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Dielectric response of PMN–0.32PT single crystal and ceramics under dc electric field

Zhenrong Li*, Zhuo Xu, Zengzhe Xi, Xi Yao

Electronic Materials Research Laboratory, Key Laboratory of the Ministry of Education, Xi'an Jiaotong University, Xi'an 710049, China

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Abstract

The temperature dependences of dielectric properties for [0 0 1] PMN–0.32PT single crystal and PMN–0.32PT ceramics under different dc electric field (E) have been investigated. A new monoclinic phase can be induced by electric field with $E = 1.5$–4.0 kV/cm, while heating, in [0 0 1] PMN–0.32PT single crystal. The phase transition process of single crystal is from rhombohedral to monoclinic, then from monoclinic to tetragonal, finally from tetragonal to cubic. With increasing electric field, all of the phase transition temperatures increased in the single crystal. Comparing with single crystal, no new phase is induced by electric field and temperature field in PMN–0.32PT ceramics. Similar to single crystal, the phase transition temperatures of PMN–0.32PT ceramics increased with increasing electric field. The difference of dielectric response under dc electric field between two materials is discussed. The formation of new monoclinic phase results from polarization rotation from [1 1 1] to [0 0 1] direction under electric field in single crystal.

Keywords: C. Dielectric properties; PMN–PT; dc electric field; Phase transition

1. Introduction

The existence of a morphotropic phase boundary (MPB) is an important feature of the solid solution between typical relaxor ferroelectrics and normal ferroelectrics $PbTiO_3$ (PT). $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) is a typical relaxor ferroelectrics. For $(1-x)$PMN–xPT system, the morphotropic phase boundary exist at $x = 0.30$–0.35 [1]. Much attention is focused on this system because of excellent dielectric and piezoelectric properties, especially PMN–PT single crystal with excellent electrostrictive properties [2]. MPB is a boundary separating rhombohedral phase, in which the electric polarization is along [1 1 1] direction, and tetragonal phases, in which the electric polarization is along [0 0 1] direction. For PMN–PT with MPB composition, as temperature increases, the phase transition process is: rhombohedral ferroelectric FE phase → tetragonal FE phase → cubic paraelectric PE phase. In addition, the ferroelectrics phase transition can be induced by external dc electric. Upon application of an electric field along $[0\,0\,1]_{cubic}$, evidence of polarization rotation via a monoclinic phase has been shown for PZN–8%PT [3]. Recently, monoclinic phase has been discovered in PMN–35%PT single crystals by means of high-resolution synchrotron X-ray diffraction. It appears at room temperature in a single crystal previously poled under an electric field of 43 kV/cm applied along the pseudocubic [0 0 1] direction, in the region of the phase diagram around the MPB between the rhombohedral and tetragonal phase [4]. As increasing electric field, the phase transition process for PZN–8%PT and PMN–35%PT undergoes: rhombohedral ferroelectric FE phase → monoclinic ferroelectric FE phase → tetragonal FE phase → cubic paraelectric PE phase.

It will be complex that the dielectric response of relaxor under combination of temperature and electric field. Besides, the dielectric response characterization depends on the manner applying of temperature and electric field. By cooling the PMN monocrystal in an electric field higher than the critical field $E_c \cong 1.7$ kV/cm or the PMN ceramics in a field higher than $E_c \cong 4.0$ kV/cm a long-range ferroelectric phase is formed [5]. Colla et al. [6] investigated dielectric properties of [0 0 1] $(PMN)_{(1-x)}(PT)_x$ single crystals for various electrical and thermal histories. Application of dc bias for $x <$

* Fax: +86-29-82668794.
E-mail address: zhrli@mail.xjtu.edu.cn (Z. Li).

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0.33 resulted in an induced transformation to a long-range ferroelectric state. For [1 1 0] and [2 1 1] PMN–32%PT single crystal, with a prior field-cooled process from the cubic state, a field-induced state, perhaps of orthorhombic symmetry, is observed and coexists with the rhombohedral symmetry in the low temperature region [7]. Yao et al. reported micro–macro-domain switching under dc bias and heating for PLZT (8/65/36) ceramics [8]. By cooling 9/65/35 PLZT ceramics in the dc bias field above E_c a relaxor to ferroelectric phase transition was induced, while by cooling below E_c the system undergoes the transition from the ergodic to the nonergodic relaxor state at a freezing temperature T_0, at which the divergence of the longest relaxation time effectively breaks ergodicity [9].

As above briefly reviewed, dielectric responses of relaxor ferroelectric are affected by the manner of applying electric field and temperature field. At the same time, the dielectric response also depends on the thermal and electric history of samples. In this report, the dielectric response of [0 0 1] PMN–0.32PT single crystal and ceramics under dc electric field while heating (FH) were investigated. The difference behavior for two materials under electric field and temperature field is discussed.

