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Specifics of polarisation switching in $PbNi_{1/3}Nb_{2/3}O_3$–$PbTiO_3$–$PbZrO_3$ ferroelectric ceramics

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Abstract

The growing interest in disordered relaxor ferroelectrics is due to unusual properties mainly related to the existence of broad phase transitions characteristic to the systems. The effects of bias field on the dielectric response and polarisation switching are studied in the 0.5 $PbNi_{1/3}Nb_{2/3}O_3$–x $PbTiO_3$–(0.5−x) $PbZrO_3$ system at different $PbTiO_3$:$PbZrO_3$ ratio. Thermal behaviour of normalised remnant polarisation P_r/P_{max} of compositions with content of lead titanate $x=0.33$ and $x=0.35$ at frequency 0.1 Hz and different values of field E_o are measured. Results of measured polarisation and depolarisation currents are compared with characteristics of polarisation switching. In the case of composition with $x=0.33$ the value of P_r/P_{max} does not depend on the field amplitude in the range 4–10 kV/cm within the thermal interval from 50 to 135 °C. In composition with $x=0.35$ the interval of P_r/P_{max} independent of E_o (5–10 kV/cm) is observed closer to the temperature of dielectric permittivity maximum $T_m \approx 180$ °C

Keywords: Ceramics; Dielectric properties; Ferroelectric properties; Perovskites; Sintering

1. Introduction

The $PbNi_{1/3}Nb_{2/3}O_3$–$PbTiO_3$–$PbZrO_3$ (PNN–PT–PZ) system has a morphotropic phase boundary at lead titanate (PT) concentration around 0.33–0.35.[1–3] At these PT concentrations the electromechanical coupling in the compound reaches 0.8.[3] On the one hand, it makes the system attractive for applications. On the other hand, the relatively low temperature of the broad phase transition makes it convenient for studies of phase transitions in ferroelectric solid solutions with components volatile at high temperatures. A rhombohedral to tetragonal (R–T) structural phase transition has been observed[1] in the composition with $x=0.33$ at temperatures $T<T_m$, where T_m is the temperature of dielectric permittivity $\varepsilon'(T)$ maximum.

However, there is no final answer so far to the question whether the phase transition is "independent" or caused by field-induced ferroelectric to paraelectric pretransition phenomena. The anomalies of $\varepsilon'(T)$ and the piezomodulus are observed only in polarised samples with $x=0.33$.[1,2] Such behaviour of electric parameters is observed in relaxor materials[4,5] and is one of the characteristics of such systems where a gradual transition (at heating of previously polarised samples) from a macro-domain to a micro-domain (cluster) state occurs. Nevertheless, in model relaxors, such as PMN or PLZT, a gradual change of structure from rhombohedral to tetragonal symmetry proceeds.

Another possible structural transformation apart from transition to the cubic phase has been reported[6] in multi-component ferroelectric ceramics (MCFEC) on the basis of PZT where the R–T transition proceeds at a temperature below T_m in the first place and then the tetragonal to cubic transition takes place at $T \approx T_m$, as in the PNN–PT–PZ system with $x=0.33$.[1] We have observed anomalous dielectric response in depolarised MCFEC samples at low measuring frequencies (of the order of 1 Hz) of $\varepsilon'(T)$. It suggests that a structural phase transition may proceed without a strong inducing electric field, which is different from a PLZT relaxor. These and other differences displayed by electrical parameters of MCFEC on the basis of PZT, as compared with typical relaxors, have been reported before.[7]

Reversible $\varepsilon'(E_=)$ measurements in the PNN–PT–PZ system have been reported earlier.[8] At a temperature close to T_m in the composition with $x=0.33$ the $\varepsilon'_r(E_=)$

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curve is well approximated by a square function of the type $\varepsilon' = A - bE^2$ with the $\varepsilon'_r(E_=)$ maximum at $E = \approx 0$ and a weak tendency to saturation at high field intensities. Such behaviour of $\varepsilon'(E_=)$ is one more evidence that manifestation of electrical properties in PNN–PT–PZ compares to relaxor materials. It should be noticed though that data on measuring frequencies in the 1–1000 kHz range[9] and the 1–1000 Hz range show no pronounced shift of T_m with the frequency, which is different from the case of PMN and PLZT relaxors. Behaviour of T_m in PNN–PT–PZ, along with the structural phase transition at $T < T_m$ and existence of morphotropic boundaries, makes this system similar to MCFEC on the basis of PZT. All the features make a good reason for some more detailed studies of the PNN–PT–PZ system. Besides, complex ferroelectric solid solutions of this kind are promising materials for ferroelectric thin film applications.[10]

The present report concerns studies of polarisation switching at infra-low frequencies in a wide range of temperatures including the temperature of the diffused phase transition in the PNN–PT–PZ system to have a better idea of the hetero-phase phenomena.

