

# DIELECTRIC AND PIEZOELECTRIC PROPERTIES OF $0.8\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3\text{-}0.2\text{BaTiO}_3$ MODIFIED WITH SODIUM NIOBATE

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In this paper, we present the dielectric and piezoelectric properties of tetragonal  $0.8\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3\text{-}0.2\text{BaTiO}_3$  modified with  $\text{NaNbO}_3$  ( $(1-x)[0.8\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3\text{-}0.2\text{BaTiO}_3]\text{-}x\text{NaNbO}_3$ ). Our experimental study has revealed that the ferroelectric phase in these compositions is suppressed with the increase of sodium niobate concentration. A broad anomaly, resembling relaxor ferroelectrics, appears in the 325–450 K temperature interval. The investigation of the electric field dependence of polarization has indicated that the double hysteresis loop behaviour is characteristic of the modified compositions, which is associated with the 1st order phase transition under the applied electric field. The experiments below room temperature have revealed that the range of stability of the ferroelectric phase is shifted to lower temperatures upon the increase of sodium niobate concentration. The electromechanical displacement in the modified compositions shows a similar maximum displacement in the whole concentration range. The electromechanical response in  $0.8\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3\text{-}0.2\text{BaTiO}_3$  solid solutions is due to the piezoelectric effect, while, in the mixed compositions, it is related to the jump-like change of the lattice constants in the vicinity of electric field-induced 1st order phase transition.

**Keywords:** dielectric spectroscopy, phase transitions, perovskites

## 1. Introduction

High-performance lead-free piezoelectrics have been sought after for more than two decades. The demands for ecological environmentally friendly piezoelectric materials have arisen in the European Union due to the RoHS directive. It was expected that the lead-free alternatives would replace Pb-based piezoceramics by now. As a result of extensive efforts, some outbreak was reached [1–3]. However, the performance of the lead-free perovskite oxides is still not sufficient for commercial applications. The high demand for new research in the area is still necessary to obtain excellent materials.

The search for lead-free piezoelectrics was concentrated on the morphotropic phase boundary

(MPB). The MPB compositions in  $\text{PbZrTi}_{1-x}\text{O}_3$  (PZT) [4] or  $(1-x)\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3\text{-}x\text{PbTiO}_3$  (PMN-xPT) [5, 6] piezoelectrics proved to have superior piezoelectric and dielectric constants. The first case is the mixture of ferroelectric lead-titanate [7, 8] with antiferroelectric lead zirconate [9]. These materials have two different crystallographic structures. If these two components are mixed, the symmetry in a particular composition range (i.e. the MPB) becomes monoclinic, lower than for its counterparts [5, 10, 11]. In the case of PZT, this composition range lies around  $x = 0.5$  [4].

$(1-x)\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3\text{-}x\text{PbTiO}_3$  system is a mixture of canonical relaxor  $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$  [12] and ferroelectric lead titanate. The MPB compositions are around  $x = 0.3$  [5]. The excellent properties in the MPB compositions were explained by

the flattening of the thermodynamic potential. This means that the polarization direction in the system can easily change on the particular monoclinic plane [13–15]. Due to this change, the system is very sensitive mechanically and exhibits both high piezoelectric coefficient and high electromechanical coupling factor ( $k > 0.9$ ).

The main research of lead-free materials is focused on sodium bismuth titanate ( $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  – NBT) [16, 17] and potassium sodium niobate ( $\text{K}_x\text{Na}_{1-x}\text{NbO}_3$  – KNN) [18]. NBT is a unique material which has a compositional disorder at the A-site of the perovskite lattice. However, there are still uncertainties about the chemical ordering of sodium and bismuth ions [19–22]. Due to the compositional disorder, NBT has a very unique sequence of phase transitions. At room temperature, NBT has a polar R3c space group [21]. Upon heating, this structure gradually transforms into an orthorhombic phase through a modulated phase (in 550–600 K temperature interval) [21, 23–25], which could possess some antipolar ordering [26]. This transformation takes place in a quite broad temperature range in which both rhombohedral and orthorhombic phases coexist [23, 25]. Above 600 K, NBT undergoes the phase transition to a tetragonal phase and finally – to a cubic phase at 800 K [21].

