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The Dielectric Response of Electrostrictive (1−*x*) PMN–*x*PZT Ceramics

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Abstract

The dielectric and pyroelectric properties of PMN–PZT ferroceramics in the area below temperature of a maximum dielectric permittivity (T_m) *were investigated. It is detected that temperature of transition from the ferroelectric phase into dipole-glass phase coincides exactly with the temperature of the maximum of repolarization currents. The reasons for the appearance of repolarization currents and correlation of dielectric and pyroelectric properties are considered.*

Keywords: PMN–PZT, dielectric properties, capacitors.

1 Introduction

It is known that relaxor ferroceramics (RFC) find a variety of applications, for example, in quality electrostrictive actuators, capacitor dielectrics, etc. The studies of the processes of phase transition (PT) in RFC are rather important from both theoretical and practical points of view.[1–4] In particular, amongst the RFC, lead magnesium niobate (PMN) -related materials have been extensively studied in recent years.[1–6] However, a full understanding of polarization behaviour of PMN-based compounds does not exist yet.

To obtain additional information about mechanisms of polarization and repolarization processes, which take place in RFC, the dielectric and pyroelectric properties of a system PMN–PZT in the area of temperatures below T_m were investigated.

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2 Specimens and Measurement Methods

Specimens of (1-x)$Pb[Mg_{1/3}Nb_{2/3}]O_3$–x$Pb[Zr_{0.53}Ti_{0.47}]O_3$ where $x = 0{\cdot}11$ mol % were obtained through usual ceramic process engineering. Plates of size $S = 5 \times 5\,mm^2$ and thickness from 0·2 to 0·5 mm were used for dielectric measurements. The electrodes were plotted by a method of burning of silver paste. The dielectric behaviour of PMN–PZT was studied on infralow (ILF) and low (LF) frequencies (ν) because the given diapason most adequately reflects the dielectric response of RFC connected with superslow process relaxation of polarization.

Real (ε') and imaginary (ε'') parts of ε^* have been measured in a broad temperature range (−185 to 85°C):

1. in a quasistatic temperature mode of heat in strong fields using the Sawyer–Tower scheme [by calculation of polarization loops (PL) on frequencies 0·1, 1 and 10 Hz];
2. by a bridge method on frequencies (1, 10, 1000 Hz) in a dynamic mode of heating with a rate about 1°C min^{-1} in the ultraweak measuring fields $E_{\sim} \approx 1\ V\,cm^{-1}$). The dependencies of dielectric permittivity from the value of an external bias field $\varepsilon'(E_{=})$ at the temperature −185°C were measured. The maximum of the bias external fields in this case was $E = 32\,kV\ cm^{-1}$ and the amplitude of measurement field at $\nu = 1000$ Hz were $1 V\,cm^{-1}$.

By means of the voltmeter–electrometer V7-30 the polarization–repolarization currents of PMN–PZT were measured. Before each experiment the samples were heated to 85°C (that exceeds by 3 times T_m on frequency 1 kHz) and thermally annealed at this temperature for about 30 min. The polarization–repolarization currents were measured in a regime of cooling and heating runs with a rate 1·4°C min^{-1}.

3 Experimental Results and Discussion

The temperature evolution of polarization loops (PL) (a) and the dependencies of dielectric permittivity on the external bias field $\varepsilon'(E_{=})$ (b) at the temperature $-185°C$ are shown in Fig. 1. The sample was previously annealed and cooled at a rate of $1°C\ min^{-1}$ to $-185°C$ in zero-field mode. One can see that the PL and $\varepsilon'(E_{=})$ have a typical form stipulated by switching of a domains structure in an electrical field that is characteristic of ferroelectric state. The coercive fields (E_c) defined from PL and from $\varepsilon'(E_{=})$ at this temperature have rather close values: $E_c = 17 kV\ cm^{-1}$ (PL by on $\nu = 0{\cdot}1$ Hz) and $E_c = 12{\cdot}5 kV\ cm^{-1}$ [at maximum of $\varepsilon'(E_{=})$]. By reviewing in detail of the forms of PL may be seen that they are displaced along an axis E at low temperatures and are unipolar (are displaced along an axis P). The field displacement PL testifies to existence in a sample of the 'internal bias' fields (E_{bf}). The fields can arise due to the superslow relaxation of structure defects or dipole defects in RFC materials. The action of E_{bf} may be as an external bias field shifting the Curie point of the polar clusters in RFC, so they form the unipolarity of a sample.[7] The value of unipolarity obtained from PL (on $\nu = 0{\cdot}1$ Hz) is nearly 10% and the difference of the magnitude of $\varepsilon'_{max}(+E_{=})$ and the magnitude of $\varepsilon'_{max}(-E_{=})$ was 8%.

