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Peculiarities of the induced phase transition in single-crystal solid solutions $\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3-5\%\text{BaTiO}_3$

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The dielectric and optical properties, as well as the time dependences of the permittivity in an electric field applied along the [001] direction, are studied in $\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3-5\%\text{BaTiO}_3$ single crystals lying near the morphotropic phase boundary. It is shown that, even in the absence of an electric field, dielectric and optical hysteresis associated with the coexistence of tetragonal and rhombohedral phases is observed in a wide temperature range, and the relative volume fractions of the two phases largely depend on temperature. It was found that at temperatures below the temperature of the morphotropic phase transition, the induction of the ferroelectric phase occurs without a delay time, which distinguishes the samples under study from $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3-x\%\text{PbTiO}_3$ solid solutions. The results obtained are explained by different sizes of polar nanoregions in the low-temperature phase.

Keywords: ferroelectricity, relaxors, induced phase transition.

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1. Introduction

The piezoelectric materials are indispensable in many devices designed to convert the mechanical energy to the electrical one, and vice versa [1]. Recent efforts for development of the lead-free piezoelectric materials have made it possible to replace the lead-based materials with ecologically clean materials, though the piezoelectric characteristics of the lead-free materials are inferior to the lead-based systems as a whole [2]. Interest in the lead-free materials being recently researched is a response to legislative compulsory measures, in particular, to the RoHS/WEEE European regulations concerning requirements for limitation of hazardous substances (for example, lead) in various products and not allowing them being internally marketed in the European Union without performing a test procedure (research, testing).

The solid solutions $\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3-x\%\text{BaTiO}_3$ (as abbreviated to $\text{NBT}-x\%\text{BT}$) belonging to the relaxors are potentially important lead-free piezoelectric systems in terms of environmental protection. The lead-containing relaxor ferroelectrics such as $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3-x\%\text{PbTiO}_3$ ($\text{PMN}-x\%\text{PT}$) and $\text{PbZn}_{1/3}\text{Nb}_{2/3}\text{O}_3-x\%\text{PbTiO}_3$ ($\text{PZN}-x\%\text{PT}$) have ultra-high piezoelectric properties near a morphotropic phase boundary (MPB). The lead-free solid solutions have a lot of discovered properties which are intrinsic to the lead-containing systems [3]. Based on that fact that adding PbTiO_3 (PT) to PMN results in the ultra-high piezoelectric properties in the solid solution ($\text{PMN}-x\%\text{PT}$), BaTiO_3 (BT) was added to $\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3$ (NBT), thereby resulting in formation of a similar solid solution between the relaxor (NBT) and

the normal ferroelectric (BT) with the MPB between the rhombohedral (R) and tetragonal (T) phases.

In $\text{NBT}-x\%\text{BT}$, the morphotropic phase boundary (MPB) exists in the concentrations Ba 6–8 mol%. In the single crystals $\text{NBT}-6\%\text{BT}$ oriented along [001] there is an evident maximum of the longitudinal piezoelectric factor $d_{33} \sim 500$ pC/N [4]. Two anomalies have been found on the temperature dependence of the permittivity in the pure NBT: one at the temperature ~ 600 K (T_{max}), which includes an evident frequency-dependent maximum, and the second one at the temperature ~ 520 K (T_{RF}), below which the NBT becomes the relaxor [5,6]. The relaxor behavior remains when doping BT, i.e. in $\text{NBT}-x\%\text{BT}$ [4–7].

Despite the anomalies and coexistence of polar nanoregions of a rhombohedral ($R3c$) and tetragonal ($P4bm$) symmetry, the solid solutions $\text{NBT}-x\%\text{BT}$ near MPB, like PMN and the solid solutions $\text{PMN}-x\%\text{PT}$, remain cubic at all temperatures without the electric field, but the $R3c$ is dominant [4,8,9]. The anomaly at T_{RF} on the temperature dependence of the permittivity is correlated to composite contribution by the transition from $R3c \rightarrow P4bm$ and to thermal evolution of the polar $P4bm$ nanoregions.