The macroscopic properties of sodium bismuth titanate are also quite complicated. The room temperature phase shows a ferroelectric behaviour, but, at certain depolarization temperature  $T_d$ , it loses ferroelectric features. The reason of the depolarization is quite robust. There are claims in the literature that it is due to the occurrence of a modulated phase in the 416–470 K temperature interval [25, 27, 28]. Below  $T_d$ , a relaxor-like dispersion is observed in NBT [28]. The material itself is widely called a relaxor ferroelectric, although its dielectric dispersion lies below 1 MHz frequency [29], while, in a canonical relaxor, the dispersion extends to the THz frequency range [30]. The whole complex dielectric spectrum of sodium bismuth titanate ceramics has been published previously [31]. The polarization dynamics in NBT was attributed to the anharmonicity of  $\text{Bi}^{3+}$  ions.

However, sodium bismuth titanate has some flaws that are not desirable for the piezoelectric applications. Its piezoelectric coefficients are significantly lower compared with those of PZT [32].

The dielectric properties are highly dependent on the stoichiometry of sodium and bismuth ions at the A-site of perovskite lattice [33]. Even a small deviation from stoichiometry causes a significant change in the ionic conductivity of NBT [34]. Thus, it is necessary to look for mixed materials to overcome the flaws of NBT. Luckily, NBT can form many solid solutions with substitutional ions both in A- and B-sites of perovskite lattice. Particularly, extensive studies of some ternary solid solutions have shown promising results [35, 36].

The most popular solid solutions of NBT is a mixture with ferroelectric barium titanate ( $\text{BaTiO}_3$  – BT).  $(1-x)\text{NBT}-x\text{BT}$  can form solid solutions in the whole range of concentrations. The morphotropic phase boundary was found in these solid solutions to be around  $x = 0.06$  [37]. The phase diagram of NBT- $x$ BT was summarized in several review papers [38, 39]. The increase of the concentration of barium titanate towards MPB develops a rather sharp jump in dielectric permittivity above which relaxor features persist. The high-temperature (around 550 K) dispersionless peak persists in the material, independently of the concentration. Its position gradually shifts to lower temperatures upon increase of  $x$ , but, above MPB, it is weakly temperature-dependent. In the compositions above MPB, the tetragonal ferroelectric phase is detected at room temperature [40] and the phase transition to a phase of cubic symmetry takes place in the range of  $T_d$  [41]. The dielectric behaviour transforms to the more classical ferroelectric one. The only difference from the compositions below MPB is that the relaxor-like dispersion is observed above the phase transition temperature [42]. Thus, the Curie–Weiss law in the cubic phase is violated – the material cannot be considered a classical ferroelectric.

Dielectric and piezoelectric properties of the tetragonal side of the phase diagram have not been so extensively studied, since it was expected to have excellent piezoelectric properties only in the vicinity of MPB. Compared to the lead-based piezoelectrics, the MPB compositions of NBT-BT solid solutions do not have such drastic improvement in dielectric and piezoelectric properties. Most of them are summarized in the review paper by Rödel [1, 39].

In this contribution, we have chosen to investigate the dielectric and piezoelectric properties of ternary solid solutions based on the 0.8NBT-0.2BT

composition, which is located in the tetragonal side of the phase diagram. This composition has the phase transition temperature around 470 K. It does not show the peculiar relaxation that is a signature feature of NBT [40]. Sodium niobate ( $\text{NaNbO}_3$  – NN) was introduced to the 0.8NBT-0.2BT system as the third component. We expected that, like in  $(0.94-x)\text{NBT}-0.06\text{BT}-x\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$  [43], NN will decrease the phase transition temperature to the room temperature range, allowing one to increase electric field-induced strain and exploiting the jump of the lattice parameter at the phase transition.

## 2. Experiment

The  $(1-x)[0.8\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3-0.2\text{BaTiO}_3]-x\text{NaNbO}_3$  samples were prepared by the conventional solid state reaction method from chemical-grade oxides and carbonates. Four different compositions with  $x = 0, 0.04, 0.05$  and  $0.08$  were prepared. They were coated with gold electrodes for the electrical contact.

Broadband dielectric properties of all the compositions were measured in two different experimental setups. The low-frequency experiments were carried out in the first setup by placing a sample in between two metal plates to form the parallel-plate capacitor. Capacitance and loss tangent were measured by an HP4284A LCR meter.

In the second setup, a sample was placed at the end of the coaxial line to form a capacitor. A vector network analyzer was used to measure the complex reflection coefficient from such a structure. The detailed description of the experimental procedure can be found in the literature [44]. All dielectric experiments were performed on cooling cycling at a rate of 1 K/min after heating the sample to 500 K.

