

# Induced phase transition in monocrystalline solids solutions $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3-29\text{PbTiO}_3$ and $\text{PbZn}_{1/3}\text{Nb}_{2/3}\text{O}_3-9\text{PbTiO}_3$ : similarity and difference

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The kinetics of the induced phase transition in single-crystal relaxor solid solutions  $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3-29\text{PbTiO}_3$  and  $\text{PbZn}_{1/3}\text{Nb}_{2/3}\text{O}_3-9\text{PbTiO}_3$  is studied when an electric field is applied along the [001] direction. At temperatures below the temperature of the morphotropic phase transition, the changes in the dielectric constant and optical transmission in electric fields are studied. It is shown that the decrease in optical transmission with time is associated only with a change in the sizes of nanoregions during the phase transition. It was found that the induced phase transition proceeds differently in these crystals. In PMN-29PT crystals, the formation of ferroelectric phases and the rapid establishment of macroscopic polarization are preceded by a certain delay time, while in PZN-9PT crystals, the ferroelectric phase is induced immediately after the application of the field without a delay time. The results obtained are explained by the different structures of the low-temperature phases in these compounds.

**Keywords:** ferroelectricity, relaxors, induced phase transition.

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## 1. Introduction

All relaxor solid solutions, of which the studied crystals are an example, have one common feature: a random distribution of ions in equivalent positions of the crystal lattice. Randomly oriented local electric and elastic fields give rise to polar nanoregions (PNRs) with chaotically distributed orientations of dipole moments. At high temperatures (several hundred degrees higher than the temperature corresponding to the maximum permittivity), relaxors are in the nonpolar paraelectric cubic phase, which is similar in many respects to the paraelectric phase of normal ferroelectrics. As the temperature decreases, relaxors undergo a transition to the ergodic relaxor state wherein PNRs (2–10 nm), which give rise to the peculiar features of relaxors, emerge at Burns temperature  $T_B \sim 620-650$  K. PNRs have manifested themselves in a number of physical phenomena: deviation of the temperature dependences of the refraction index and the sound velocity from the normal linear dependence [1–3], acoustic emission [4], etc.

Several other characteristic temperatures are found in relaxors below  $T_B$ . These are frequency-dependent temperature  $T_m$  of the permittivity maximum and temperature  $T$  of the ferroelectric phase transition or (if the ferroelectric phase transition is not observed) freezing temperature  $T_f$  (Vogel–Fulcher temperature).

Although they have a number of common features, different relaxors also exhibit significant differences related to the emergence of the ferroelectric phase [5,6]. For example, the structure of classical relaxor  $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$

(PMN) remains cubic with nanometric inclusions of polar regions down to low temperatures. The ferroelectric phase may emerge in PMN either in an electric field or when the  $(\text{Mg}_{1/3}\text{Nb}_{2/3})$  complex is substituted partially with  $\text{Ti}^{4+}$  ions. At the same time, disordered  $\text{PbSc}_{1/2}\text{Nb}_{1/2}\text{O}_3$  (PSN) may undergo a spontaneous phase transition to the ferroelectric phase even in zero electric field.

Lead zinc niobate  $\text{PbZn}_{1/3}\text{Nb}_{2/3}\text{O}_3$  (PZN) falls in between these two relaxors: a diffuse phase transition to the ferroelectric phase was found in it [6]. These differences in behavior observed in transition to the ferroelectric phase in three classes of compositionally disordered perovskites may be related to the differences in kinetics of PNR development.

It is known fairly well how the ferroelectric phase transition is induced in PMN,  $\text{PMN}-x\text{PbTiO}_3$  ( $\text{PMN}-x\text{PT}$ ) solid solutions [7–12], and several other relaxors [12–14]. In the process of cooling from the ergodic paraelectric phase, PNRs grow in size down to temperature  $T_f$ . At temperatures lower than  $T_f$ , the size of PNRs remains almost constant (10–30 nm for PMN), and only the orientation of their dipole moments changes. A nonergodic glass phase with frozen local polarization emerges, and the ferroelectric phase transition in PMN is induced only in an electric field.