At the same time, the authors of the paper [10] think that the middle structure of the NBT single crystals is not consistent with the rhombohedral system, and it is better to describe it by means of a monoclinic spatial group.

There are different points of view as to phase transitions in $\text{NBT}-x\%\text{BT}$. Thus, the authors of the papers [11,12] consider a low-temperature transition as a transition to the antiferroelectric (AFE) phase, and a maximum of permittivity as a transition from the antiferroelectric to paraelectric phase. Although results of the paper [11] on the

presence of the transition into the AFE-phase were accepted by many researchers, it had not been verified in no way thereafter. Authors of the other works [6,9,13–15] referring to no structural changes below T_{RF} , unanimously claim that constrictions occurring in hysteresis loops, which have been earlier regarded as a specific proof of the transition to AFE, are a mere consequence of an electric field-induced relaxor–ferroelectric transition.

All relaxor solid solutions, of which the crystals being presently studied are an example, have one common feature: a random distribution of ions in equivalent positions of the crystal lattice. All the early studied relaxors, such as PMN, PZN, etc., and the solid solutions based thereon, the random distribution of the ion was observed in the *B* position of the ABO_3 oxygen octahedron, in contrast to the presently studied solid solutions, in which the *A* position is occupied by two different ions. Although they have a number of common features, such relaxors also exhibit significant differences correlated to a nature of an emerging ferroelectric phase [16,17]. Thus, in a number of combinations, such as $\text{PMN}-x\% \text{PT}$ and others [18–21], sizes of the polar nanoregions (PNR) below a temperature of the morphotropic phase boundary (MPB) remain the same, but with a change of their dipole moments only, thereby leading to occurrence of a nonergodic glass phase. At the same time, in other relaxors, such as PZN, $\text{PZN}-x\% \text{PT}$, even below the MPB temperature, PNR continues to be increasing without changing a direction of their dipole moments, and the nonergodic glass phase seems to be absent [16,17,22].

There is no study of the nature of the relaxor state in the presently studied compounds, in which the relaxor properties are correlated to disorder in the *A* position of the ABO_3 oxygen octahedron. In connection therewith, it was interesting to study an induction process of the ferroelectric phase, as well as the nucleation kinetics of ordered ferroelectric phases. It will be a study of dielectric and optic properties, as well as time dependences of the permittivity in the electric field in the NBT–5%BT single crystal with a composition near MPB.

2. Examined samples and experimental procedure

The NBT–5BT single crystals have been selected as objects to be studied. Although the solid solutions with the BaTiO_3 content of 6 and 7% exhibit the best piezoelectric and dielectric properties, but it is very difficult to control their properties because of coexistence of the two phases [23,24]. For this reason, for the studies we have selected the single crystals with the $95\%(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3-5\% \text{BaTiO}_3$ (NBT–5%BT) composition, which are mainly of a rhombohedral structure and in terms of the composition located in direct vicinity of the morphotropic phase boundary and which can expectedly have high piezoelectric characteristics.

Growing of the NBT–5%BT single crystals is described in detail in the paper [4]. The initial Ba concentration was determined by means of the atomic emission spectrometry. The dielectric measurements were performed at the frequency of 1 kHz. The electric field was applied along the direction [001]. The He–Ne-laser ($\lambda = 0.63 \mu\text{m}$, a continuous mode) was used for the optic measurements.

Before each measurement, the samples were heated in a zero field to a temperature exceeding the temperature of T_{max} by ~ 50 K and held at this temperature for ~ 30 min in order to suppress the memory effects correlated to the application of the electric field. In order to measure the time dependences of permittivity, the annealed samples were cooled in a zero field to a room temperature below the MPB temperature at which a constant electric field was applied thereto. Following the application of the electric field, the process of variation of the permittivity was timed. These measurements were carried out directly after annealing of the sample.