Polarization and displacement hysteresis loops were measured by an AixACCT TF2000 analyzer which is equipped with a 4 kV voltage supply and a single beam interferometer. The triangular-shaped voltage signal of 10 Hz frequency was applied on all the samples under test. The temperature was measured with a 100  $\Omega$  platinum resistor. Temperature was stabilized for 10 min before each measurement.

## 3. Results and discussion

Figure 1 summarizes the temperature dependences of complex dielectric permittivity for all

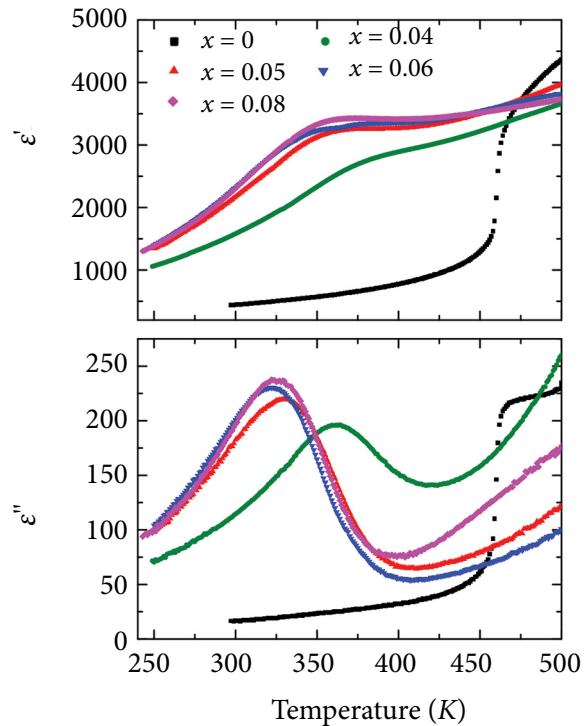


Fig. 1. Temperature dependence of the complex dielectric permittivity for all investigated  $(1-x)[0.8\text{NBT}-0.2\text{BT}]-x\text{NN}$  compositions.

the compositions at frequency  $f = 100$  kHz. The initial composition (0.8NBT-0.2BT) shows a typical ferroelectric-like behaviour. The sharp increase above 450 K indicates the 1st order ferroelectric phase transition. The high-temperature phase is cubic, while below the phase transition it is tetragonal. Even though the dielectric properties resemble the classical ferroelectric material, we have a deviation from the Curie–Weiss law due to an intrinsic disorder.

The addition of sodium niobate changes the dielectric properties quite drastically. First of all, the sharp increase of permittivity that would resemble a phase transition is absent. Instead, we have a broad anomaly in the 325–450 K temperature interval. This anomaly resembles the one observed in pure sodium bismuth titanate. It is not related to any phase transition, but it is known that above the anomaly a ferroelectric phase cannot be induced. Further increase of sodium niobate concentration shifts the anomaly to lower temperatures, but it becomes concentration-independent in the  $x = 0.05$ – $0.08$  composition range. It is important to note that the breadth of the anomaly is barely dependent on the composition as well.

In order to understand the impact of sodium niobate, we present the temperature dependence of 0.96[0.8NBT-0.2BT]-0.04NN composition at different frequencies in Fig. 2. It is evident that the dielectric anomaly around 350 K is mostly expressed at low frequencies. It is barely observed above 1 MHz. This is nearly the same scenario as in pure sodium bismuth titanate [29]. The temperature dependence of the imaginary part of dielectric permittivity shows a quite similar behaviour to the canonical relaxor lead magnesium niobate [45]. It seems that there is another anomaly above 500 K. However, this temperature region is out of our experimental capabilities. So, all the features in the dielectric data show that the NBT-like behaviour have been restored with the addition of sodium niobate.

Figure 3 represents the displacement and polarization hysteresis for all the compositions at room temperature (295 K). Ferroelectric behaviour is observed for the composition below  $x = 0.05$  concentration. Obviously, the displacement hysteresis is due to the piezoelectric effect. The displacement at larger electric fields exceeds 0.3%, which is a rather