2. Samples and methods

Ceramic samples of the PNN–PT–PZ ferroelectric solid solution were made at the Institute of Solid State Physics of the University of Latvia by conventional ceramics technology. For studies the 0.5PNN–0.33PT–0.17PZ and 0.5PNN–0.35PT–0.15PZ compositions were chosen.

Solid solutions were obtained from oxides: PbO, Nb_2O_5, TiO_2, NiO, ZnO by solid state reactions. Regimes for calcination were chosen on the basis of differential thermal analysis and X-ray phase analysis with account of previous experience. The first calcination was made for 5 h at 850–900 °C, the second—for 5 h at 1000–1030 °C. After each thermal treatment the mixture was ground in ethanol environment and the slurry was desiccated for 4 h at 250°C. As a result a homogeneous mixture of perovskite structure was obtained.

Ceramic samples were obtained by conventional ceramic technology at 1080–1120 °C depending on the composition; duration of sintering: 1–3 h. Hot pressing at temperature 1120–1150 °C during 1–2 h under the pressure of 20 MPa provides better ceramics, the sample density is 98% of the calculated value from X-ray data. To eliminate evaporation of PbO from the mixture above 900 °C (PbO melts at 850–880 °C) a PbO—rich environment in closed platinum crucibles was provided for thermal treatment. The loss of PbO did not exceed 1.0 wt.%. All the solid solution samples have the perovskite structure with densely packed grains of average size 4–5 μm. Porosity does not exceed 2%. Silver paste electrodes were fired at temperature 600–800 °C on samples of the size 5×5×1 mm.

Maximum polarisation P_{max}, remnant polarisation P_r, effective dielectric permittivity ε'_{eff}, and the dielectric loss ε''_{eff} were measured in Volgograd State Architectural and Engineering Academy on an automated Sawyer–Tower circuit at frequencies 0.1, 1, and 10 Hz and rising the temperature from the temperature of liquid nitrogen to $T > T_m$ (the accuracy of measurements 2%). Parameter values were calculated from polarisation loops according to relations: $\varepsilon'_{eff} = P/\varepsilon_o E_o$, $\varepsilon''_{eff} = S/\varepsilon_o \pi E_o^2$, where P is polarisation, E_o—the amplitude of the measuring field, ε_o—the universal dielelectric constant, and S—the loop area.

The DC bias field $E_=$ is applied at a temperature below T_m—the temperature of the dielectric permittivity $\varepsilon'(T)$ maximum before heating the sample, according to the method used in studies of relaxor materials. An anomaly of ε' is observed at $T < T_m$ on the $\varepsilon'(T)$ curve at frequencies $\nu < 10$ Hz. The anomalies are related to the induced morphotropic phase transition at PT concentration $x = 0.35$. Analogous phase transition has been reported in a similar system at PT concentration equal to 0.33.

3. Results and discussion

The P_r/P_{max} ratio as a function of temperature in compositions with $x = 0.33$ and $x = 0.35$ are shown in Fig. 1. In this case the P_r/P_{max} ratio is normalised with respect to a given E_o at a given temperature but not with respect to P_r maximum of the whole thermal interval as the usual practice is. So the P_r/P_{max} ratio is characteristic to the rate of change of P_r with respect to the rate of change of P_{max} with the sample temperature. To some extent it illustrates, within the wide range of temperature, the ratio of contributions of domains subject and not subject to decay at the change of E_o.

As seen from Fig. 1, within the given interval of amplitudes E_i, there is a region where the P_r/P_{max} ratio in both the compositions becomes independent of the amplitude. In case of $x = 0.33$ (Fig. 1a) this region is much wider extending from $T \approx 30$–40 °C up to $T > T_m$ (at the frequency of 1 Hz $T_m \approx 140$ °C). In the other composition ($x = 0.35$) this region is close to T_m (≈180 °C).

The features of the behaviour of P_r/P_{max} are in good agreement with the relevant $\varepsilon'_{eff}(T)$ and $\varepsilon''_{eff}(T)$ curves in compositions with $x = 0.33$ (Fig. 2a) and $x = 0.35$ (Fig. 2b). As seen from Fig. 2a, there is an anomaly of $\varepsilon'_{eff}(T)$ at $T \approx 50$ °C, where the region of independent P_r/P_{max} ratio begins at all E_o values. Another anomaly—a maximum of $\varepsilon'_{eff}(T)$ occurs at $E_o = 3.3$ kV/cm in the first place. As E_o increases from 5.1 to 8.6 kV/cm, the maximum broadens and levels flat over the 50–120 °C interval.