3. Experimental results and discussion

The Fig. 1 shows the temperature dependences of the permittivity ϵ (the curves 1, 2) and dielectric loss angle $\tan \delta$ (the curve 1') for the NBT–5%BT non-polarized crystals oriented along the axis [001] as measured in the mode of heating (ZFH) (the curves 1 and 1') and cooling (ZFC) (the curve 2). Except for the main maximum at the temperature of $\sim 555-558$ K (the Curie temperature T_c), which corresponds to the transition from the tetragonal ferroelectric phase to the tetragonal paraelectric phase, there is an evident small inflection in the ZFH mode at the temperature $\sim 433-443$ K, which is especially noticeable during cooling (ZFC) at the temperature ~ 423 K (the

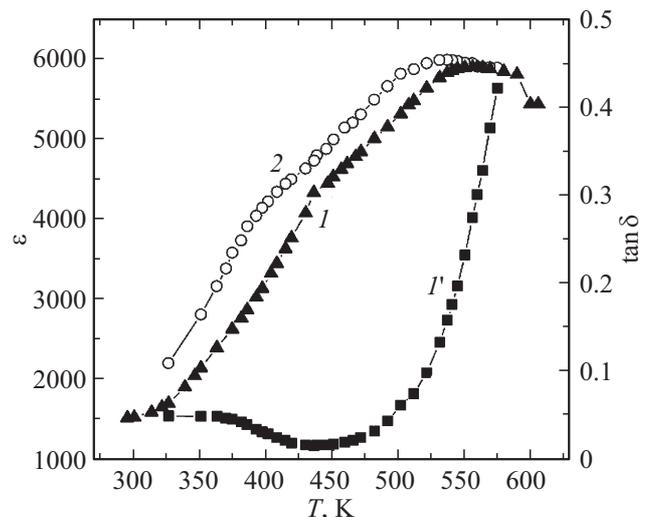


Figure 1. Temperature dependences ϵ (the curves 1, 2) and $\tan \delta$ (the curve 1') for the non-polarized NBT–5%BT crystals oriented along the axis [001], as obtained during heating (the curves 1, 1') and cooling (the curve 2).

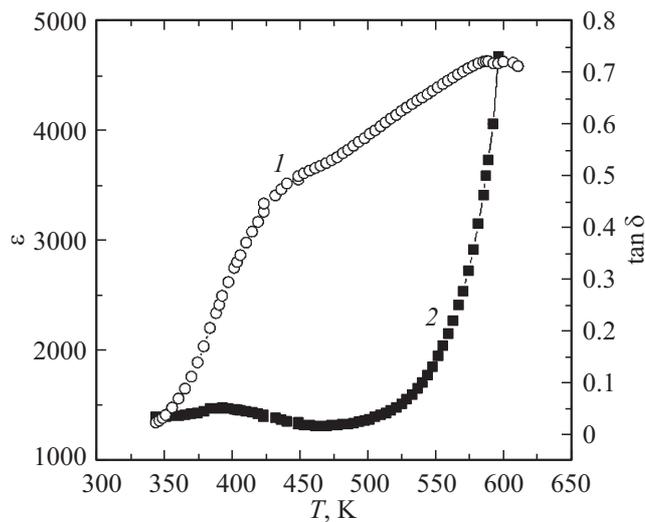


Figure 2. Temperature dependences ε (the curve 1) and $\tan \delta$ (the curve 2) for the crystal oriented along the axis [001] and pre-polarized in the field of 12 kV/cm, as obtained during heating.

curve 2). This temperature corresponds to the phase transition from the ferroelectric phase to the relaxor phase (T_{RF}). It should be clarified here that in further discussion of the experimental data we will stick to conclusions of the papers [13,6,14,15], in which this transition is regarded as the relaxor–ferroelectric transition, but not a ferroelectric–antiferroelectric one [11,12]. As it is clear from the figure, the thermal hysteresis is observed in a wide range of the temperatures up to the temperature T_c , but it is the most substantial — within the phase transition T_{RF} . The presence of the dielectric hysteresis is attributable to coexistence of the tetragonal and rhombohedral phases in a wide range of the temperatures, where relative volume fractions of the two phases substantially depend on the temperature.