The properties of a crystal in this nonequilibrium state should be time-dependent. As was detailed in [7–14], the logarithmically wide spectrum of relaxation times and the presence of an incubation period before a ferroelectric transition with long-range order is induced in an electric field provide direct evidence in favor of nonergodicity of the relaxor (glass) phase.

It is also possible that the ferroelectric phase with long-range order may be induced in a manner unlike that of PMN and solid solutions based on it. This alternative scenario may manifest itself, e.g., in PZN compounds, where a diffuse phase transition to the ferroelectric phase was observed in zero field.

The kinetics of PNR development in PZN occurring while the ferroelectric phase is induced remains understudied. It was suggested in [5,6] that the ferroelectric phase in PZN is more likely to be induced by the PNR size increase than by the interaction between polar nanoregions, since this interaction initiates the emergence of the glass-like nonergodic relaxor state and gives rise to a certain time delay in inducing the phase transition.

It is entirely unknown how the ferroelectric phase is induced in relaxor ferroelectric single-crystal  $\text{PbZn}_{1/3}\text{Nb}_{2/3}\text{O}_{3-y}\text{PbTiO}_3$  (PZN- $y$ PT) ( $y = 7.9\%$ ) solid solutions, which are at the morphotropic phase boundary (MPB). These materials are of both theoretical and practical interest. They are regarded as advanced materials for future high-performance converters, sensors, and actuators. They feature excellent piezoelectric and electromechanical characteristics (e.g., PZN-9PT has  $d_{33} \sim 2500\text{--}3000$  pC/N,  $k_{33} > 92\%$ ). PZN-PT single crystals offer several advantages over the more readily available PMN-PT materials: (a) easily attainable uniformity of composition in the process of crystal growth; (b) superior piezoelectric properties (25–40% better); (c) strong coercive fields; (d) the elastic flexibility is 50–100% higher; (e) the temperature of the morphotropic phase transition (MPT) is 10–20°C higher [15,16].

In view of this, it appears to be of some interest to examine the kinetics of nucleation of ordered ferroelectric phases in the glass-like relaxor state, determine how the ferroelectric phase is induced in PZN-9PT compounds, and compare the findings with the available data on the corresponding processes in PMN-29PT crystals. Time dependences of the permittivity and the optical transmission in an electric field in these single crystals will be studied.

## 2. Samples and experimental procedure

PMN-29PT and PZN-9PT single crystals located in the vicinity of MPB were chosen as the objects to be studied. These crystals were grown directly from solution in melt using the modified Bridgman method [17].

Conflicting data on the structure of PZN-9PT compounds in zero electric field are found in literature. Having examined nonpolarized PZN-9PT compounds, the authors of [18] concluded that only rhombohedral ( $R$ ) and tetragonal ( $T$ ) phases coexist in them at room temperature, which is lower than the MPT temperature. It was reported in [19], however, that the orthorhombic phase ( $O$ ) is also present. The latest X-ray and synchrotron studies [20] suggest that only orthorhombic and tetragonal phases are present at room temperature. Note that the orthorhombic phase is

very close in energies to the monoclinic phase ( $Mc$ ) and is thus difficult to distinguish from it (the  $O$  phase is the limiting case of  $Mc$  [21]). The following sequence of phases is observed as the temperature increases: ( $O + T$ )- $T$ -cubic ( $C$ ).

