxor-based piezo-/ferroelectric $(1\text{-}x)Pb(Mg_{1/3}Nb_{2/3})O_3$-$xPbTiO_3$ single crystals," *J. Appl. Phys.*, 2000, vol. 87, pp. 2312 (8).
32. A. E. Glazunov, A. K. Tagantsev, "Direct evidence of Vogel-Fulcher freezing in relaxor ferroelectrics," *Appl. Phys. Lett.*, 1998, vol. 72, pp. 1048-1050.
33. F. Cordero, M. Corti, F. Craciun, C. Galassi, D. Piazza, F. Tabak, "Polar and nonpolar atomic motions in the relaxor ferroelectric $Pb_{1-3x/2}La_xZr_{0.2}Ti_{0.8}O_3$ from dielectric, anelastic and NMR relaxation," *Phys. Rev. B*, 2005, vol. 71, pp. 094112 (9).
34. A. C. Larson, R. B. von Dreele, "General structure analysis aystem (GSAS)," Los Alamos National Laboratory Report, 1994, LAUR, pp. 86-748.

35. B. H. Toby, “EXPGUI, a graphical user interface for GSAS,” *J. Appl. Cryst.*, 2001, vol. 34, 210-213.
36. R. Taukulis, “Segnetoelektrisku relaksoru elektromehāniskās īpašības,” Bakalaura darbs, Rīga: LU, 2010. 17.-33. lpp.
37. X. Dai, A. DiGiovanni, D. Viehland, “Dielectric properties of tetragonal lanthanum modified lead zirconate titanate ceramics,” *J. Appl. Phys.*, 1993, vol. 74, pp. 3399-3405.
38. O. Noblanc, P. Gaucher, G. Calvarin, “Structural and dielectric studies of $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ ferroelectric solid solutions around the morptotropic boundary,” *J. Appl. Phys.*, 1996, vol. 79, pp. 4291-4297.
39. O. Bidault, M. Licheron, E. Husson A. Morell, The onset of an electric field-induced ferroelectric-like phase in the perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$,” *J. Phys.: Condens. Mat.*, 1996, vol., pp. 8.
40. Z.-Y. Cheng, R. S. Katiyar, X. Yao, A. Guo, “Dielectric behaviour of lead magnesium niobate relaxors,” *Phys. Rev. B*, 1997, vol. 55, pp. 8165-8174.
41. A. Khodorov, A. Tsotsorin, “Glassy-like dielectric spectrum behaviour in PMN-PZT solid solution,” *Ferroelectrics*, 2002, vol. 270, pp. 167-172.
42. S. A. Prosandeev, “Orientational and fluctuation polarizations of langevin dipoles in a random electric field,” *Phys. Solid State*. 2003, vol. 45, pp. 1774-1779.
43. H. Arndt, G. Schmidt, “Thermal expansion in relaxor ferroelectrics,” *Ferroelectrics,* 1988, vol. 79, pp. 443-446.
44. A. S. Bhalla, R. Guo, L. E. Cross, G. Burns, F. H. Dacol, R. R. Neurgaonkar, “Measurements of strain and the optical indices in the ferroelectric $Ba_{0.4}Sr_{0.6}Nb_2O_6$: Polarization effects,” *Phys. Rev. B*, 1987, vol. 36, pp. 2030-2035.
45. M. Gorec, V. Bondarev, I. Flerov, M. Maglione, A. Simon, P. Sciau, M. Boulos, S. Guillemet-Fritsch, “Thermal expansion, polarization and phase diagrams of $Ba_{1-y}Bi_{2y/3}Ti_{1-x}Zr_xO_3$ and $Ba_{1-y}La_yTi_{1-y/4}O_3$ compounds,” *J. Phys.: Condens.Mat.*, 2009, vol. 21, pp. 075902 (7).
46. E. Birks, M. Dunce, and A. Sternberg, “High Electrocaloric Effect in Ferroelectrics,” *Ferroelectrics*, 2010, vol. 400, pp. 336-343.
47. V. V. Shvartsman, W. Kleemann, J. Dec, Z. K. Xu, S. G. Lu, “Diffuse phase transition in $BaTi_{1-x}Sn_xO_3$ ceramics. An intermediate state between ferroelectric and relaxor behaviour,” *J. Appl. Phys.*, 2006, vol. 99, pp. 124111 (8).
48. Y. Hiruma, H. Nagata, Y. Hidaka, S. Tsukada, S. Kojima, T. Takenaka, “Depolarization temperatures and piezoelectric properties of $(Bi_{0.5}Na_{0.5})TiO_3$ ceramics and single crystals,” *Ferroelectrics*, 2010, vol. 404, pp. 162-166.
49. E. Aksel, J. S. Forrester, B. Kowalski, M. Deluca, D. Damjanovic, J. L. Jones, “Structure and properties of Fe-modified $Na_{0.5}Bi_{0.5}TiO_3$ at ambient and elevated temperature,” *Phys. Rev. B*, 2012, vol. 85, pp. 024121 (11).