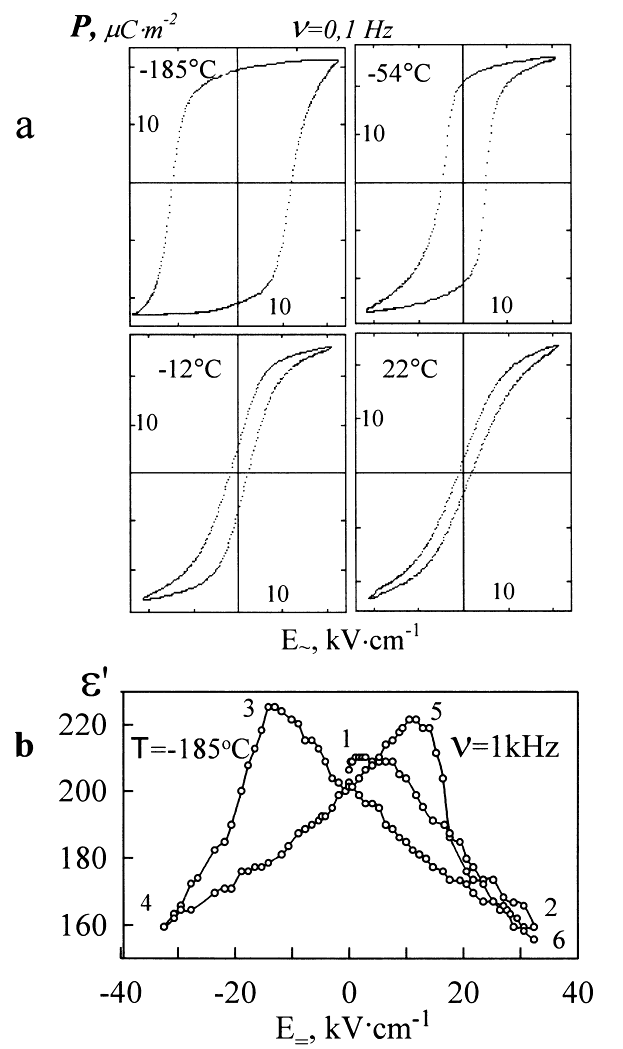

Fig. 1. The typical polarization loops at selected temperatures on frequency 0·1 Hz (a) and reversal dependence of dielectric permittivity as function of bias fields $\varepsilon'(E_{=})$ by frequency 1 kHz of measuring field ($E \sim = 1\ V\ cm^{-1}$) (b) for PMN–PZT ceramic.

The temperature dependencies of both the remain polarization $P_r(T)$ and the repolarization currents $-(i_r)$ obtained in a mode of heat for PMN–PZT ferroceramic are shown in Fig. 2. The analysis of such temperature dependencies reveals a probable temperature of a depolarization of PMN–PZT or, as according to Ref. 8 of PMN–PT. It is the temperature of transition from the macrodomain state to the microdomain state. Thus, the temperature of a depolarization will coincide with the temperature of the greatest rate of a change of spontaneous polarization $P_s(T)$ or of remain polarization $P_r(T)$.

It should be noted that in a temperature interval from -185 to $-50°C$ the pyrocurrent is stipulated probably by the contribution of a 'difference' of currents which appeared because there are the opposite directions of P_s created by separate polar clusters. So this difference connected with unipolarity of a sample, as was mentioned above. The insignificant change i_p in the shown temperature interval can testify to an arising of the regular polar or 'domainlike' (macroscopic) configuration. According to Ref. 9 such polar structure can be formed in relaxor phase by nucleation and interaction of polar nanoregions with the structure defects and further will be formed in the larger polar configurations (by cooling). It is necessary to remark that the behaviour of pyrocurrents correlates well with a small decreasing $P_r(T)$ in the same

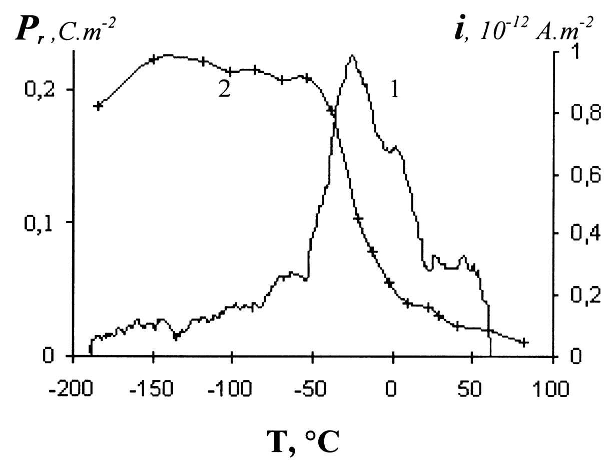

Fig. 2. Temperature dependence of the repolarization currents $-i_r$ (curve 1) and the remaning polarization P_r (curve 2) in PMN–PZT ferroceramic.

temperature area (Fig. 2). By the further increasing of temperature the dependence $i_r(T)$ passes through a maximum at $T \approx -20°C$ (Fig. 2, curve 1) That coincides exactly with the temperature of a point of twist on dependence $P_r(T)$ (Fig. 2, curve 2). The nature of a maximum $i_r(T)$ probably has been connected to intensive destruction of the frozen polar configuration, which confirms the suppositions made in Refs. 8 and 9. It seems the given maximum reflects the total contribution of polarization and depolarization currents.

4 Conclusions

1. In area of low temperature ($-185 \div -50°C$) the PMN–PZT may have the regular polar 'domainlike' structure.
2. Pyrocurrent existing in the certain temperature interval is stipulated probably by the unipolarity arising from the existence of the 'internal bias' field.
3. It is shown, that temperature of a maximum of the depolarization current which is connected to a disintegration of a frozen polar configuration coincides with critical temperature of transition from ferroelectric phase to a mixed phase.

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