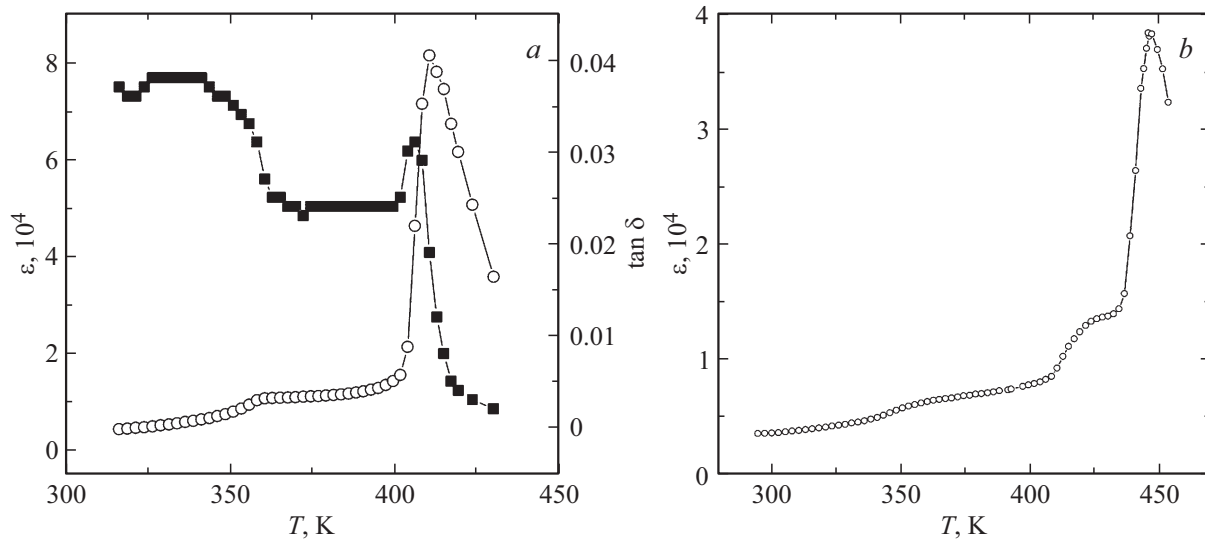
At room temperature, PMN-29PT crystals are in a cubic disordered matrix with PNRs introduced into it. The majority of these PNRs have local rhombohedral symmetry, and their spontaneous polarization vector is oriented along one of the [111] directions. Therefore, the local symmetry of the sample is rhombohedral [22]. Individual PNRs of monoclinic, orthorhombic, and tetragonal phases are also present [23]. The following sequence of phase transitions is observed in nonpolarized samples as the temperature increases: rhombohedral ( $R$ )-tetragonal ( $T$ )-cubic phase ( $C$ ) [24]. An intermediate monoclinic phase ( $Ma$ ) emerges in an electric field, and the following phase sequence is observed:  $R$ - $Ma$ - $T$ - $C$ .

The electric field was applied along the [001] direction. The optical transmission was measured in the direction perpendicular to that of the field. A He-Ne laser ( $\lambda = 0.63 \mu\text{m}$ , continuous mode) and a semiconductor laser ( $\lambda = 1.3 \mu\text{m}$ , pulsed mode) were used in these optical measurements. The dielectric measurements were performed at a frequency of 1 kHz.

Before each measurement, the samples were heated in zero field to a temperature  $\sim 100$  K higher than  $T_{\text{max}}$  and held at this temperature for 30 min in order to suppress the memory effects associated with the application of the electric field. In order to measure the time dependences of permittivity  $\epsilon$  and the optical transmission, annealed samples were cooled in zero field to a temperature below the MPT temperature at which a constant electric field was applied. Following the application of the electric field, the process of variation of the permittivity and the optical transmission was timed. These measurements were carried out directly after annealing.

## 3. Experimental results and discussion

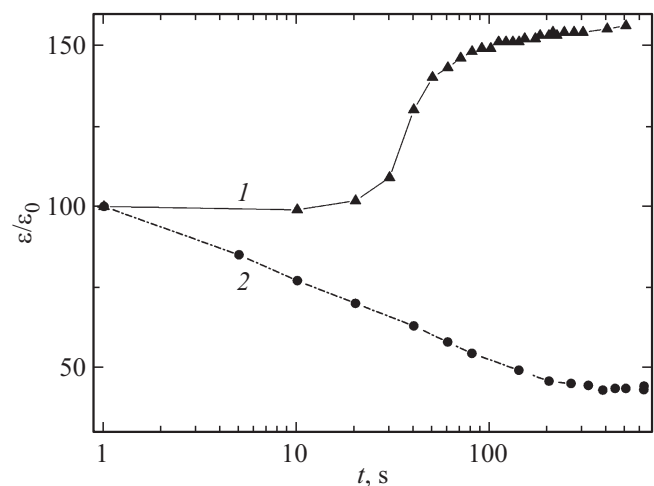
The temperature dependences of  $\epsilon$  and  $\tan \delta$  for [001]-oriented nonpolarized PMN-29PT and PZN-9PT crystals measured in the ZFH mode are presented in Fig. 1, *a* and Fig. 1, *b*, respectively. It can be seen that the primary maximum in both crystals, which corresponds to the transition to the cubic ( $C$ ) phase, is accompanied by a minor anomaly associated with the MPT to the tetragonal phase. In PMN-29PT, the initial phase for this MPT is rhombohedral ( $T \sim 360\text{--}370$  K); in PZN-9PT, the initial phase is the mixed ( $O + T$ ) one ( $T \sim 355\text{--}375$  K). The PZN-9PT crystal (Fig. 1, *b*) also features a third anomaly at a temperature of  $\sim 410\text{--}440$  K. A similar temperature dependence of the permittivity of PZN-9PT crystal was observed in [20]. The origin of the third anomaly is still debatable. There is no indication that a structural phase transition occurs at this temperature, while X-ray and