Author's Publication List

SCI Publications

1. M. Dunce, E. Birks, M. Antonova, A. Plaude, R. Ignatans, A. Sternberg, "Structure and dielectric properties of $Na_{1/2}Bi_{1/2}TiO_3$-$BaTiO_3$ solid solutions," *Ferroelectrics*, 2013, vol. 447, pp. 1-8.
2. M. Dunce, E. Birks, M. Antonova, A. Plaude, A. Sternberg, "Phase transitions in Li, K and Ag modified $Na_{1/2}Bi_{1/2}TiO_3$-$SrTiO_3$-$PbTiO_3$ solid solutions," *Ferroelectrics*, 2012, vol. 436, pp. 12-18.
3. J. Hagberg, M. Dunce, E. Birks, M. Antonova, A. Sternberg, "Electrocaloric effect in $Na_{1/2}Bi_{1/2}TiO_3$-$SrTiO_3$-$PbTiO_3$ solid solutions," *Ferroelectrics*, 2012, vol. 428, pp. 20-26.
4. Š. Svirskas, M. Ivanov, Š. Bagdzevičius, M. Dunce, M. Antonova, E. Birks, A. Sternberg, J. Banys, "Dynamics of phase transition in 0.4NBT-0.4ST-0.2PT solid solution," *Integr. Ferroelectr.*, 2012, vol. 134, p. 81-87.
5. M. Dunce, E. Birks, M. Antonova, M. Kundzinsh, A. Sternberg, "Relation of dielectric permittivity and electric field dependence of polarization in some relaxors with perovskite structure," *Ferroelectrics*, 2011, vol. 424, pp. 21-27.
6. M. Dunce, R. Taukulis, E. Birks, I. Aulika, A. Fuith, M. Antonova, A. Sternberg, "Thermal expansion, Burns temperature and electromechanical properties in $Na_{1/2}Bi_{1/2}TiO_3$-$SrTiO_3$-$PbTiO_3$ solid solutions," *Ferroelectrics*, 2011, vol. 424, pp. 15-20.
7. M. Dunce, E. Birks, M. Antonova, V. Zauls, M. Kundzinsh, A. Fuith, "Structure and Physical Properties of $Na_{1/2}Bi_{1/2}TiO_3$-$CdTiO_3$ Solid Solutions," *Ferroelectrics*, 2011, vol. 417, pp. 93-99.
8. M. Dunce, E. Birks, M. Antonova, A. Sternberg, "Phase Transitions in Modified $Na_{1/2}Bi_{1/2}TiO_3$-$SrTiO_3$-$PbTiO_3$ Solid Solutions," *Ferroelectrics*, 2011, vol. 114, pp. 190-194.
9. M. Dunce, E. Birks, M. Antonova, M. Kundzinsh, "Description of relaxor state in $Na_{1/2}Bi_{1/2}TiO_3$-$SrTiO_3$-$PbTiO_3$ system of solid solutions," *Integr. Ferroelectr.*, 2011, vol. 123, pp. 40-46.
10. M. Dunce, M. Antonova, E. Birks, A. Sternberg, "Phase transitions in $Na_{1/2}Bi_{1/2}TiO_3$-$SrTiO_3$-$PbTiO_3$ solid solutions," *Ferroelectrics*, 2010, vol. 405, pp. 57-61.
11. E. Birks, M. Dunce, A. Sternberg, "High electrocaloric effect in ferroelectrics," *Ferroelectrics*, 2010, vol. 400, pp. 336-343.
12. M. Dunce, M. Antonova, E. Birks, M. Kundzinsh, A. Sternberg. "Phase transitions in $Na_{1/2}Bi_{1/2}TiO_3$-$SrTiO_3$-$PbTiO_3$ solid solutions," *Integr. Ferroelectr.*, 2009, vol. 108, pp. 125-133.