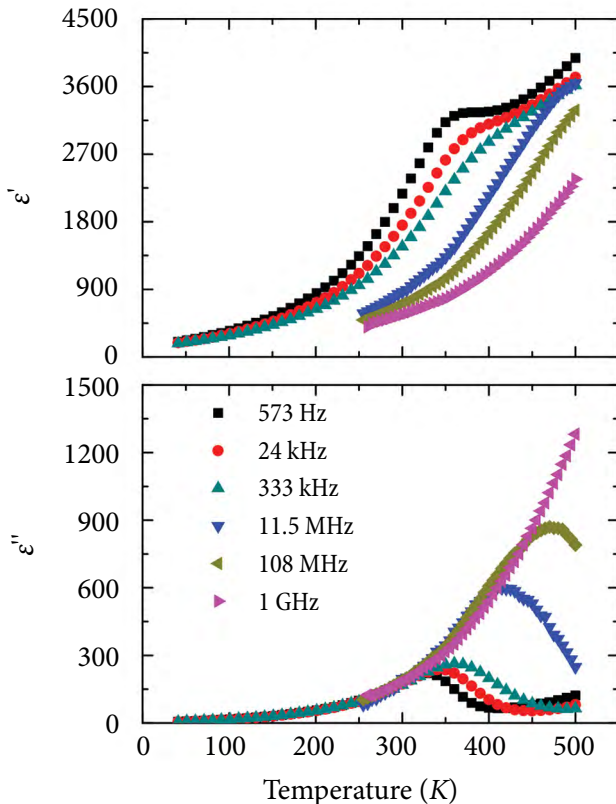


Fig. 2. Temperature dependence of the complex dielectric permittivity for the 0.96[0.8NBT-0.2BT]-0.04NN composition.

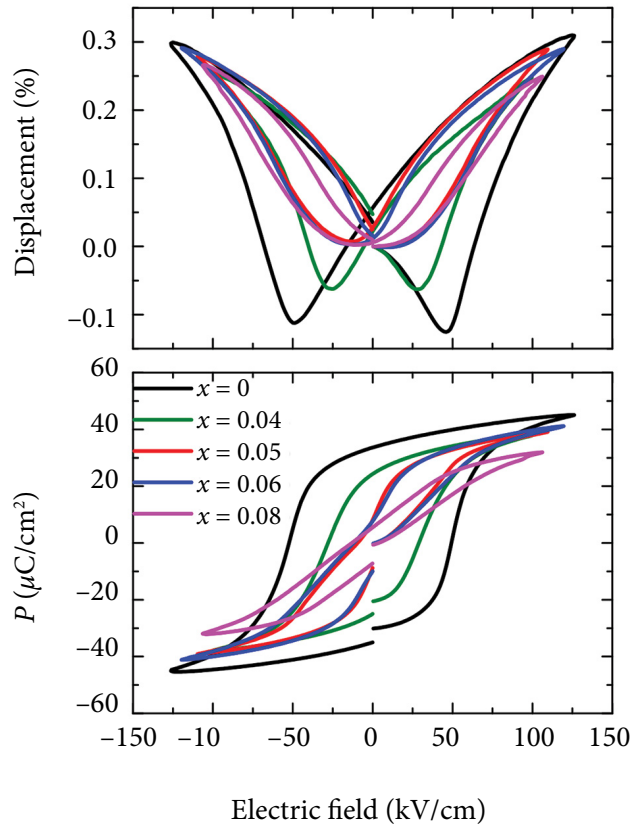


Fig. 3. Displacement (top panel) and polarization (bottom panel) hysteresis in all investigated compositions at room temperature.

high value for the lead-free piezoceramics. It is comparable to the morphotropic phase boundary compositions of NBT-BT.

The increase of sodium niobate concentration reduces the coercive field at room temperature. The ferroelectric behaviour at room temperature is suppressed in the  $x = 0.05$ – $0.08$  compositional range. The electric field dependence of polarization does not retain the character of typical ferroelectric loop. The compositions containing 5 and 6% of sodium niobate show inclined double hysteresis loops. The remanent polarization is rather small in these compositions. However, the maximum polarization is close to the values at lower temperatures, in a stable ferroelectric state. Such behaviour indicates that the ferroelectric long-range order can be induced by the external electric field. This ferroelectric phase does not sustain after the electric field is switched off. It is often observed at some temperature range in canonical relaxor ferroelectrics and antiferroelectrics. The sample containing 8% of sodium niobate show a much slimmer loop. The double hysteresis is not so evident from Fig. 3.

The displacement hysteresis resembles the electrostrictive behaviour.