The Fig. 2 shows the temperature dependences ε (the curve 1) and $\tan \delta$ (the curve 2) for the crystal oriented along the axis [001] and pre-polarized in the field of 12 kV/cm, as measured during heating. Besides the ε main maximum, the ε curve shows other two anomalies: the depolarization temperature ($T_d \approx 395$ K), at which there is evidently the biggest change of the inclination on the ε curve, and $\tan \delta$ has a slight maximum. In addition to this anomaly, the ε curve also has a slight inflection at the temperature T_{RF} , which is approximately equal to 438–443 K. It should be noted here that the depolarization temperature T_d is below the temperature T_{RF} approximately by 40 K. This agrees with the literature data obtained for other compounds containing NBT [25–27]. The different temperatures of depolarization T_d and ferroelectric–relaxor transition T_{RF} in the relaxor ferroelectrics based on NBT make them different from the lead-containing relaxors, in which these temperatures are the same. It means that the depolarization process in the NBT-containing solid solutions is of another origin. It can be assumed that

when being heated at the temperature T_d ferroelectric macrodomains occurring during polarization of the sample in the electric field lose their ferroelectric nature and decompose to nanodomains. There is a relaxor state within the temperatures between T_d and T_{RF} . It may be correlated to that fact that the ferroelectric polar state formed during sample polarization is a metastable one with large elastic energy. With increase in the temperature, a value of the potential barrier decreases and the system tries to minimize the elastic energy by reverse switching into a random state. It can explain the fact that the depolarization temperature T_d is always lower than T_{RF} . The authors propose another explanation in the paper [28]. They correlate a difference in the temperatures to the fact that heating above T_d destroys the macroscopic polarization only. The domains start to vibrate due to thermal activation, but the interrelation of the local dipoles inside the domains is not lost. The domains decompose into PNR only when the material is heated to the temperature T_{RF} and above.

It is still debatable whether an intermediate monoclinic phase exists in the electric field, which assumes continuous rotation between pseudo-cubic directions [111] (the rhombohedral phase) and [100] (the tetragonal phase) similar to the lead-containing solid solutions. The complexity of determination of the monoclinic phase is correlated to big disorder in the A sublattice due to coexistence of ions of a various charge (Na^+ , Bi^{3+} and Ba^{2+}) [29].

The optic measurements are more sensitive in comparison with the dielectric ones. They help to obtain additional data on physical properties of a substance, especially when studying changes of heterogeneity sizes in the phase transitions. The Fig. 3 shows temperature dependences of optical transmission for a nonpolarized sample, which are obtained in the mode of heating (the curve 1) and cooling (2)

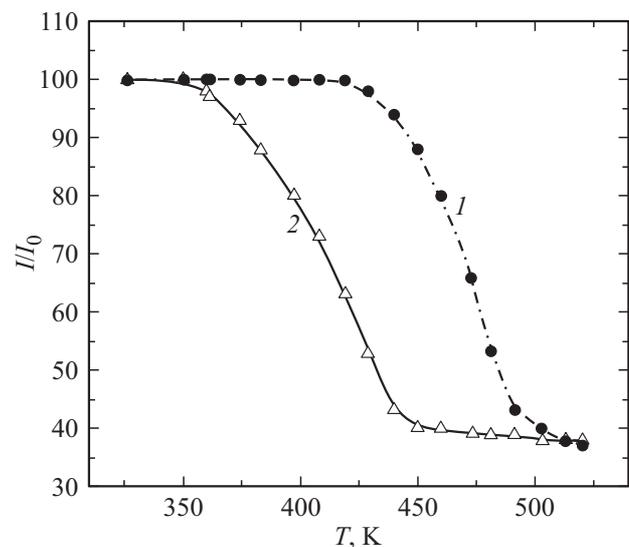


Figure 3. Temperature dependences of optical transmission for a nonpolarized sample in the mode of heating (1) and cooling (2), (I_0 — a value in the zero field).