Other Publications

13. A. Plaude, R. Ignatans, E. Birks, M. Dunce, M. Antonova, A. Sternberg, "Structure and dielectric properties at phase transition of $Na_{1/2}Bi_{1/2}TiO_3$-$BaTiO_3$ solid solutions," *J. Phys.: Conf. Ser*. (iesniegts publicēšanai)
14. E. Birks, M. Dunce, M. Antonova, A. Sternberg, "Phase transitions in modified $Na_{1/2}Bi_{1/2}TiO_3$-$SrTiO_3$ solid solutions," *Phys. Status Solidi C*, 2009, vol. 6, pp. 2737-2739.

Participation in Conferences

1. M. Dunce, E. Birks, J. Peräntie, J. Hagberg, M. Antonova, A. Sternberg, "Phase transitions and electrocaloric effect in Ca modified $Na_{1/2}Bi_{1/2}TiO_3$-$SrTiO_3$-$PbTiO_3$ solid solutions," *In: International Symposium on the Applications of Ferroelectrics 2013 (2013 Joint UFFC, EFTF and PFM Symposium)*, Prague, Czech Republic, July 21-25, 2013, Abstracts, ISAF-P1A-6.
2. Š. Svirskas, M. Ivanov, Š. Bagdzevičius, J. Banys, J. Dec, S. Miga, M. Dunce, E. Birks, M. Antonova, A. Sternbergs, "Linear and nonlinear dielectric properties of ternary solid solutions $0.4Na_{0.5}Bi_{0.5}TiO_3$-$(0.6\text{-}x)SrTiO_3$-$xPbTiO_3$," *In: International Symposium on the Applications of Ferroelectrics 2013 (2013 Joint UFFC, EFTF and PFM Symposium)*, Prague, Czech Republic, July 21-25, 2013, Abstracts, ISAF-P3C-38.
3. M. Dunce, E. Birks, M. Antonova, A. Mishnov, M. Kundzinsh, A. Sternberg, "Phase transitions and physical properties in Ca modified $Na_{1/2}Bi_{1/2}TiO_3$-$SrTiO_3$-$PbTiO_3$ solid solutions. *In: International Conferece "Functional Materials and Nanotechnologies 2013"*, Tartu, Estonia, April 21-24, 2013, Abstracts, PO-109.
4. R. Ignatans, A. Plaude, M. Dunce, M. Antonova, E. Birks, "Structure and dielectric properties of $Na_{1/2}Bi_{1/2}TiO_3$-$BaTiO_3$ solid solutions in the phase transition region," *In: International Conferece "Functional Materials and Nanotechnologies 2013"*, Tartu, Estonia, April 21-24, 2013, Abstracts, PO-95.
5. M. Dunce, Ē. Birks, M. Antonova, A. Mišņovs, A. Šternbergs, "Fāžu pārejas ar Ca modificētos $Na_{1/2}Bi_{1/2}TiO_3$-$SrTiO_3$-$PbTiO_3$ cietajos šķīdumos," *No: LU Cietvielu Fizikas institūta 29. Zinātniskā konference*, Rīga, 20.-22. februāris, 2013, Konferences tēzes, 33. lpp.
6. M. Dunce, E. Birks, M. Antonova, A. Plaude, R. Ignatans, A. Sternberg, "Structure and phase transitions in $Na_{1/2}Bi_{1/2}TiO_3$ $BaTiO_3$ solid solutions," *In: First Baltic School on Application of Neutron and Synchrotron Radiation in Solid State Physics and Material Science*, Riga, Latvia, October 1-4, 2012, Abstracts, p. 29.
7. Š. Svirskas, M. Ivanov, Š. Bagdzevičius, J. Banys, M. Dunce, M. Antonova, E. Birks, A. Sternberg, "Dielectric dispersion and phase diagram of 0.4NBT-(0.6-x)ST-xPT ceramics," *In: The 11th Russia/CIS/Baltic/Japan Symposium on Ferroelectricity,* Ekaterinburg, Russia, August 20-24, 2012, Abstracts, p. 47.
8. M. Dunce, E. Birks, M. Antonova, A. Plaude, R. Ignatans, A. Sternberg, "Structure and dielectric Properties of $Na_{1/2}Bi_{1/2}TiO_3$-$BaTiO_3$ Solid Solutions," *In: 21st International Symposium on Applications of Ferroelectrics - 11th European Conference on Applications of Polar Dielectrics - 4th Conference Piezoresponse Force Microscopy and Nanoscale Phenomena in Polar Materials*, Aveiro, Portugal, July 9-13, 2012, Abstracts, p. 68.
9. M. Dunce, E. Birks, M. Antonova, A. Sternberg, "Phase transitions in Li, K and Ag modified $Na_{1/2}Bi_{1/2}TiO_3$-$SrTiO_3$-$PbTiO_3$ solid solutions," *In: International conference "Functional materials and nonotechnologies"*, Riga, Latvia, April 17-20, 2012, Abstracts, p. 139.
10. Š. Svirskas, M. Ivanov, Š. Bagdzevičius, J. Banys, M. Dunce, M. Antonova, E. Birks, A. Sternberg, "Dynamics of phase transition in $0.4Na_{0.5}Bi_{0.5}TiO_3$-$(0.6\text{-}x)SrTiO_3$-

