Dimensional t -factor variation and increase of stability of the ferroelectric state in $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3$ -based solid solutions

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The influence of the B -site ion substitutions in $(1-x)(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ - $x\text{BaTiO}_3$ system of solid solutions on the relative stability of the antiferroelectric (AFE) and ferroelectric (FE) phases has been studied. The ions of zirconium, tin, and $(\text{In}_{0.5}\text{Nb}_{0.5})$, $(\text{Fe}_{0.5}\text{Nb}_{0.5})$, $(\text{Al}_{0.5}\text{V}_{0.5})$ ion complexes have been used as substituting elements. An increase in the concentration of the substituting ion results in a near linear variation in the size of the crystal lattice cell. Along with the cell size variation, a change in the relative stability of the AFE and FE phases takes place according to the changes of the tolerance factor of the solid solution. An increase in the tolerance factor leads to the increase in the temperature of the FE-AFE phase transition, and vice versa. Obtained results indicate the way for raising the temperature of the FE-AFE phase transition in $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ -based solid solutions.

Keywords: Lead-free piezoelectrics; solid solutions; ion substitutions; phase transitions.

1. Introduction

The lead zirconate-titanate (PZT), lead magnesium niobate, and lead zinc niobate and solid solutions on their base are known to have the largest values of piezoelectric parameters at present. PZT-based solid solutions are the most popular commercial ceramic materials for different applications. The need to replace the lead-containing compounds has inspired an interest and stimulated intensive studies of the $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ (BNT)-based piezoelectric ceramics.

Majority of researchers hold to an accepted point of view^{1–4} that the following sequence of the structural phase transformations takes place in BNT:

$$R3c \leftrightarrow R3c + P4bm \leftrightarrow P4bm \leftrightarrow Pm3m.$$

The low-temperature rhombohedral phase ($R3c$) is a ferroelectric (FE). This state persists at heating up to $\sim 200^\circ\text{C}$. In the interval of temperatures from ~ 200 to $\sim 330^\circ\text{C}$, the stable state with tetragonal crystal structure ($P4bm$) is a nonpolar antiferroelectric (AFE) phase. At higher temperatures BNT has a cubic crystal structure ($Pm3m$) and the dipole ordering does not exist. For the whole temperature range above 330°C , the dipole state of BNT is defined as a paraelectric (PE) (independent of high-temperature structural transition). There exist intermediate regions of temperature within which adjacent phases coexist in the BNT and BNT-based solid solutions.

The $(1-x)(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ - $x\text{BaTiO}_3$ (BNT – 100xBT) series of solid solutions is among the most thoroughly investigated BNT-based compounds. The sequence of phases and phase diagrams of this series of solid solutions have been the object of numerous studies^{5–12} (here we give references to the most recent studies; the number of earlier works is referenced in Refs. 6 and 8). The promising piezoelectric behavior of BNT – 100xBT is attributed to the existence of a morphotropic phase boundary in the range of composition $x = 0.05$ – 0.07 , similar to the morphotropic boundary in the PZT.^{10,13–15} Nonetheless these solid solutions have a number of disadvantages, such as a low temperature of transition from the polar FE pure nonpolar phase or into the state of the so-called relaxor AFE.⁸ All the above cited studies demonstrate a decrease of this characteristic temperature with an increase of the BaTiO_3 content in the interval $0 \leq x \leq 0.05$ and a very low value of this temperature (of the order of 130°C) in solid solutions belonging to the morphotropic region. Low values of the piezoelectric module d_{33} (160–180 pC/N) are also characteristic for BNT – 100xBT series of solid solutions.

In the majority of publications on properties of BNT-based solid solutions, the samples have been obtained by substitutions in the A -site of the perovskite crystal lattice. But in all these cases, this substitution led to a depression of the FE-AFE phase transition temperature (in comparison with

Fig. 1. Depolarization temperature, T_d , as a function of content of substituting ions in: $[(\text{Bi}_{1-x}\text{Ln}_x^{3+})_{1/2}\text{Na}_{1/2}]\text{TiO}_3$ (a) and $[(\text{Bi}_{1/2}\text{Na}_{1/2})_{1-x}\text{A}_x^{2+}]\text{TiO}_3$ (b) solid solutions.¹⁶

the value of this temperature in the prime BNT). The variation of the solid solution's depolarization temperature with changes in the content of divalent and trivalent elements used for substitutions in the A-site is given in Fig. 1 adapted from Ref. 16. Moreover, even in the BNT-based solid solutions containing the high-temperature FEs such as PbTiO_3 or BiFeO_3 , the point of destruction of the polar FE state decreased (as in $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ – BiFeO_3 solid solutions¹⁷), or just did not increase (as in $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ – PbTiO_3 solid solutions^{18,19}).