**Figure 1.** Temperature dependences of  $\varepsilon$  and  $\tan \delta$  for [001]-oriented nonpolarized PMN-29PT (a) and PZN-9PT (b) crystals measured in the ZFH mode.

synchrotron studies reveal only the existence of a sequence of phase transitions  $(O + T) \rightarrow T \rightarrow C$ . It was suggested in [20] that this unique phase transition in PZN-9PT may be related closely to the evolution of hierarchical nanosized ferroelastic domains that is observed when the temperature increases and gives rise to the third anomaly. The evidence in favor of this assumption were also presented in [20]. Having analyzed the Laue diffraction patterns, the authors concluded that the coexistence of the  $O$  and  $T$  phases gradually transforms into the  $T$  phase. Meanwhile, ferroelastic domains of the  $O$  and  $T$  phases transform into the ferroelastic domain of the  $T$  phase. The evolution of ferroelectric and ferroelastic domains is what gives rise to the anomalous dielectric phase. Additional detailed studies are needed to gain a deeper understanding of temperature-dependent phase evolutions.

Fig. 2 presents the time dependences of the permittivity for PMN-29PT (curve 1) and PZN-9PT (curve 2) crystals measured in an electric field at room temperature. It is evident that  $\varepsilon$  varies significantly with time in both crystals, thus providing evidence of an induced phase transition. However, the manner in which this transition is induced differs between these two crystals. In PMN-29PT crystals, the induced phase transition occurs with a time delay, while the transition in PZN-9PT starts right after the field is applied. This behavior of  $\varepsilon$  in PMN-29PT crystals agrees with the data obtained for PMN- $x$ PT solid solutions with different  $x$  values and a number of other relaxors [7–14]. The properties of a crystal in this nonequilibrium state should be time-dependent. The presence of an incubation period preceding an induced ferroelectric transition with long-range order in an electric field is direct proof of nonergodicity of the relaxor (glass) phase, which exists below the MPT temperature, and suggests that only the orientation of dipole moments of PNRs changes below the

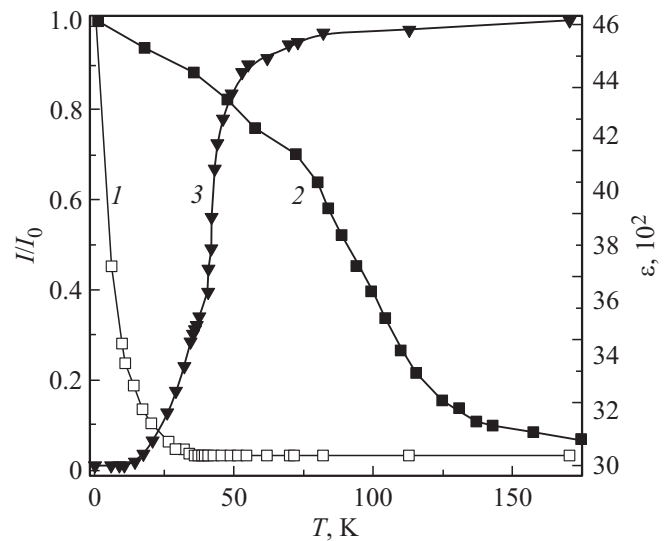


**Figure 2.** Time dependences of the permittivity measured at room temperature for PMN-29PT (curve 1) in an electric field of 1.23 kV/cm and PZN-9PT (curve 2) in an electric field of 3.3 kV/cm ( $\varepsilon_0$  is the permittivity in zero field).