In order to understand the development of ferroelectric order, polarization and displacement hysteresis at different temperatures was studied. The temperature dependences of remnant polarization for all the compositions are depicted in Fig. 4. The ferroelectric phase in the 0.8NBT-0.2BT sample persists at least up to 440 K. Some of the curves exhibit a maximum of remnant polarization. This maximum results from the fact that the coercive field increases when the temperature is decreased. In order to get fully saturated hysteresis loops, it is necessary to apply much stronger electric field than the coercive field  $E_c$  (usually  $1.5 E_c$  is sufficient). The decrease of remnant polarization with the decrease of temperature indicates that the field is too weak and the polarization is not fully switched on.

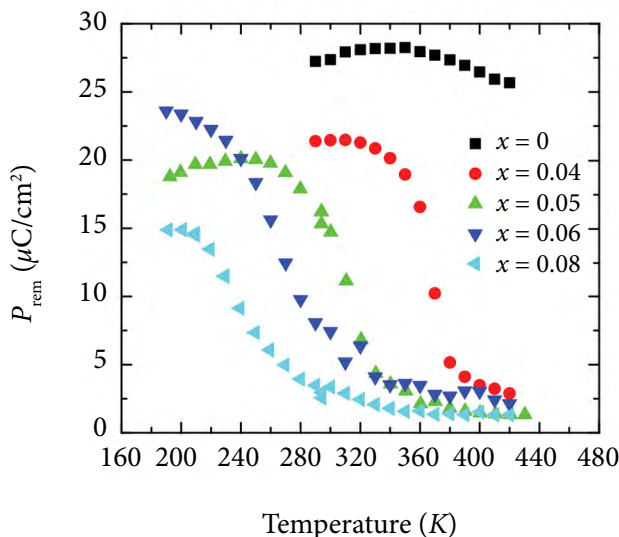


Fig. 4. Temperature dependence of the remnant polarization for all investigated compositions.

The steepest part of  $P_{\text{rem}}(T)$  dependence shifts to lower temperatures if the concentration of NN increases. This means that the range of stability of the ferroelectric phase in these compositions is shifted to lower temperature. The only composition that has the steepest part of  $P_{\text{rem}}(T)$  dependence below room temperature is 0.92[0.8NBT-0.2BT]-0.08NN. The ferroelectric phase range is shifted out of our experimental temperature range.

The temperature evolution of polarization and strain hysteresis is depicted in Fig. 5 by choosing the 0.94(0.8NBT-0.2BT)-0.06NN composi-

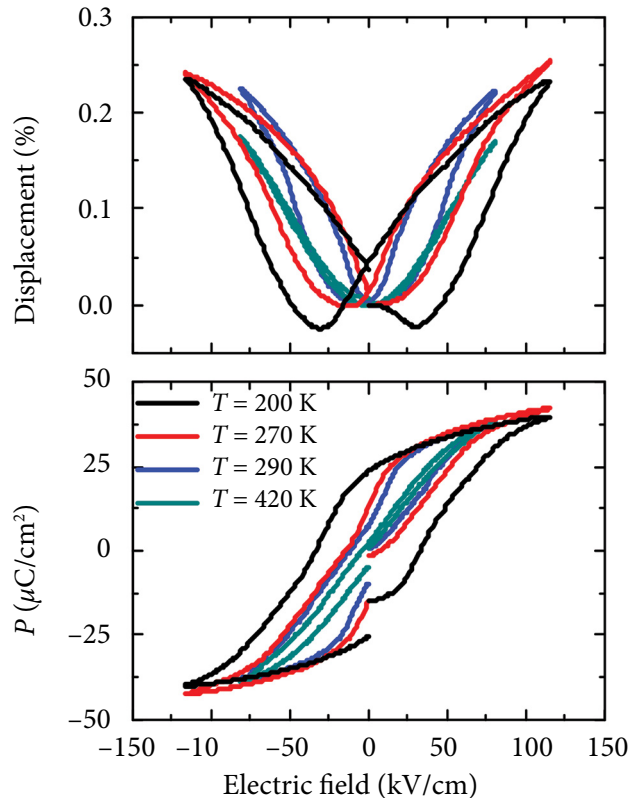


Fig. 5. Electric field dependence of the displacement and polarization of 0.94(0.8NBT-0.2BT)-0.06NN solid solution at different temperatures.