Large values of the piezoelectric parameters in lead-containing piezoelectric substances are reached as a consequence of B-site substitutions. PZT , $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ – PbTiO_3 , and $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ – PbTiO_3 solid solutions are good examples of this statement. In PZT solid solutions, one of the components (PbTiO_3) is a FE and the other one (PbZrO_3) is an AFE. An increase in the concentration of a substituting ion that has a larger size than the size of the titanium ion leads to the stabilization of a nonpiezoelectric AFE phase.^{20–23} Conversely a decrease in the size of the ion substituting for the B-site ion leads to the stabilization of a FE state.

There are very few reports in the literature (see Refs. 24–26, for example) on the BNT-based solid solutions with substitutions of zirconium for titanium. The number of publications devoted to B-site substitutions by other ions is even less.^{27–30} As expected, the AFE state in BNT–BT was also stabilized when the substitutions of ions with a size larger than the size of the Ti^{4+} -ion took place.^{31,32} As mentioned above, substitutions of smaller ions in B-site of crystal lattice can stabilize the FE state. Therefore, for investigations

of the influence of substitutions for titanium ion on the relative stability of the FE and AFE states, we have chosen the $[(\text{Na}_{0.5}\text{Bi}_{0.5})_{0.8}\text{Ba}_{0.2}]\text{TiO}_3$ as a base solid solution. The solid solution with such composition is located within the FE region in the diagram of the phase states of the $[(\text{Na}_{0.5}\text{Bi}_{0.5})]\text{TiO}_3$ – BaTiO_3 system.^{5,33} This compound undergoes a phase transition from the FE state into the AFE state when heated and has a subsequent phase transition into the PE state at higher temperatures. We have also studied solid solutions with smaller barium content located in the vicinity of the morphotropic region.

The aim of our studies is to investigate the influence of the size of ions substituting the B-site in the chosen system of BNT-based solid solutions on the relative stability of the FE and AFE states and to determine the physical factors that promote the increase of the temperature range of existence of the FE state.

In this paper, we present studies of the solid solutions with compositions located in two different areas of the diagram of phase states of $[(\text{Na}_{0.5}\text{Bi}_{0.5})]\text{TiO}_3$ – $100x\text{BaTiO}_3$, namely, solid solutions with compositions positioned away from the morphotropic region (corresponding to the interval of composition from 5 to 7 mol% of BaTiO_3) and solid solutions with composition in the vicinity of the morphotropic region (but not in the said region).

2. Experimental Methods

The traditional solid state synthesis method has been used for manufacturing of BNT-based solid solutions. Reagent grade oxides and carbonates of corresponding metals were used as starting materials that were mixed in the appropriate stoichiometry (except for Bi_2O_3 , which we have taken in the excess of 0.5 wt.%) by ball milling during 12 h. The mixed powders were calcined at 850 °C for 6 h. The sintering of ceramic samples was carried out at 1200 °C for 6 h.

The studies of crystal structure were performed using DRON-3 X-ray diffractometer in the Bragg–Brentano geometry with CuK_α -radiation ($\lambda = 1.5418 \text{ \AA}$), Ni-filter for the incident beam and the graphite monochromator in the diffracted beam. The angular range was $20^\circ \leq 2\theta \leq 90^\circ$, the scan step was 0.02° , and the accumulation time in each point was 2 s. The X-ray diffraction patterns showed perfect single-phase state of the samples prepared for further studies. X-ray diffraction patterns for the solid solutions with the zirconium substituted for titanium are presented in Fig. 2 as an example.

We have given this example, since the process of obtaining of single-phase solid solutions is the most difficult when titanium is replaced by zirconium.^{31,32} This is due to the Ti^{4+} and Zr^{4+} ions have the largest dimension difference of among all the replacing ions studied in the present paper.

Synthesized powders were axially pressed into disks with a diameter of 12 mm and a thickness of 1 mm and then sintered at 1150–1200 °C to manufacture samples for dielectric measurements. Fire-on silver paste was used to make

Fig. 2. X-ray diffraction patterns for the $[(\text{Na}_{0.5}\text{Bi}_{0.5})_{0.8}\text{Ba}_{0.2}](\text{Ti}_{1-y}\text{Zr}_y)\text{O}_3$ system of solid solutions. Zr-content (y): 1 – 0.00, 2 – 0.05, 3 – 0.10, 4 – 0.30.

electrodes on disk's surfaces. Temperature dependencies of the dielectric constant, $\varepsilon(T)$, were measured in an AC electric field with a frequency of 1 kHz using a precision QuadTech 7600 LCR meter. D-E hysteresis loops were observed using the standard Sawyer–Tower circuit at 10^{-2} Hz.

3. Influence of Ion Substitutions on Phase Transformations

3.1. $[(\text{Na}_{0.5}\text{Bi}_{0.5})_{0.8}\text{Ba}_{0.2}]\text{TiO}_3$ -based solid solutions

As noted before, our goal is to study the influence of substitutions on the relative stability of the FE and AFE states in BNT – 100xBT solid solutions located in the vicinity of the morphotropic (MPB) region of the BNT – 100xBT phase diagram. We also consider the solid solutions containing 20 mol% of BaTiO_3 since in these compounds the FE state is more stable than the AFE one. Here, we also need to note that as a rule, a little attention has been paid to the region of AFE states in publications on BNT–BT compounds. Such situation could be due to the desire of finding the substitute for PZT-based materials and majority of studies were devoted to the MPB region of the BNT – 100xBT phase diagram. Because of this, we give a discussion of BNT–BT solid solutions with large barium content.