$xPbTiO_3$ solid solutions," *In: International conference "Functional materials and nonotechnologies",* Riga, Latvia, April 17-20, 2012, Abstracts, p. 140.

11. M. Dunce, Ē. Birks, M. Antonova, A. Plaude, R. Ignatāns, "Fāžu pārejas un fizikālās īpašības $Na_{1/2}Bi_{1/2}TiO_3$-$BaTiO_3$ cietajos šķīdumos," *No: LU Cietvielu Fizikas institūta 28. Zinātniskās konference*, Rīga, 8.-10. februāris, 2012, Konferences tēzes, 26. lpp.
12. M. Dunce, E. Birks, M. Antonova, M. Kundzinsh, "Electric field dependence of dielectric permittivity and polarization in some relaxors with perovskite structure," *In: 13th International conference-school "Advanced Materials and Technologies"*, Palanga, Lithuania, August 27-31, 2011, Abstracts, P72.
13. J. Banys, Š. Svirskas, M. Ivanov, Š. Bagdzevičius, M. Dunce, M. Antonova, E. Birks, A. Sternberg, "Dielectric investigation of 0.4NBT-(0.6-x)ST-xPT solid solutions," *In: ISIF-2011*, Cambridge, England, July 31 – August 4, 2011, Abstracts, p. 109.
14. M. Dunce, E. Birks, M. Antonova, M. Kundzinsh, V. Zauls, A. Sternberg, "Electrocaloric effect in $Na_{1/2}Bi_{1/2}TiO_3$-$SrTiO_3$-$PbTiO_3$ solid solutions," *In: EMF-12*, Bordeaux, France, June 26 – July 1, 2011, Abstracts, P3-2.
15. Š. Svirskas, M. Ivanov, Š. Bagdzevičius, J. Banys, M. Dunce, M. Antonova, E. Birks, A. Sternberg, "Broadband dielectric spectroscopy of $0.4Na_{1/2}Bi_{1/2}TiO_3$-$(0.6\text{-}x)SrTiO_3$-$xPbTiO_3$ solid solutions," *In: EMF-12*, Bordeaux, France, June 26 – July 1, 2011, Abstracts, P3-12.
16. M. Dunce, E. Birks, M. Antonova, M. Kundzinsh, A. Sternberg, "Relation of dielectric permittivity and electric field dependence of polarization in some relaxors with perovskite structure," *In: International conference "Functional materials and nonotechnologies"*, Riga, Latvia, April 5-6, 2011, Abstracts, p. 220.
17. M. Dunce, R. Taukulis, E. Birks, I. Aulika, A. Fuith, M. Antonova, A. Sternberg, "Thermal expansion, Burns temperature and electromechanical properties in $Na_{1/2}Bi_{1/2}TiO_3$-$SrTiO_3$-$PbTiO_3$ solid solutions," *In: International conference "Functional materials and nonotechnologies"*, Riga, Latvia, April 5-6, 2011, Abstracts, p. 219.
18. Š. Svirskas, M. Ivanov, Š. Bagdzevičius, J. Banys, M. Dunce, M. Antonova, E. Birks, A. Sternberg, V. Zauls, "Dielectric properties of of $0.4Na_{1/2}Bi_{1/2}TiO_3$-$(0.6\text{-}x)SrTiO_3$-$xPbTiO_3$ solid solutions," *In: International conference "Functional materials and nonotechnologies"*, Riga, Latvia, April 5-6, 2011, Abstracts, p. 210.
19. M. Dunce, A. Fuith, Ē.Birks, M.Antonova, "Bērnsa temperatūra – noteikšana un interpretācija," *No: LU Cietvielu Fizikas institūta 27. Zinātniskās konference*, Rīga, 14.-16. februāris, 2011, Konferences tēzes, 32. lpp.
20. M. Dunce, E. Birks, M. Antonova, K. Kalninsh, M. Kundzinsh, "Structure and physical properties of $Na_{1/2}B_{1/2}TiO_3$-$CdTiO_3$ solid solutions," *In: I Lithuanian-Ukrainian-Polish Meeting on Ferroelectrics Physics*, Vilnius, Lithuania, September 13-16, 2010, Abstracts, p. 69. *(Saņemta godalga "outstanding contribution")*
21. M. Dunce, E. Birks, M. Antonova, M. Kundzinsh, "Phase transitions in modified $Na_{1/2}Bi_{1/2}TiO_3$-$SrTiO_3$ solid solutions," *In: The 12-th International Conference "Advanced Materials and Technologies"*, Palanga, Lithuania, August 27-31, 2010, Abstracts, p. 80.
22. M. Dunce, E. Birks, M. Antonova, A. Sternberg, "Phase transitions in modified $Na_{1/2}B_{1/2}TiO_3$-$SrTiO_3$ solid solutions," *In: The 10th Russia/CIS/Baltic/Japan Symposium on Ferroelectricity*, Yokohama, Japan, June 20-24, Abstracts, 2010.