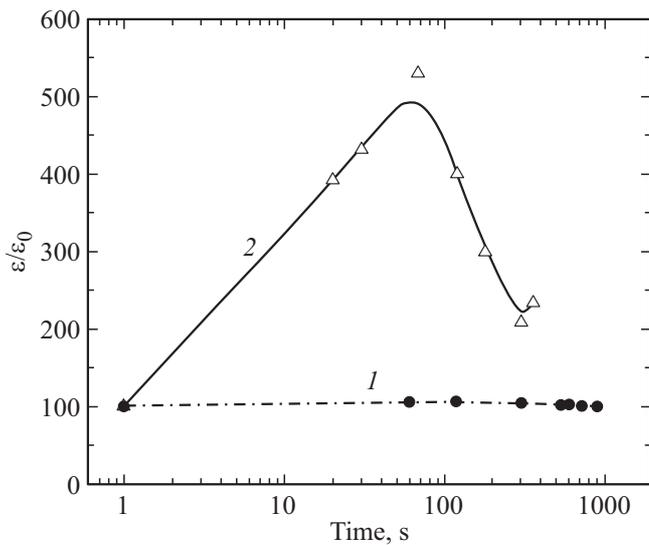


Figure 4. Time dependences of the magnitude $\varepsilon/\varepsilon_0$ at the room temperature for the NBT–5%BT crystals in the electric field 10 kV/cm (the curve 1) and 13.8 (kV/cm) (the curve 2), where ε — permittivity in the presence of the field at various moments of time, ε_0 — permittivity in the zero field.

(the curve 2). It is clear from the figure that when the sample is heated, the optical transmission sharply reduces near T_{RF} , thereby meaning enlarged dimensions of the polar regions. It agrees with results of the paper [26], in which it was found that a volume fraction with the nanodomains increases at the temperature was approaching T_{RF} . The hysteresis observed means that this transition is a transition of the first order. However, in the paper [29] the authors cast doubt on whether this transition is the transition of the first order and suppose that it shares similarities of the phase transition of the second order.

In order to study a process of induction of the ferroelectric phase in our crystals, in which the relaxor properties are correlated to disorder in the A position of the ABO_3 oxygen octahedron, the time dependences of permittivity were measured in different electric fields. The measurement results are given in the Fig. 4 (the curves 1, 2), where ε_0 — permittivity prior to application of the field, ε — permittivity in the presence of the field in different moments of time. It is clear that in the fields significantly lower than the coercive field (the curve 1), almost no change of the magnitude $\varepsilon/\varepsilon_0$ is found. In the fields close to the coercive field, just after switching on the field, first there is sharp increase in the magnitude $\varepsilon/\varepsilon_0$, with its subsequent decrease (the curve 2).

As it is clear from the figure, the time dependences $\varepsilon/\varepsilon_0$ have a number of features. The first feature of the observed dependences of the Fig. 4 is increase in the magnitude $\varepsilon/\varepsilon_0$ and appearance of the maximum after some time since switching on the field, if the field exceeds the coercive field E_c . The formation of this maximum and the observed increase of $\varepsilon/\varepsilon_0$ may be correlated to activation of switching processes of the tetragonal domains observed

when $E > E_c$, and to increase in mobility of domain walls during the sample polarization. The ongoing polarization may include formation of macroscopic tetragonal domains. After the maximum there is an evident sharp decrease in the magnitude $\varepsilon/\varepsilon_0$, thereby meaning a beginning transition into the ferroelectric phase (supposedly, the tetragonal one) with the macroscopic domain structure. Unfortunately, it was not possible to observe the full transition into the tetragonal phase, as significant dielectric losses in the sample did not allow applying big electric fields.