The first “composition–temperature” diagram of phase states for the $(1-x)(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3-x\text{BaTiO}_3$ system of solid solution was presumably published in Ref. 33. This phase diagram was rather schematic reflecting only general

tendencies in the formation of different phase states in this series of solid solutions. The region of the AFE states located between the regions of the FE and PE states was shown in this phase diagram. The study in Ref. 5 contained the most complete phase diagram for ceramic samples of solid solutions with BaTiO_3 -content in the interval from 0.00% to 0.15%. Authors of this paper demonstrated that the temperature region for the AFE states is located between the temperature regions for the FE and PE states. There were also additional phase boundaries present within the region of the AFE states in this phase diagram.⁵ Probably their presence was a feature of the AFE region itself but it could also be a consequence of using of ceramic samples for all studies. The phase diagram obtained on single crystals of the same series of the $(\text{Bi}_{1/2}\text{Na}_{1/2})1-x\text{BaTiO}_3$ system of solid solutions was published in Ref. 12. High precision investigations of crystal structure using synchrotron radiation as well as dielectric measurements on crystals in a wide temperature interval were carried out in this study. Authors of Ref. 12 have also indicated the presence of the intermediate region of AFE states. It must be emphasized that the authors of Ref. 5 did not find any additional transitions within the region of AFE states or they did not mention their presence. Summarizing all this, one can conclude that the vast majority of authors have clearly pointed out the existence of the AFE states in the BNT – 100xBT solid solutions with BaTiO_3 -content up to 15%.

Very few publications on BNT – 100xBT solid solutions with higher content of barium titanate are available. As we mentioned above, the reason for this may be due to the primary interest in BNT – 100xBT solid solutions from the MPB region.

The boundaries of the AFE states region do not collapse when the concentration of BaTiO_3 reaches 15% and continue to be present even at higher BaTiO_3 -content (this AFE region is an intermediate area between the FE and PE regions in the phase diagram). There are very few publication devoted to studies of the BNT – 100xBT compounds with higher content of BaTiO_3 . The whole series of BNT – 100xBT solid solutions with BaTiO_3 -content up to 90% was investigated in Ref. 34. It was shown that there is a phase transition in the temperature region of 160°C – 170°C besides of the phase transition into the PE state at 300°C in the solid solution with 20% of BaTiO_3 . Turning back to the phase diagram in Ref. 2, one can see that this transition temperature “rests” on the extension of the line of the FE–AFE phase transition. In addition to all above-said, one has to mention the Ref. 35, where the phase diagram of BNT – 100xBT with 20% of BaTiO_3 is presented. Authors of this paper observed the presence of two phase transitions (from the FE to AFE state and from the AFE to PE state at heating) in this solid solution. If to compare this phase diagram with all other known phase diagrams, one can clearly see that this intermediate state between the FE and PE states is the AFE state.

Our discussions of the AFE state and the FE–AFE phase transition in this study have not been based on the

Fig. 3. Imaginary part of the dielectric constant versus temperature for the $[(\text{Na}_{0.5}\text{Bi}_{0.5})_{0.80}\text{Ba}_{0.20}](\text{Ti}_{1-y}\text{Zr}_y)\text{O}_3$ solid solutions (a) without and (b) under the action of the an electric field of 1100 V/mm. Zr-content (y): 1 – 0.00, 2 – 0.05. The “composition-temperature” phase diagram for the $[(\text{Na}_{0.5}\text{Bi}_{0.5})_{1-x}\text{Br}_x]\text{TiO}_3$ series from Ref. 35 is shown in the insert.

above-mentioned results only. We carried out measurements of temperature dependencies of the dielectric characteristics of our samples subjected to the action of an external electric field. Temperature dependencies of the imaginary part of dielectric constant measured without external electric field and in the presence of a field of 1100 V/mm are given in Fig. 3. Here we need to note that the anomaly in the $\epsilon''(T)$ dependence in the vicinity of the PE phase transition is very weakly pronounced and is not visible on a scale of Fig. 3.

The temperature of the low-temperature transition increases with an increase in the electric field intensity at a rate of $19^\circ\text{C}/(\text{kV}/\text{mm})$ while the temperature of the high-temperature transition decreases at a rate of $1.5^\circ\text{C}/(\text{kV}/\text{mm})$. Such type of changes in the temperatures of the phase transitions in the presence of external electric field and a weak decrease in the temperature of PE transition are characteristic specifically for the state with the AFE-type of electric-dipole ordering.^{23,36,37}

The rate of displacement of the temperature of the low-temperature phase transition (which we identify as the FE–AFE phase transition) in external electric field observed in our measurements is close to the rate of displacement of the FE–AFE phase transition in solid solutions with small BaTiO_3 -content where the AFE phase has been unambiguously identified. These results are presented in Fig. 2 of Ref. 38. The influence of the Zr-ion content on the position of the high-temperature AFE–PE phase transition is weak. The temperature, at which the low-temperature FE–AFE phase transition takes place, decreases significantly when the content of zirconium ion in the solid solution increases.