MPT temperature right after the application of the field, while their sizes remain almost the same. 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. It can be seen that  $\varepsilon$  in the PMN-29PT crystal (curve 1) grows with time if the field is applied along the [001] direction. The probable explanation for this is as follows: when the field is applied in this direction, the polarization plane of rhombohedral regions rotates from the [111] direction to [001] via an intermediate monoclinic phase that is characterized by a significantly higher  $\varepsilon$  value than the rhombohedral multidomain phase existing in zero field.

A different pattern is seen in PZN-9PT (curve 2). The induced phase transition from the mixed ( $O + T$ ) phase to the  $T$  phase occurs right after the field is applied. The observed  $\epsilon$  reduction is associated with the reduction in the number of relaxing elements (specifically, domain boundaries and interphase boundaries) that contribute to the permittivity. The lack of a delay seen in PMN-29PT (curve 1) suggests that PNRs and domains in PZN-9PT crystals continue to grow in size below the MPT temperature. PNRs formed at high temperatures in PZN-9PT are larger in size, while their density is lower, since the phase transition in PZN compounds is less diffuse than the one in PMN-containing crystals. The distance between PNRs is greater, and some of them may grow to mesoscopic sizes with decreasing temperature. This growth continues below the MPT temperature due to the increase in ferroelectric distortion and the transformation of regions with a reduced local Curie temperature to the ferroelectric phase. This process was discovered in diffraction experiments [5]. The obtained data suggest that the phase below the MPT temperature in PZN-9PT solid solutions is not a nonergodic glass one.

The dependence of transmission  $I$  on the wavelength is associated with the change in the size of nanoregions in the process of phase transition; i.e., the optical transmission is a size effect that depends on the wavelength of incident light, and its variation is associated only with the change in the size of inhomogeneities and the enhancement of scattering. When the size of inhomogeneities exceeds the wavelength of incident light, the value of  $I$  decreases. Temporal variations of the optical transmission are not necessarily coincident with the time dependences of acoustic and dielectric properties. This is illustrated by Fig. 3,  $I$ – $3$  presents the time dependences of the optical transmission at two wavelengths ( $I$ ,  $2$ ) and the permittivity ( $3$ ) at room temperature in PMN-29PT crystals in an electric field applied along [001]. It can be seen that the transmission decreases with time at both wavelengths. It is also evident that the optical transmission is at its maximum before the measurements (in zero field). This implies that all inhomogeneities in zero field are smaller in size than both wavelengths ( $0.63 \mu\text{m}$  and  $1.3 \mu\text{m}$ ). When the electric field is applied, the optical transmission decreases very slowly in the infrared region at a wavelength of  $1.3 \mu\text{m}$  (curve 2), but drops rapidly in the visible range at  $0.63 \mu\text{m}$  (curve 1). The difference in time needed for regions of different sizes to undergo a phase transition is probably indicative of the fact that the sample is not polarized completely in the process of phase transition: the polarization of regions  $1.3 \mu\text{m}$  in size (and larger ones) requires more time and stronger electric fields. In addition, the times of the maximum change of dielectric (curve 3) and optical (curves  $I$ ,  $2$ ) properties do not match. The sharp reduction in the optical transmission in the visible range is shifted to earlier time relative to the permittivity anomaly, while the transmission reduction in the infrared region is stretched over a wider time interval and is observed even after the  $\epsilon$  anomalies. It is the