The second feature is the fact the magnitude $\varepsilon/\varepsilon_0$ changes just after switching on the field without a delay time. No incubation period was observed earlier in the $\text{PbZn}_{1/3}\text{Nb}_{2/3}\text{O}_3-9\% \text{PbTiO}_3$ (PZN–9%PT) crystal solid solutions [30]. It may be correlated to a continuing increase in the PNR sizes and domains below the MPB temperature, too; unlike PMN crystals and solid solutions based thereon, in which the PNR do not change. Indeed, the paper [27] found that at the room temperature, which is below the MPB temperature, in the crystals under study sizes of the ferroelectric domains were ~ 100 nm, which is significantly bigger than in the PMN (20–30 nm) crystals, in which the induced phase transition occurs after some delay time. It can be assumed that no incubation period is correlated to a various degree of diffuseness of the phase transition in a dominant component of the solid solution. The PMN crystals have a ferroelectric state only in the presence of the electric field, as PZN has an evident diffuse phase transition into the ferroelectric state even without the electric field. In the crystals under study, in a dominant NBT component, without the electric field there is a fuzzy phase transition into the ferroelectric state [31]. It means that the diffuseness degree of the phase transition is less than for the PMN-containing crystals and, therefore, the PNR concentration is less. This leads to increase in the distance between the PNR, thereby enabling increase in the PNR sizes even below the MPB temperature. There is no such possibility in the PMN-containing crystals, as a number of the polar regions is high due to large diffuseness of the phase transition. With decrease in the PMN temperature, the PNR sizes increase, the distance therebetween is decreasing up to the MPB temperature, below which the PNR sizes remain almost the same and only a direction of their dipole moments is changing. It is only after a certain time passes from the moment of application of the electric field that PNRs start to grow and a ferroelectric transition to the phase with long-range order is induced. The presence of the incubation period during induction of the ferroelectric transition with a long-range order in the electric field is one of direct proofs in favor of nonergodicity of the relaxor (glass) phase. As it follows from the Fig. 4, no time delay in the induced phase transition allows assuming that in the NBT–5%BT solid solutions the phase below the MPB temperature is not a nonergodic glass phase.

4. Conclusion

The present paper has studied influence of the electric field on the phase transitions in the lead-free ferroelectric NBT–5%BT crystals near MPB. It is discovered that the wide range of temperatures has dielectric and optic hysteresis correlated to the coexistence of the phases.

Just after switching on the field exceeding the coercive field, the time dependences of the permittivity first exhibit a sharp increase in the magnitude $\varepsilon/\varepsilon_0$. After a certain time, there is an evident maximum, with decrease in $\varepsilon/\varepsilon_0$ thereafter. Most likely, the observed maximum is correlated to activation of the switching processes of the tetragonal domains and increased mobility of the domain walls. After the activation of the switching processes, it is found that the magnitude $\varepsilon/\varepsilon_0$ is sharply decreasing, thereby meaning the induced transition into the tetragonal ferroelectric phase with the macroscopic domain structure. The ferroelectric phase is induced without time delay.

It is hypothesized that no time delay is correlated to a lesser diffuse degree of the phase transition in the NBT–5%BT crystals in comparison with the PMN relaxor and a continuing PNR increase in the phase below the MPB temperature without changing the direction of their dipole moments.

It can be concluded from the data obtained that the phase below the MPB temperature is nonergodic in the NBT–5%BT relaxors, in which there is a fuzzy phase transition into the ferroelectric phase even without the electric field. It is also confirmed by the results obtained earlier for the PZN– x %PT solid solutions.

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Conflict of interest

The author declares that he has no conflict of interest.

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