At the first stage, we have carried out substitutions of zirconium and tin ions for titanium ions. The results of such substitutions have been discussed in details.^{31,32}

In the $[(\text{Na}_{0.5}\text{Bi}_{0.5})_{0.80}\text{B}_{0.20}](\text{Ti}_{1-y}\text{Zr}_y)\text{O}_3$ (the Zr ionic radius is larger than the one of titanium) solid solutions with different zirconium content, the two phase transitions were clearly observed. The first of them (the low temperature one) corresponds to the FE–AFE phase transition and the second one corresponds to the transition from the AFE (nonpolar) to the PE phase (the attribution of phases was made according to Refs. 5, 34, 35 and 39). The temperature, at which the low-temperature phase transition takes place, decreases significantly when the zirconium content in the solid solution rises. The effect of variation of the zirconium concentration on the position of the high-temperature phase transition is weak.

The study of the crystal structure of solid solutions showed that an increase in the zirconium content led to a linear increase in the size of the unit cell and to a rapid decrease in the degree of tetragonal distortions of the crystal cell, and at $x > 0.10$ it was difficult to say anything about the type of distortion of the crystal lattice. Figure 4 shows the dependencies of the crystal lattice parameter, calculated in pseudocubic approximation, on the zirconium content. As we can see, the linear dependence is performed with good accuracy.

Similar results were obtained for solid solutions with substitutions of titanium by tin. Tin ion has a smaller ionic radius in comparison with zirconium but the ionic radius of tin is still larger than the ionic radius of titanium. The growth of the tin content led to an increase in the unit cell size (Fig. 4), however, since the size of the tin ion is smaller than that of zirconium, the rate of the lattice parameter increase was lower in this case. The temperature of the phase transition between the FE and AFE states decreased when the tin content increased.³¹

Fig. 4. The dependence of the crystal lattice parameter (in pseudocubic approximation) on the content of the substituting element, y , in the $[(\text{Na}_{0.5}\text{Bi}_{0.5})_{0.80}\text{Ba}_{0.20}](\text{Ti}_{1-y}\text{B}_y)\text{O}_3$. Substituting elements: 1 – Zr, 2 – Sn, 3 – $(\text{Fe}_{1/2}\text{Nb}_{1/2})$.

The influence of zirconium and tin ions substitutions on the relative stability of the FE and AFE states can be explained on the basis of the size effect, as it has been done in relation to the stability of the same phases in the PZT-based solid solutions. The tolerance factor $t = (R_A + R_O)/\sqrt{2}(R_B + R_O)$ is usually taken into account as an estimation parameter. The FE state in the PZT is stable at large values of t ($t > 0.9090$), whereas for small values of t ($t < 0.9080$) the stable state is the AFE one.²¹ As it easy to see, an increase in the ionic radius of the *B*-site ion (when ions Ti^{4+} are substituted by Zr^{4+} , Sn^{4+} ions) leads to a decrease of the t -factor. Just this effect occurs in the case of substitutions of zirconium (as well as tin) for titanium in $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3$ -based solid solutions. Such a conclusion has been confirmed by results obtained on the BNT – 100xBT solid solutions with substitutions of the Ti^{4+} ion by the complex $(\text{In}_{1/2}\text{Nb}_{1/2})^{4+}$. The average ionic radius of the $(\text{In}_{1/2}\text{Nb}_{1/2})^{4+}$ complex is larger than the radius of Ti^{4+} ion. According to approach based on consideration of the tolerance factor, the stability of the FE state has to be depressed against the stability of the AFE state, when the content of $(\text{In}_{1/2}\text{Nb}_{1/2})^{4+}$ complex rises, and the temperature of FE–AFE phase transition decreases. Such behavior has been observed in our experiments.

3.2. Substitutions of titanium by the $(\text{Fe}_{0.5}\text{Nb}_{0.5})$ -complex

As the next step of our studies to verify the proposed mechanism of influence of the size of ionic radius of substituting ions on the FE → AFE phase transition in the BNT-based solid solutions, we carried out substitutions of both zirconium and titanium ions by the $(\text{Fe}_{0.5}\text{Nb}_{0.5})^{4+}$ complex with the same valence as the replaceable ions. Two

samples of the BNT – 100xBT system were obtained $[(\text{Na}_{0.5}\text{Bi}_{0.5})_{0.80}\text{Br}_{0.20}]\{[(\text{Ti}_{0.90}(\text{Fe}_{0.5}\text{Nb}_{0.5})_{0.1})]_{0.90}\text{Zr}_{0.10}\}\text{O}_3$ (the substitution of the $(\text{Fe}_{0.5}\text{Nb}_{0.5})^{4+}$ complex for Ti^{4+}) and $[(\text{Na}_{0.5}\text{Bi}_{0.5})_{0.80}\text{Br}_{0.20}]\{(\text{Ti}_{0.90}[\text{Zr}_{0.08}(\text{Fe}_{0.5}\text{Nb}_{0.5})_{0.02}]_{0.10})\}\text{O}_3$ (the substitution of the $(\text{Fe}_{0.5}\text{Nb}_{0.5})^{4+}$ complex for Zr^{4+}).