2. Experimental procedure

Reagent grade PbO, MgO, Nb_2O_5, TiO_2 powders were used as raw materials. The single crystal of the composition PMN–0.32PT was grown using an accelerated crucible rotation technique (ACRT) and Bridgman method [10]. The single crystal was oriented along pseudocubic [0 0 1] directions by means of XRD. The sample of size of 5 mm × 5 mm × 0.8 mm was used for dielectric measurements.

The Columbite precursor method was used to prepare PMN–0.32PT ceramics. The mixture of MgO and Nb_2O_5 powders calcined at 1000 °C for 6 h to form $MgNb_2O_6$. Then $MgNb_2O_6$ was mixed with PbO and TiO_2 powder. The mixture was ball milled and then calcined at 850 °C for 4 h. The resultant powders were pressed using PVA binder into pellets of 15 mm in diameter and 2–3 mm in thickness. The samples were then fired at 1200 °C for 2 h in a sealed alumina crucible. To compensate the PbO loss from pellets during sintering, a PbO-rich atmosphere was maintained by placing an equimolar mixture of PbO and ZrO_2 inside the crucible.

Dielectric measurements were conducted on an automated system, where a computer controlled a Delt temperature box, a HP4284A LCR meter and high voltage generator. Dielectric properties were measured at 0.1, 1, 10 and 100 kHz, in the temperature range of room temperature to 200 °C with a heating rate of 3 °C/min. As sample history has a strong influence on the dielectric response, the sample was annealed at 300 °C for 2 h before dielectric measurement. For the field-heated (FH), the dielectric properties were measured under dc field while heating. The applied electric field was along the [0 0 1] direction for single crystals.

3. Results and discussions

Fig. 1 shows the temperature dependence of dielectric constant and dissipation factor without dc electric field for [0 0 1] PMN–0.32PT single crystal. Two phase transition peaks are present. Low temperature peak is around 80 °C, which corresponding to phase transition from rhombohedral to tetragonal phase. A high temperature peak around 140 °C is corresponding to phase transition from tetragonal to cubic phase. The relaxor characterization of phase transition was discussed previously [10]. As decreasing temperature, paraelectric phase is transformed into weak relaxor at $T = T_{max}$, then to normal ferroelectrics by a first-order transformation. The temperature dependence of dielectric constant and dissipation factor under $E = 2.0$ kV/cm for [0 0 1] PMN–0.32PT single crystal is shown in Fig. 2. The interesting abnormal dielectric peaks appear in rhombohedral phase region. Corresponding to the curve of tg δ versus T, there is a sharp peak at around 70 °C. Comparing dielectric properties under $E = 0$ kV/cm with those under dc field $E = 2.0$ kV/cm, the frequency diffusion of dielectric constant is weaken under $E = 2$ kV/cm. Application of an electric field results

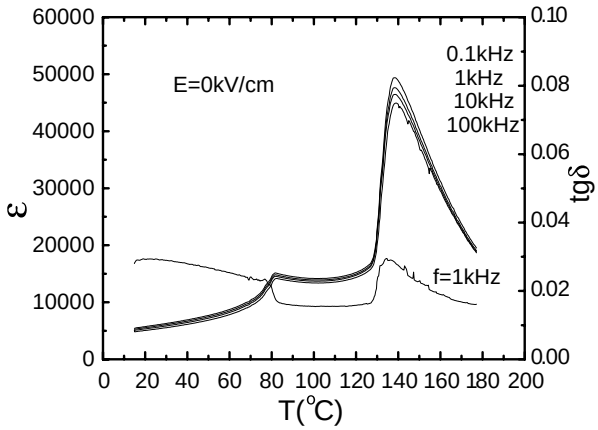

Fig. 1. Temperature dependence of dielectric constant and dissipation factor without dc electric field for [0 0 1] PMN–0.32PT single crystal.

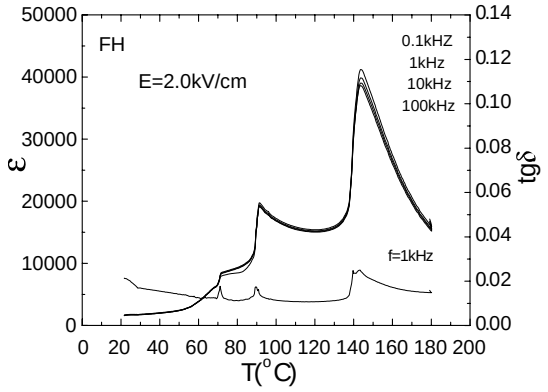

Fig. 2. Temperature dependence of dielectric constant and dissipation factor under $E = 2$ kV/cm (FH).