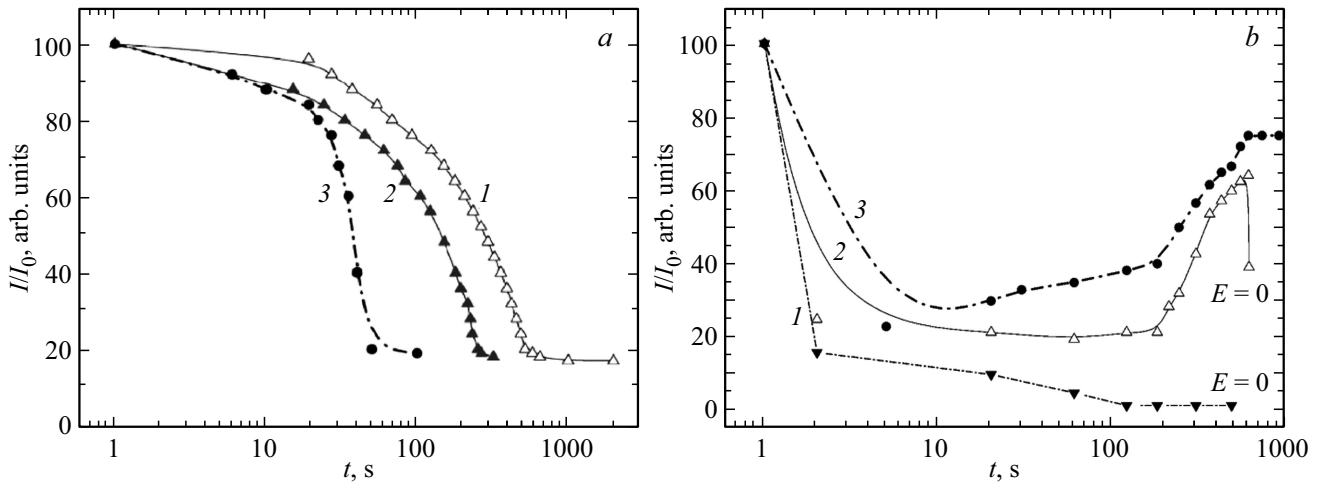


**Figure 3.** Time dependences of optical transmission  $I/I_0$  ( $I$ ,  $2$ ) at different wavelengths and the permittivity ( $3$ ) of the PMN-29PT crystal in electric field  $E = 1.23 \text{ kV/cm}$  applied along [001],  $\lambda$ ,  $\mu\text{m}$ :  $I$  —  $0.63$ ,  $2$  —  $1.3$  ( $\epsilon_0$  and  $I_0$  are the values in zero field).

dielectric properties (as well as the acoustic ones) of a crystal that are highly sensitive to changes in the sample structure. Therefore, when the monoclinic phase is induced, the electric fields applied in the [001] direction in our experiments trigger only partial polarization of the sample, and long-range order is established only in a certain fraction of the crystal volume. We have also observed the emergence of long-range order in a fraction of the sample volume in experiments on inducing the monoclinic phase in several other crystals [11,12].

In [12], we have carried out simultaneous comprehensive measurements of the acoustic, dielectric, and optical properties of the PMN-29PT crystal and their variations in the process of inducing a phase transition by an electric field applied in the [110] and [111] directions. It was found that, in contrast to the monoclinic phase induced in a field applied along [001], the phases (rhombohedral and rhombohedral, respectively) induced even in weak fields applied in these directions are single-domain. This was evidenced by the fact that the maximum changes of all the three studied characteristics were observed within the same time interval; in addition, the time dependences of the optical transmission at different wavelengths were matching. The emergence of the single-domain phase was evidenced by the measured increase in the optical transmission after the phase transition.

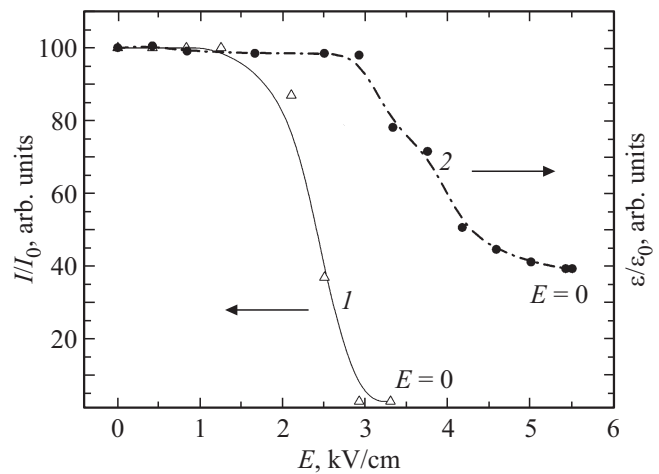
Although the optical transmission data do not render a true temporal pattern of the phase transition, such measurements are more sensitive than, e.g., dielectric measurements and provide additional information both on the initiation of the phase transition in a crystal and on the type of polarization (complete or partial) of the sample. This is illustrated by Fig. 4. Fig. 4 presents