In the first case, the average ionic radius of the $(\text{Fe}_{0.5}\text{Nb}_{0.5})^{4+}$ complex is greater than the radius of the substituted titanium ion; in the second case, the average ionic radius of $(\text{Fe}_{0.5}\text{Nb}_{0.5})^{4+}$ is smaller than the radius of zirconium ion. Figure 5 shows the temperature dependencies of the imaginary part of the dielectric constant for these solid solutions. As one can see, in the first case (in full agreement with the proposed model), the stability of the AFE state with respect to the FE state increases, and the FE → AFE transition temperature decreases. In the second case, both the stability of the FE state and the temperature of the FE → AFE phase transition increase.

3.3. $[(\text{Na}_{0.5}\text{Bi}_{0.5})]\text{TiO}_3$ – BaTiO_3 with compositions in the vicinity of the morphotropic region

Results presented in previous section demonstrate the possibility for increasing the stability of the FE state relative to the AFE one and as consequence a possibility to increase the temperature of the FE–AFE phase transition. To achieve this, one has to substitute the titanium ion by ions or ion complexes with smaller ionic radii.

The search for ions of chemical elements or ion complexes that can stabilize the FE state with the only titanium substitution was the next stage of our research. There is no suitable ions of simple chemical elements which have size lower than the size of Ti^{4+} and are specific for *B*-site of the perovskite crystal lattice of the $[(\text{Na}_{0.5}\text{Bi}_{0.5})_{1-x}\text{Ba}_x]\text{TiO}_3$ solid solutions. Therefore, we have selected the ion complex $(\text{Al}_{0.5}^{3+}\text{V}_{0.5}^{5+})^{4+}$ with an average ion radius of 0.54 Å which is smaller then the radius of the Ti^{4+} ion equal to 0.605 Å. We have analyzed two base solid solutions in our studies, namely, the $[(\text{Na}_{0.5}\text{Bi}_{0.5})_{0.97}\text{Ba}_{0.03}]\text{TiO}_3$ and $[(\text{Na}_{0.5}\text{Bi}_{0.5})_{0.90}\text{Ba}_{0.10}]\text{TiO}_3$ (with 3% and 10% of Ba-content). The compositions of these compounds are located in the vicinity of the morphotropic region in phase diagram of BNT – 100xBT. The first of these solid solutions is located in the region of the phase diagram containing solid solutions with rhombohedral crystal structure. The second compound belongs to the region of solid solutions with tetragonal crystal structure.

The replacement of Ti^{4+} -ions by the complex $(\text{Al}_{0.5}^{3+}\text{V}_{0.5}^{5+})^{4+}$ does not lead to a change in the type of distortion of the perovskite crystal lattice. So the solid solution $[(\text{Na}_{0.5}\text{Bi}_{0.5})_{0.97}\text{Ba}_{0.03}][\text{Ti}_{1-x}(\text{Al}_{0.5}\text{V}_{0.5})_x]\text{O}_3$ with $x = 0.10$ is characterized by the following parameters of the rhombohedral unit cell: $a_{\text{Rh}} = 3.887$ Å and $\alpha_{\text{Rh}} = 89.75^\circ$. The $[(\text{Na}_{0.5}\text{Bi}_{0.5})_{0.90}\text{Ba}_{0.10}][\text{Ti}_{1-x}(\text{Al}_{0.5}\text{V}_{0.5})_x]\text{O}_3$ solid solution with $x = 0.10$ is characterized by parameters of the tetragonal unit cell: $a_T = 3.905$ Å, $c_T = 3.952$ Å and $c/a = 1.012$. The degree of distortion of the crystal lattice is somewhat

Fig. 5. Imaginary part of dielectric constant versus temperature for the $[(\text{Na}_{0.5}\text{Bi}_{0.5})_{0.80}\text{Br}_{0.20}](\text{Ti}_{0.9}\text{Zr}_{0.10})\text{O}_3$ based solid solutions. 1 — dependence for $[(\text{Na}_{0.5}\text{Bi}_{0.5})_{0.80}\text{Br}_{0.20}](\text{Ti}_{0.9}\text{Zr}_{0.10})\text{O}_3$ without substitutions for Ti and Zr, 2 — dependence for $[(\text{Na}_{0.5}\text{Bi}_{0.5})_{0.80}\text{Ba}_{0.20}]\{[\text{Ti}_{0.9}(\text{Fe}_{0.5}\text{Nb}_{0.5})_{0.10}]\text{Zr}_{0.10}\}\text{O}_3$ with substitution of Ti by the $(\text{Fe}_{0.5}\text{Nb}_{0.5})$ complex, 3 — dependence for $[(\text{Na}_{0.5}\text{Bi}_{0.5})_{0.80}\text{Ba}_{0.20}]\{\text{Ti}_{0.90}[\text{Zr}_{0.08}(\text{Fe}_{0.5}\text{Nb}_{0.5})_{0.02}]_{0.10}\}\text{O}_3$ with substitution of Zr by the $(\text{Fe}_{0.5}\text{Nb}_{0.5})$ complex.