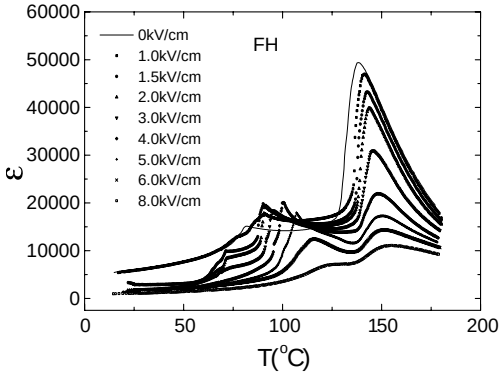

Fig. 3. Temperature dependence of dielectric constant under different dc field for [0 0 1] PMN–0.32PT single crystal ($f = 1$ kHz, FH).

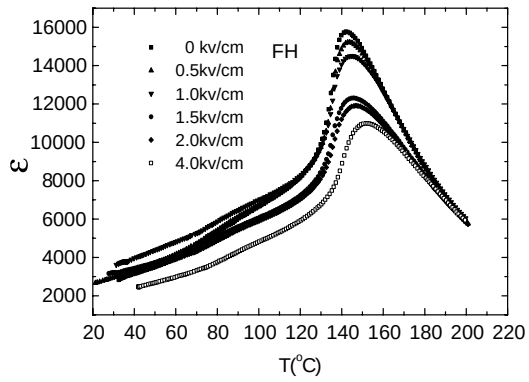

Fig. 5. The temperature dependence of dielectric constant under different dc field for PMN–0.32PT ceramics ($f = 1$ kHz, FH).

in transformation the weak relaxor to a long-range ordering (LRO). But the frequency diffusion of dielectric constant exists above T_{max} in Fig. 2. It indicates that superparaelectric state or polar microregions exist. Due to these polar microregions with a different response to frequency, frequency dispersion of dielectric properties is exhibited. Fig. 3 shows the temperature dependence of dielectric constant under different dc field for [0 0 1] PMN–0.32PT single crystal ($f =$ 1 kHz, FH). The abnormal dielectric peaks appear in rhombohedral phase region under applying dc field in the range of $E = 1.5$–3.0 kV/cm. When $E = 4.0$ kV/cm, the abnormal dielectric peaks are not evident and degenerate into a turning point. When $E = 5.0$–8.0 kV/cm, the abnormal dielectric peaks disappear. With further increasing dc bias, the phase transition temperatures shift to high temperature, at the same time, dielectric constants decrease obviously.

Fig. 4 shows the temperature dependence of dielectric constant and dissipation factor without dc electric field for PMN–0.32PT ceramics. High temperature peak around 140 °C is corresponding to phase transition from tetragonal to cubic phase. There is a shoulder around 80 °C, corresponding to phase transition from rhombohedral to tetragonal phase. The characterization of relaxor ferroelectrics is presented. The temperature dependence of dielectric constant under different dc field for PMN–0.32PT ceramics ($f = 1$ kHz, FH) is shown in Fig. 5. Increasing dc electric field, the T_{max} increase and the maximum dielectric constant decreases. But the abnormal dielectric peak does not appear. Comparing Fig. 1 with Fig. 4, the difference between $T_{max,100\,kHz}$ and $T_{max,0.1\,kHz}$, $\Delta T_{max}(T_{max,100\,kHz} - T_{max,0.1\,kHz})$ is 0.4 and 2.9 °C for single crystal and ceramics, respectively. The relaxor extent of PMN–0.32PT ceramics is stronger than that of single crystal, and the maximum dielectric constant of PMN–0.32PT ceramics is less than that of PMN–0.32PT single crystal. The difference between PMN–0.32PT ceramics and single crystal is due to ceramics with grain boundary and pores that result in relaxation and decreasing of dielectric constant.

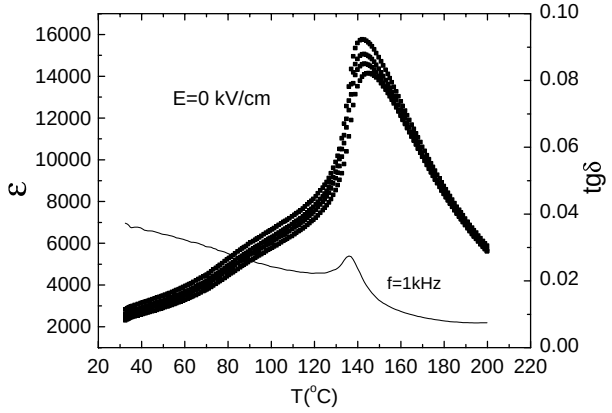

Fig. 4. Temperature dependence of dielectric constant and dissipation factor without dc electric field for PMN–0.32PT ceramics.