The $\varepsilon''_{eff}(T)$ curve has a similar behaviour. As E_o increases, the low-temperature anomaly—a weak maximum on the $\varepsilon''_{eff}(T)$ curve at $T \approx 50$ °C, fades and the

main maximum essentially broadens while shifting to lower temperatures. Similar behaviour of ε'_{eff} and ε''_{eff} has been observed in PZT MCFEC with the difference that the additional anomalous maximums on the $\varepsilon''_{eff}(T)$ and $\varepsilon''_{eff}(T)$ curves are more distinct.

In composition with $x=0.35$ the anomaly on ε'_{eff} (T) at $T<T_m$ ($T\approx$140–150 °C) is much less pronounced than in the composition with $x=0.33$. The anomaly of dielectric response in this range of temperatures is more distinctly manifested on the ε''_{eff} (T) curve on which, as in the case of $x=0.33$, there are two maximums: one at $T\approx$140 °C and the other at $T<T_m$ ($T\approx$140–150 °C). Both turn into "steps" on the ε''_{eff} (T) curve.

Thus, specific behaviour of P_r/P_{max}, $\varepsilon'_{eff}(T)$, and $\varepsilon''_{eff}(T)$ is observed in both compositions. In case of composition with $x=0.33$ the polarisation anomalies correspond to data of structure analysis[1] showing a R–T phase transition at $T\approx$70 °C and a tetragonal to cubic

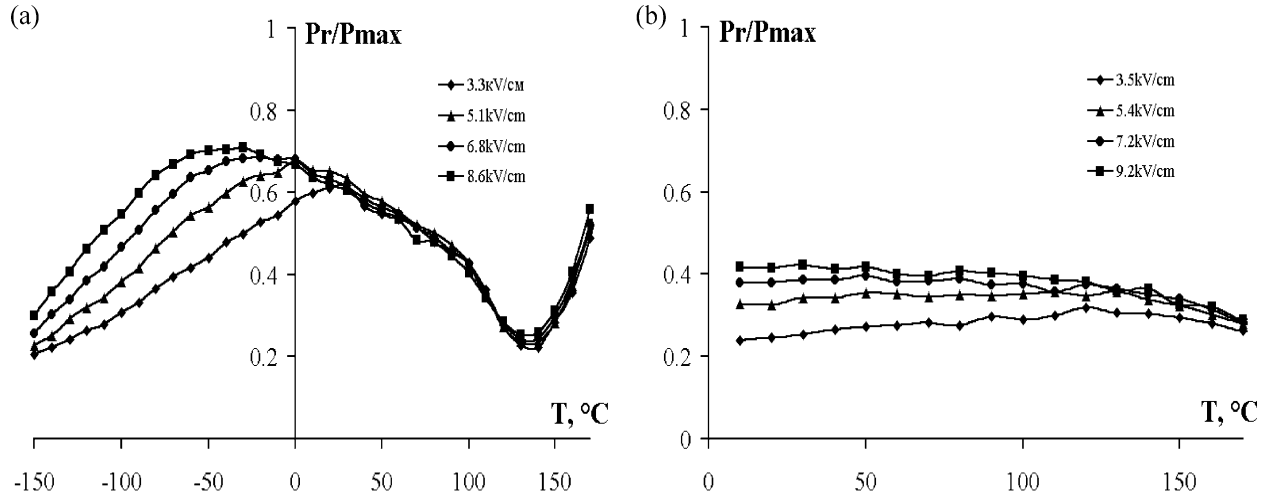

Fig. 1. Thermal behaviour of Pr/Pmax determined from polarisation loops at the frequency of 0.1 Hz at different field amplitudes in ferroelectric ceramics 0.5PNN–0.33PT–0.17PZ (a) and 0.5PNN–0.35PT–0.15PZ (b).