**Figure 4.** Variation of optical transmission  $I/I_0$  ( $I_0$  is the value in zero field) with time at different temperatures (K) in PMN-29PT (a) and PZN-9PT (b) crystals in an electric field (kV/cm), a:  $E = 0.75$ ; 1 — 321, 2 — 333, 3 — 350; b:  $E = 3.3$ ; 1 — 297, 2 — 311, 3 — 320.

the time dependences of the optical transmission in an electric field in PMN-29PT (a) and PZN-9PT (b) crystals measured at different temperatures. It can be seen that the transmission decreases with time in both crystals. Even a very weak (just 0.75 kV/cm) field is sufficient to induce the ferroelectric transition to the monoclinic single-domain phase in PMN-29PT crystal at room temperature. However, this field is not sufficient to induce the single-domain state if the measurement temperature becomes close even to the MPT temperature (Fig. 4, a, curve 3). The coercive fields in PZN-9PT are stronger than the ones in PMN-29PT, and stronger fields are needed to induce a phase transition in these crystals. It can be seen from Fig. 4, b that the phase transition from the mixed ( $O + T$ ) phase to the tetragonal phase occurred in a field of 3.3 kV/cm at room temperature (curve 1). This phase is multi-domain. When the measurement temperature becomes closer to the MPT temperature, the optical transmission starts increasing after a certain short time interval (curves 2, 3). Since no phases other than tetragonal were found in these crystals in experiments with an applied electric field [21], the observed transmission increase proves that the sample gradually becomes single-domain. The emerging single-domain state of the tetragonal phase is not stable, and the sample reverts partially to the multidomain state when the field is switched off (curve 2).

Fig. 5 presents the dependences of the variation of the optical transmission ( $I/I_0$ ) (curve 1) and the permittivity (curve 2) on the electric-field intensity measured at room temperature in the PZN-9PT crystal. It can be seen that both quantities decrease with increasing electric-field intensity. The reduction in transmission is attributable to the growth of electrically induced polar regions or domains. The emergence of a partially ordered ferroelectric structure or large domains in an electric field may result in the formation of large domain boundaries, which scatter incident light.



**Figure 5.** Dependences of the variation of the optical transmission ( $I/I_0$ ) (curve 1) and the permittivity (curve 2) on the electric-field intensity measured at room temperature in the PZN-9PT crystal.

It should be noted here that compared to the variation of  $\epsilon$ , the reduction in transmission is initiated in weaker fields. These results agree with the time dependences of the optical transmission for the PMN-29PT crystal in Fig. 3 and confirm once again that the optical transmission is a size effect and is associated with changes in the size of those inhomogeneities that become larger than the wavelength of incident light. The partially ordered tetragonal single-domain phase emerging in the electric field remains stable even after the field is switched off.

#### 4. Conclusion

Temporal variations of the permittivity and the optical transmission in two classes of relaxor solid solutions

(PMN-29PT and PZN-9PT) located at the morphotropic phase boundary were studied in different electric fields.

It was demonstrated that although polar nanoregions (PNRs) are present in the high-temperature phase in both relaxors, they exhibit both common and discrepant features in the way the ferroelectric phase transition is induced.

The permittivity and the optical transmission decrease sharply with time in both crystals at temperatures below the MPT temperature in electric fields stronger than a certain threshold field. These temporal variations are indicative of an induced phase transition and suggest that the volume fraction of the ferroelectric phase increases. The polarized phase emerging in an electric field remains stable in both crystals even after the field is switched off.

It was found that the low-temperature phases in these compounds have different structures. This translates into significant differences in the process of inducing the ferroelectric phase. It was demonstrated that a certain time delay, which is one of the distinctive features of a nonergodic glass phase, precedes the formation of ferroelectric phases and the rapid establishment of macroscopic polarization in PMN-29PT crystals in an electric field applied at temperatures below the MPT temperature. The glass phase emerges due to the fact that the size of PNRs remains unchanged below the MPT temperature; the only thing that changes is the orientation of their dipole moments.

A different pattern is observed in PZN-9PT compounds: the ferroelectric phase is induced directly after the application of an electric field without any delay. This suggests that the nonergodic glass phase does not emerge below the MPT temperature. This may be attributed to the growth of PNRs (with no changes in the orientation of their dipole moments) that continues at temperatures below the MPT temperature.