23. M. Dunce, R. Taukulis, E. Birks, I. Aulika, A. Fuith, M. Antonova, A. Sternberg, "Thermal expansion and electromechanical properties in $Na_{1/2}Bi_{1/2}TiO_3$-$SrTiO_3$-$PbTiO_3$ solid solutions. *In: Electroceramics XII*, Trondheim, Norway, June 13-16, 2010, Abstracts, p. 156.
24. M. Dunce, E. Birks, M. Antonova, M. Kundzinsh, "Description of relaxor state in $Na_{1/2}Bi_{1/2}TiO_3$-$SrTiO_3$-$PbTiO_3$ system of solid solutions," *In: International Baltic Sea Region conference "Functional materials and nonotechnologies"*, Riga, Latvia, March 16-19, 2010, Abstracts, p. 53.
25. M. Dunce, M. Antonova, M. Kundziņš, Ē. Birks, "Relaksoru stāvokļa apraksts NBT-ST-PT cieto šķīdumu sistēmā," *No: LU CFI 26. zinātniskās konference*, Rīga, 17.-19. februāris, 2010, Konferences tēzes, 40. lpp.
26. M. Dunce, E. Birks, M. Antonova, and A. Sternberg, "Phase transitions in $Na_{1/2}Bi_{1/2}TiO_3$-$SrTiO_3$-$PbTiO_3$ solid solutions," *In: 12th International Meeting on Ferroelectricity & 18th IEEE International Symposium on the Application of Ferroelectrics,* Xi'an, China, August 23-27, 2009, Abstracts, EP-001.
27. M. Dunce, M. Antonova, E. Birks, A. Sternberg, "Phase transitions in modified $Na_{1/2}Bi_{1/2}TiO_3$-$SrTiO_3$-$PbTiO_3$ solid solutions," *In: 15th Semiconducting and Insulating Materials Conference,* Vilnius, Lithuania, June 15-19, 2009, Abstracts, p. 118.
28. M. Dunce, M. Antonova, E. Birks, M. Kundzinsh, A. Sternberg, "Phase transitions in modified $Na_{1/2}Bi_{1/2}TiO_3$-$SrTiO_3$-$PbTiO_3$ solid solutions," *In: International Baltic Sea Region conference "Functional materials and nonotechnologies"*, Riga, Latvia, March 31 – April 3, 2009, Abstracts, p. 51.
29. Ē. Birks, M. Dunce, M. Kundziņš, M. Antonova, A. Mišņovs, "$Na_{1/2}Bi_{1/2}TiO_3$-$SrTiO_3$-$PbTiO_3$ cieto šķīdumu dielektriskās īpašības," *No: LU Cietvielu Fizikas institūta 25. Zinātniskās konference.* Rīga, 11.-13. februāris, 2009, Konferences tēzes, 58. lpp.

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