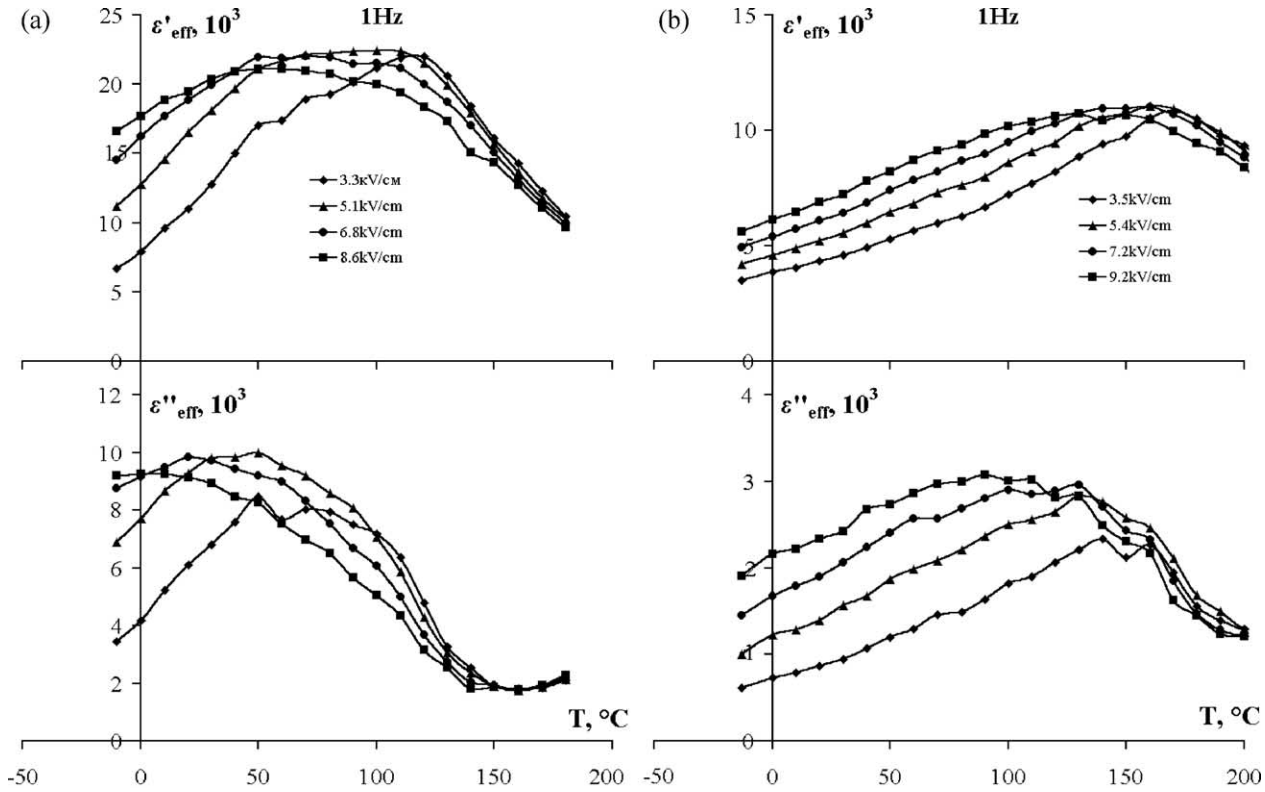

Fig. 2. Thermal behaviour of the effective dielectric permittivity and dielectric loss in PNN–PT–PZ ceramics with $x=0.33$ (à) and $x=0.35$ (b) at the frequency of 1 Hz at different field amplitudes.

transition at $T \approx 130$ °C. Both transitions are broad,[1] which also is in good agreement with results of the present studies (Figs. 1 and 2). A narrow interval between the two phase transitions is one of the reasons the P_r/P_{max} ratio is independent of the field amplitude in the interval from $T = 30$–40 °C to $T > T_m$. Consequently, both P_r and P_{max} may change equally fast under coexistence of phases (the first because of "ease" the polarisation is switched, the other because of the "ease" the polarisation is induced within the region of phase transition).

Additional anomaly of $\varepsilon''(T)$ in a close vicinity of T_m in composition with $x = 0.35$ may be related to processes usual in relaxor materials in the reagion of T_m.[5] In the given case a transition proceeds from the ferroelectric (macroscopic domain) state to the relaxor (microscopic domain) state, then to the paraelectric phase accompanied by a gradual change of the structural symmetry from tetragonal to cubic as observed in a ferroelectric solid solution with $x = 0.35$.[1] The anomaly of $\varepsilon'(T)$ slightly below T_m is well pronounced on the reported $\varepsilon'(T)$ curves[1] but the authors have not paid attention to it.

Compared to other compounds a relatively extended interval of temperatures $T < T_m$ is revealed in $0.5PbNi_{1/3}Nb_{2/3}O_3$–$0.17PbZrO_3$–$0.33PbTiO_3$ where the $\varepsilon_r'(E_=)$ maximum occurs at $E_= \approx 0$. It shows that solid solutions $0.5PbNi_{1/3}Nb_{2/3}O_3$–$0.5Pb(Zr,Ti)O_3$ exhibit distinct relaxor properties at 33% of $PbTiO_3$, which is consistent with other data.[8,9] The features of $\varepsilon_r'(E_=)$ are related to field induced phase transformations and provide evidence to essentially broadened morphotropic boundary in the given system of trine solid solutions.[8]

4. Conclusion

Results obtained in the present study allow to conclude that the complex multistage morphotropic phase boundary in $PbNi_{1/3}Nb_{2/3}O_3$–$PbTiO_3$–$PbZrO_3$ ferroelectric ceramics at the examined concentrations of lead titanate manifests itself in the specific features of polarisation characteristics of the material.

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