Fig. 6. Real (a) and imaginary (b) parts of permittivity versus temperature for the $[(\text{Na}_{0.5}\text{Bi}_{0.5})_{0.90}\text{Br}_{0.10}][\text{Ti}_{1-y}(\text{Al}_{0.5}\text{V}_{0.5})_y]\text{O}_3$ solid solutions. y : 1 – 0.00, 2 – 0.05, 3 – 0.10. The arrows in the Fig. 6(a) indicate temperatures of the FE–AFE transition.

higher (albeit insignificantly) than in unsubstituted solid solutions.¹⁰ It will be demonstrated below that the introduction of the $(\text{Al}_{0.5}^{3+}\text{V}_{0.5}^{5+})^{4+}$ ion complex into the crystal lattice leads to an increase in the temperature of destruction of the FE ordering.

An example of temperature dependencies of the dielectric constant for the series of solid solutions with 10% of barium in the A-sites of the perovskite crystal lattice of $[(\text{Na}_{0.5}\text{Bi}_{0.5})_{0.90}\text{Ba}_{0.10}][\text{Ti}_{1-x}(\text{Al}_{0.5}\text{V}_{0.5})_x]\text{O}_3$ are shown in Fig. 6. The dependencies $\varepsilon'(T)$ and $\varepsilon''(T)$ for solid solutions containing 3% of Ba in the A-sites of perovskite lattice have analogous character.

The dependence of the temperature of the FE–AFE phase transition on the content of $(\text{Al}_{0.5}^{3+}\text{V}_{0.5}^{5+})^{4+}$ ion complex for the two series of the solid solutions is shown in Fig. 7.

As it is clearly seen, an increase of the content of the $(\text{Al}_{0.5}^{3+}\text{V}_{0.5}^{5+})^{4+}$ ion complex leads to the rise of the temperature of the FE–AFE phase transition.

Thus, substitutions of the $(\text{Al}_{0.5}^{3+}\text{V}_{0.5}^{5+})^{4+}$ ion complex increase of the stability of the FE phase against the AFE one. The latter define the increase in the degree of distortion of the crystal lattice. The larger rate of increase of the FE–AFE

Fig. 7. The temperature of the FE–AFE phase transition versus content of the $(\text{Al}_{0.5}\text{V}_{0.5})$ complex: (a) $[(\text{Na}_{0.5}\text{Bi}_{0.5})_{0.97}\text{Br}_{0.03}][\text{Ti}_{1-y}(\text{Al}_{0.5}\text{V}_{0.5})_y]\text{O}_3$ solid solutions. (b) $[(\text{Na}_{0.5}\text{Bi}_{0.5})_{0.90}\text{Br}_{0.10}][\text{Ti}_{1-y}(\text{Al}_{0.5}\text{V}_{0.5})_y]\text{O}_3$ solid solutions during the heating (1) and cooling (2).

transition temperature has been observed for the series of solid solutions containing 3% of the barium.

4. Conclusions

We have investigated the influence of ion substitutions in the B-site of the crystal lattice of $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3$ -based solid solutions on the temperature of the FE–AFE phase transition.

An increase in the content of the substituting ions results in the variation of the size of the crystal cell according to a nearly linear law. At the same time, there exists a coordination of the relative stability of the AFE and FE phases with the variation of the tolerance factor of the solid solution.

The substitution of titanium ion by ions of zirconium and tin or by $(\text{In}_{0.5}\text{Nb}_{0.5})$ complex leads to a decrease in the tolerance factor and to an increase of the stability of the AFE phase relative to the stability of the FE phase.

The influence of substitutions of the $(\text{Fe}_{0.5}\text{Nb}_{0.5})$ complex depends on the type of the ion in the B-site which is substituted by this complex. When the $(\text{Fe}_{0.5}\text{Nb}_{0.5})$ complex is substituted for a zirconium ion, the tolerance factor increases and the temperature of the phase transition rises (it means the increase of the FE phase stability), whereas when the $(\text{Fe}_{0.5}\text{Nb}_{0.5})$ complex is substituted for a titanium ion, the transition temperature decreases as the result of a decrease of the tolerance factor (it means the increase of the AFE phase stability).

The substitution of the ion in the B-site by the $(\text{Al}_{0.5}\text{V}_{0.5})^{4+}$ complex leads to the increase of the stability of the FE phase and the increase in the temperature of the FE–AFE phase transition.