tion as an example. Above 400 K temperature, we observe the slim loop-like dependence of polarization vs electric field. The displacement curve shows the pure electrostrictive behaviour. Upon cooling, double hysteresis occurs. The electromechanical response in this double-hysteresis regime resembles the electrostrictive behaviour at a weak electric field regime. After the phase transition is induced, this character is no longer electrostrictive. Finally, at 200 K, we see ferroelectric-like loops and the displacement is due to the piezoelectric effect. However, the remnant polarization is not as large as in the compositions with a lower NN content and a significant polarization relaxation is evident – the hysteresis starts at non-zero polarization because the sample was pre-poled before the measurement. The measurement cycle ends up with a much larger remnant polarization. After removing electric field, the remnant polarization drops quite drastically. The drop in 0.8NBT-0.2BT is much smaller (see Fig. 3). This feature can arise due to several reasons. One of them is the finite conductivity in the materials,

but this can be safely neglected since the dielectric data at low frequencies does not show a typical conductivity behaviour. It seems that, after removing the external electric field, some of the polarization persists in the system. It is unclear how long it stays stable. It might have some longer relaxation time.

From the displacement hysteresis loops, we have calculated a large-signal piezoelectric coefficient  $d_{33}$  of the ferroelectric samples at room temperature.  $d_{33}$  for 0.8NBT-0.2BT is 200 pm/V, while for 0.96[0.8NBT-0.2BT]-0.04NN it is 280 pm/V. These are much higher coefficients than the ones found for the MPB compositions of NBT-BT. However, these values are not as superior as for the lead-free materials with additional co-doping.

#### 4. Conclusions

We have revealed that sodium niobate impacts the ferroelectric phase of 0.8NBT-0.2BT by shifting depolarization temperature to lower temperatures. In the compositions  $(1-x)[0.8\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3-0.2\text{BaTiO}_3]-x\text{NaNbO}_3$  with  $x = 0.05$  and  $0.06$ , the reversible electric field-induced phase transition is observed at room temperature. However, the contribution of the jump of lattice parameter at this induced phase transition does not create a significantly higher field-induced strain, compared with the 0.80NBT-0.20BT composition where such strain is apparently created by domain reorientation. Most probably it is related with reducing of polarization upon increase of  $x$ . The maximal strain value at room temperature is observed for the composition  $x = 0.06$  and exceeds 0.25% at 80 kV/cm. The dielectric anomalies in the system become more similar to the peculiar ones observed in pure NBT.

Our data has also revealed that the morphotropic phase boundary of NBT-BT system is not so extraordinary in terms of superior piezoelectric properties. The tetragonal composition has similar or larger piezo coefficients than the MPB compositions at room temperature. The ternary compositions despite their complexity show electromechanical properties quite similar to the neat composition (i.e. 0.8NBT-0.2BT), despite the fact that the displacement has an electrostrictive character at a weak electric field regime. Nevertheless, large displacements in the mixed compositions are

preserved due to the 1st order electric field-induced phase transition.

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## $0,8\text{Na}_{0,5}\text{Bi}_{0,5}\text{TiO}_3-0,2\text{BaTiO}_3$ , MAIŠYTO SU NATRIO NIOBATU, DIELEKTRINIŲ IR PJEZOELEKTRINIŲ SAVYBIŲ TYRIMAS

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### Santrauka

Šiame darbe buvo tiriamos tetragoninio  $0,8\text{Na}_{0,5}\text{Bi}_{0,5}\text{TiO}_3-0,2\text{BaTiO}_3$ , maišyto su  $\text{NaNbO}_3$ , dielektrinės ir pjezoelektrinės savybės. Tyrimai atskleidė, kad didinant  $\text{NaNbO}_3$  koncentraciją  $x$ , feroelektrinė fazė yra slopinama kambario temperatūroje. Maišytose kompozicijose išryškėja plati anomalija 325–450 K temperatūrų intervale. Ši anomalija primena feroelektriniams relaksoriams būdingus bruožus. Detaliau ištyrus poliarizacijos ir poslinkio histerezės kilpas buvo nustatyta, kad maišytose kompozicijose formuojasi dvigubos histerezės

kilpos, būdingos elektriniu lauku indukuojamiems 1-os rūšies faziniams virsmams. Buvo nustatyta, kad kuo didesnė natrio niobato koncentracija, tuo žemesnėje temperatūroje stebimos feroelektrinės poliarizacijos kilpos. Elektromechaninės sistemos savybės skirtingose kompozicijose yra panašios, pasiekiami gana dideli pjezoelektriniai poslinkiai. Grynoje medžiagoje elektromechaninis atsakas yra susijęs su pjezoefektu, o maišytose kompozicijose – su dideliu gardelės parametų pokyčiu, indukuojant 1-os rūšies fazinį virsmą elektriniu lauku.