The experiments on inducing the multidomain phase in the PMN-29PT crystal revealed a temporal mismatch between the anomalies of dielectric and optical (measured at two wavelengths: 1.3 and 0.63  $\mu\text{m}$ ) properties. It was therefore concluded that the wavelength dependence of the optical transmission is associated only with the change in the sizes of nanoregions in the process of phase transition.

## Conflict of interest

The author declares that she has no conflict of interest.

## References

- [1] I.W. Chen. *J. Phys. Chem. Solids* **61**, 197 (2000).
- [2] G. Burns, F.H. Dacol. *Solid State Commun.* **48**, 853 (1983).
- [3] H. Arndt, F. Schmidt. *Ferroelectrics* **79**, 149 (1988).
- [4] M. Roth, E. Mojaev, E. Dul'kin, P. Gemeiner, B. Dkhil. *Phys. Rev. Lett.* **98**, 265701 (2007).
- [5] Y-H. Bing, A.A. Bokov, Z.-G. Ye, B. Noheda, G. Shirane. *J. Phys.: Condens. Matter* **17**, 2493 (2005).
- [6] Y-H. Bing, A.A. Bokov, Z.-G. Ye. *Current Appl. Phys.* **11**, 14 (2011).
- [7] E.V. Colla, E.Y. Koroleva, N.M. Okuneva, S.B. Vakhrushev. *Phys. Rev. Lett.* **74**, 1681 (1995).
- [8] E.V. Colla, M.B. Weissman. *Phys. Rev. B* **72**, 104 106 (2005).
- [9] E.V. Colla, D. Vigil, J. Timmerwilke, M.B. Weissman. *Phys. Rev. B* **75**, 214 201 (2007).
- [10] E.V. Colla, N. Jurik, Y. Liu, M.E.X. Delgado, M.B. Weissman, D.D. Vieland, Z.-G. Ye. *J. Appl. Phys.* **113**, 184104 (2013).
- [11] L.S. Kamzina, L.A. Kulakova, *Phys. Solid State* **59**, 10, 1945 (2017).
- [12] L.S. Kamzina, L.A. Kulakova, *Phys. Solid State* **60**, 5, 955 (2018).
- [13] L.S. Kamzina, L.A. Kulakova. *Phys. Solid State* **58**, 1, 177 (2016).
- [14] L.S. Kamzina, L.A. Kulakova. *Phys. Solid State* **57**, 11, 2165 (2015).
- [15] S.J. Zhang, F. Li, X. Jiang, J. Kim, J. Luo, X. Geng. *Prog. Mater. Sci.* **68**, 1 (2015).
- [16] E.W. Sun, W.W. Cao. *Prog. Mater. Sci.* **65**, 124 (2014).
- [17] J. Xu, S. Fan, B. Lu, J. Tong, A. Zhang. *Jpn. J. Appl. Phys.* **41**, 7000 (2002).
- [18] I. Bhaumik, G. Singh, S. Ganesamoorthy, A.K. Karnal, V.S. Timari, V.K. Wadhawan. *Ferroelectrics* **326**, 73 (2005).
- [19] D.E. Cox, B. Noheda, G. Shirane, Y. Uesu, K. Fujishiro, Y. Yamada. *Appl. Phys. Lett.* **79**, 400 (2001).
- [20] T. Li, Z. Dud, N. Tamura, Mao Ye, S. Inguva, Wei Lu, X. Zeng, S. Ke. *J. Eur. Ceram. Society* **38**, 1488 (2018).
- [21] B. Noheda, D.E. Cox, G. Shirane, S.E. Park, L.E. Cross. *Phys. Rev. Lett.* **86**, 3891 (2001).
- [22] H. Cao, J. Li, D. Vieland, G. Xu. *Phys. Rev. B* **73**, 184110 (2006).
- [23] S.J. Zhang, L. Lebrun, S. Rhee, C.A. Randall, T.R. Shrout. *Appl. Phys. Lett.* **81**, 892 (2002).
- [24] M. Davis, D. Damjanovic, N. Setter. *Phys. Rev. B* **73**, 014115 (2006).