All results presented in this paper show a predominant influence of the ion size factor on the relative stability of the FE and AFE states in the $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3$ -based solid

solutions in the case of *B*-site substitutions and point at the method allowing to raise the temperature of the FE–AFE phase transition.

References

- ¹G. O. Jones and P. A. Thomas, Investigation of the structure and phase transitions in the novel A-site substituted distorted perovskite compound $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$, *Acta Crystallogr. Sect. B* **58**, 168 (2002).
- ²V. Dorcet, G. Trolliard and P. Boullay, The structural origin of the antiferroelectric properties and relaxor behavior of $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$, *J. Magn. Mater.* **321**, 1758 (2009).
- ³V. Dorcet, G. Trolliard and P. Boullay, Reinvestigation of phase transitions in $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ by TEM. Part I: First order rhombohedral to orthorhombic phase transition, *Chem. Mater.* **20**, 5061 (2008).
- ⁴V. Dorcet and G. Trolliard, Reinvestigation of phase transitions in $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ by TEM. Part II: Second order orthorhombic to tetragonal phase transition, *Chem. Mater.* **20**, 5074 (2008).
- ⁵F. Cordero, F. Craciun, F. Trequattrini, E. Mercadelli and C. Galassi, Phase transitions and phase diagram of the ferroelectric perovskite $(\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3)_{1-x}\text{Ba}_x\text{TiO}_3$ by anelastic and dielectric measurements, *Phys. Rev. B* **81**, 144124 (2010).
- ⁶Y.-Q. Lu and Y.-X. Li, A review on lead-free piezoelectric ceramics studies in China, *J. Adv. Dielectr.* **1**, 269 (2011).
- ⁷C. Ma and X. Tan, Phase diagram of unpoled lead-free $(1-x)(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ – $x\text{BaTiO}_3$ ceramics, *Sol. State Comm.* **150**, 1497 (2010).
- ⁸X. Tan, C. Ma, J. Frederick, S. Beckman and K. G. Webber, The antiferroelectric $\leftrightarrow$ ferroelectric phase transition in lead-containing and lead-free perovskite ceramics, *J. Amer. Ceram. Soc.* **94**, 4091 (2011).
- ⁹C. Ma and X. Tan, *In situ* transmission electron microscopy study on the phase transitions in lead-free $(1-x)(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ – $x\text{BaTiO}_3$ ceramics, *J. Amer. Ceram. Soc.* **94**, 4040 (2011).
- ¹⁰W. Jo, J. E. Daniels, J. L. Jones, X. Tan, P. A. Thomas, D. Damjanovic and J. Rödel, Evolving morphotropic phase boundary in lead-free $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ – BaTiO_3 piezoceramics, *J. Appl. Phys.* **109**, 014110 (2011).
- ¹¹C. Ma, H. Guo and X. Tan, A new phase boundary in $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ – BaTiO_3 revealed via a novel method of electron diffraction analysis, *Adv. Funct. Mater.* **23**, 5261 (2013).
- ¹²W. Ge, C. Luo, Q. Zhang, Y. Ren, J. Li, H. Luo and D. Viehland, Evolution of structure in $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ single crystals with BaTiO_3 , *Appl. Phys. Lett.* **105**, 162913 (2014).
- ¹³P. K. Panda, Review: Environmental friendly lead-free piezoelectric materials, *J. Mater. Sci.* **44**, 5049 (2009).
- ¹⁴J. Rödel, W. Jo, K. T. P. Seifert, E.M. Anton, T. Granzow and D. Damjanovic, Perspective on the development of lead-free piezoceramics, *J. Amer. Ceram. Soc.* **92**, 1151 (2009).
- ¹⁵B. Parija, S. Panigrahi, T. Badaranda and T. P. Sinha, Morphotropic phase boundary and dielectric relaxation study of lead free ceramic, *J. Adv. Dielect.* **2**, 125008 (2012).
- ¹⁶Y. Hiruma, Y. Watanabe, H. Nagata and T. Takenaka, Phase transition temperatures of divalent and trivalent ions substituted $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ ceramics, *Key Eng. Mater.* **350**, 93 (2007).
- ¹⁷J. M. Kim, Y. S. Sung, J. H. Cho, T. K. Song, M. H. Kim, H. Chong, T. G. Park, D. Do and S. S. Kim, Piezoelectric and dielectric properties of lead-free $(1-x)(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ – $x\text{BiFeO}_3$ ceramics, *Ferroelectrics* **404**, 88 (2010).
- ¹⁸S.-E. Park and K. S. Hong, Phase relations in the system $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ – PbTiO_3 . I. Structure, *J. Appl. Phys.* **79**, 383 (1996).
- ¹⁹K. S. Hong and S.-E. Park, Phase relations in the system $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ – PbTiO_3 . II. Dielectric properties, *J. Appl. Phys.* **79**, 388 (1996).