Comparing dielectric response of [0 0 1] PMN–0.32PT single crystal and ceramics under dc electric field (see Figs. 3 and 5), the similar change is that the maximum dielectric constant decreases and T_{max} increases with increasing dc electric field, and the obvious difference is that the abnormal dielectric peak induced by dc electric field appear in rhombohedral phase region for [0 0 1] PMN–0.32PT single crystal and no abnormal dielectric peak appears for PMN–0.32PT ceramics.

When dc electric field is applied, the effects of the alignment of polar domains make more thermal energy needed to disrupt the alignment resulting in samples with high phase transition temperature. Additionally, antipolarization electric field in samples is induced under dc bias. The lattice polarizability lower and dielectric constant decrease.

In PMN–PT or PZN–PT system, spontaneous polarization is along [1 1 1] direction. If dc bias is applied along [0 0 1], polarization rotation takes place from rhombohedral to tetragonal phases via monoclinic phase [3,4]. So, it is supposed that the abnormal dielectric peaks may correspond to the phase transition from rhombohedral to monoclinic phases under dc bias. When dc bias is low or even tends to zero, there does not exist abnormal dielectric peaks. It

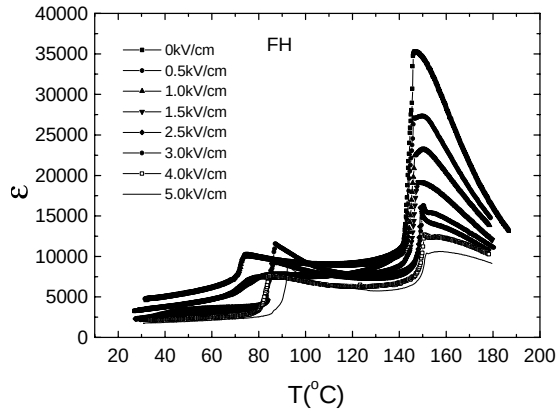

Fig. 6. Temperature dependence of dielectric constant under different dc field for [1 1 1] PMN–0.32PT single crystal ($f = 1$ kHz, FH).

indicates that dc bias is too small to induce phase transition from rhombohedral to monoclinic phases during heating process. When dc field is 1.5–4 kV/cm, induced phase transitions take place in single crystal with heating. However, when dc field is higher than 4 kV/cm, the abnormal dielectric peaks disappear. It shows that the dc bias is high enough resulting in the polarization rotation quickly and the induced phase transition from rhombohedral to monoclinic phases is not exhibited at ε–T curve during heating process. That is to say, application of high electric field and heating make the polarization rotation quickly and the temperature stable regions of monoclinic phase disappear. Fig. 6 shows the curve of dielectric constant vs. temperature under dc bias for [1 1 1] PMN–0.32PT single crystal. There is not exhibiting abnormal dielectric peaks. It further indicates that there does not exist polarization rotation due to the same direction for spontaneous polarization and application dc bias.

The random directions of the crystallographic axes of the crystallites of a ceramic limit the extent to which spontaneous polarization can be developed. So, the properties of ferroelectrics ceramics can be significantly different from the intrinsic behaviors of ferroelectrics single crystals because of grain boundary and multidomain effects. Koo and Cheong's results showed that X-ray peak position shifts under electric field for MPB ($x = 33$–34%) in PMN–xPT ceramics, which may be associated with the recently discovered monoclinic phase [11]. It demonstrated that the intrinsic dielectric and piezoelectric response result from structural change under electric field. It implied that monoclinic phase transition could happen for MPB composition ceramics in PMN–PT system under electric field. In our results of PMN–0.32PT ceramics, monoclinic phase transition does not be found in FH process. Maybe the phase transition is weak that it cannot be present in ε–T curve under this condition, because ceramics have multigrain and isotropic structure, and electric field is not strong enough to induce phase transition.

4. Conclusions

The temperature dependences of dielectric properties for [0 0 1] PMN–0.32PT single crystal and ceramics under different dc electric field (FH) have been compared. The similar change is that the maximum dielectric constant decreases and T_{max} increases with increasing dc electric field, and the obvious difference is that the abnormal dielectric peak induced by dc electric field ($E = 1.5$–4.0 kV/cm) appear in rhombohedral phase region for [0 0 1] PMN–0.32PT single crystal and no abnormal dielectric peak appears for PMN–0.32PT ceramics. The abnormal dielectric peak corresponds to the phase transition from rhombohedral to monoclinic phase, resulting from polarization rotation from [1 1 1] to [0 0 1] direction under electric field.

Acknowledgements

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