- ²⁰B. Jaffe, W. R. Cook and H. Jaffe, *Piezoelectric Ceramics*, Chaps. 7 and 8 (Academic Press, London, New York, 1971).
- ²¹M. Troccaz, P. Gonnard, Y. Fetteau and L. Eyraud, Goldschmidt factor and phase diagrams of doped PZT, *Ferroelectrics* **14**, 769 (1976).
- ²²P. Gonnard and M. Troccaz, Dopant distribution between A and B sides in PZT ceramics of type ABO_3 , *J. Solid State Chem.* **23**, 321 (1978).
- ²³M. E. Lines and A. M. Glass, *Principles and Application of Ferroelectric and Related Materials*, Chap. 8 (Clarendon Press, Oxford, 1977).
- ²⁴L. K. Kumari, K. Prasad and R. N. P. Choudhary, Impedance analysis of $(\text{Na}_{0.5}\text{Bi}_{0.5})(\text{Zr}_{0.25}\text{Ti}_{0.75})\text{O}_3$ ceramic, *Indian J. Energy Mater. Sci.* **15**, 147 (2008).
- ²⁵C. Peng, J.-F. Li and W. Gong, Preparation and properties of $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ – $\text{Ba}(\text{Ti},\text{Zr})\text{O}_3$ lead-free piezoelectric ceramics, *Mater. Lett.* **59**, 1576 (2005).
- ²⁶B. Tilak, Ferroelectric relax behavior and spectroscopic properties of Ba^{2+} and Zr^{4+} modified sodium bismuth titanate, *Amer. J. Mater. Sci.* **2**, 110 (2014).
- ²⁷E. Aksel, J. S. Forrester, B. Kowalski and M. Deluca, Structure and properties of Fe-modified $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ at ambient and elevated temperature, *Phys. Rev. B* **85**, 024121 (2012).
- ²⁸W. Bai, Y. Bian, J. Hao, B. Shen and J. Zhai, Composition and temperature-dependent structure evolution and large strain response in $(1-x)(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ – $x\text{Ba}(\text{Al}_{0.5}\text{Ta}_{0.5})\text{O}_3$ ceramics, *J. Am. Ceram. Soc.* **96**, 246 (2013).
- ²⁹E. A. Patterson and D. P. Cann, Relaxor to ferroelectric transitions in $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ – $\text{Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3$ solid solutions, *J. Am. Ceram. Soc.* **95**, 3509 (2012).
- ³⁰J. H. Cho, S. C. Lee, L. Wang, H. G. Yeo, Y. S. Sung, M. H. Kim and T. K. Song, Dielectric properties and phase transitions in hetero-valent-ion-substituted $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ ceramics, *J. Korean Phys. Soc.* **56**, 457 (2010).
- ³¹V. M. Ishchuk, L. G. Gusakova, N. G. Kisel, D. V. Kuzenko, N. A. Spiridonov and V. L. Sobolev, Zr and Sn substituted $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3$ -based solid solutions, *Math. Res. Express* **3**, 2 (2016).
- ³²V. M. Ishchuk, L. G. Gusakova, N. G. Kisel, N. A. Spiridonov and V. L. Sobolev, Zr-substituted $(\text{Na}_{0.5}\text{Bi}_{0.5})_{1-x}\text{Ba}_x\text{TiO}_3$ -based solid solutions, *J. Amer. Ceram. Soc.* **99**, 1786 (2016).
- ³³T. Takenaka, K. Maruyama and K. Sakata, $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ – BaTiO_3 system for lead-free piezoelectric ceramics, *Jpn. J. Appl. Phys.* **30**, 2236 (1991).
- ³⁴M. Duncce, E. Birks, M. Antonova, A. Plaude, R. Ignatans and A. Sternberg, Structure and dielectric properties of $\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3$ – BaTiO_3 solid solutions, *Ferroelectrics* **447**, 1 (2013).
- ³⁵Y. Hiruma, K. Yoshii, H. Nagata and T. Takenaka, Investigation of phase transition temperatures on $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ – $(\text{Bi}_{1/2}\text{K}_{1/2})\text{TiO}_3$ and $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ – BaTiO_3 lead-free piezoelectric ceramics by electrical measurements, *Ferroelectrics* **346**, 114 (2007).

- ³⁶G. Shirane, E. Savaguchi and Y. Tagaki, Dielectric properties of lead zirconate, *Phys. Rev.* **84**, 476 (1951).
- ³⁷J. C. Burfoot and G. W. Taylor, *Polar Dielectrics and Their Applications* (University of California Press, Berkeley, 1979).
- ³⁸E. Sapper, S. Schaab, W. Jo, T. Granzow and J. Rödel, Influence of electric fields on the depolarization temperature of Mn-doped $(1-x)\text{Bi}_{1/2}\text{Na}_{1/2}\text{TiO}_3 - x\text{BaTiO}_3$, *J. Appl. Phys.* **111**, 014105 (2012).
- ³⁹R. Garg, B. N. Rao, A. Senyshyn, P. S. R. Krishna and R. Ranjan, Lead-free piezoelectric system $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3\text{--BaTiO}_3$: Equilibrium structures and irreversible structural transformations driven by electric field and mechanical impact, *Phys. Rev. B* **88**, 014103 (2013).