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Electric field effects on the domain structures and the phase transitions of $0.62Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.38PbTiO_3$ single crystals with different orientations

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Abstract

The domain states and phase transitions in $0.62Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.38PbTiO_3$ single crystals with different orientations were investigated through biased dielectric measurement, thermally stimulated discharging current (TSDC) and polarization–electric field (P–E) hysteresis loop measurements. The biased dielectric response shows that the crystals have a macrodomain tetragonal ferroelectric state in the ferroelectric phase under zero dc bias. An external bias field could modulate the domain state and induce a phase transition in the crystals. Also, it is proposed that a bias field applied along the ⟨011⟩ direction of the original tetragonal phase could induce triple like P–E hysteresis loops and an orthorhombic ferroelectric phase in an intermediate temperature range.

1. Introduction

Relaxor-based ferroelectric single crystals $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3$–$xPbTiO_3$ (PMN–PT) with compositions near the morphotropic phase boundary (MPB) between ferroelectric rhombohedral (FE_r) and tetragonal (FE_t) phases, have promising potential for applications in transducers, sensors and actuators due to their ultrahigh electromechanical coupling factors ($k_{33} > 90\%$), high piezoelectric coefficients ($d_{33} > 2000$ pC N^{-1}) and high strain levels up to 1.7% [1–4]. The excellent piezoelectric properties shown in the composition range have been studied in relation to the polarization rotation through mesostates under electric or mechanical force [5]. A dominant monoclinic ferroelectric (FE_m) phase could be induced by a large

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poling field applied along the ⟨001⟩ direction in PMN–PT single crystals with compositions near the MPB [6–8], which has been used to interpret the origin of the ultrahigh piezoelectric property. The ferroelectric orthorhombic (FE_o) phase could also be induced by an external electric field applied along the ⟨011⟩ direction of the original rhombohedral single crystal near the MPB [9–11].

The 0.62PMN–0.38PT single crystal has a FE_t phase at room temperature, which has a spontaneous polarization along the ⟨001⟩ direction. It is also promising for potential application in electro-optical (EO) devices due to the temperature independence of its high EO coefficients and the absence of complicated structure-produced strong light scattering [12, 13]. In practical applications, a steady performance of piezoelectric materials is desirable. Thus it is of significant importance to reveal the influence of an electric field at changing temperatures on the domain configurations and the phase transitions of the single crystals. In this paper, we study the electric field effects on the phase transition behaviour in 0.62PMN–0.38PT single crystals with different orientations by *in situ* observation of the dielectric property under the bias fields and P–E loop measurements.

2. Experiment

The 0.62PMN–0.38PT single crystals were grown directly from the melt by a modified Bridgman technique [14]. The crystals oriented along the ⟨001⟩, ⟨011⟩ and ⟨111⟩ directions were prepared with dimensions of $\sim 5 \times 5 \times 1\ mm^3$ and coated with silver electrodes. The poling was carried out using a poling field of 1 kV mm^{-1} for 15 min at 150 °C in silicone oil. The dielectric response as a function of frequency (0.1, 1 and 10 kHz) and temperature (between 25 and 230 °C) was measured using a HP4192A impedance analyser, and the applied dc bias field ranges from 0 to 300 V mm^{-1}. The rate of temperature change is 1 °C min^{-1} in the biased heating process and −1 °C min^{-1} in the biased cooling process. Each time before the dc bias was applied, the crystals were thermally depoled by heating up to 240 °C. The piezoelectric constant d_{33} was measured using a Berlincourt-type quasistatic d_{33} meter at 55 Hz at room temperature. The discharging current in the poled crystals was measured using a Keithley 6517A electrometer at a heating rate of 1 °C min^{-1} in the temperature range between 25 and 230 °C. P–E loop measurements were made by a modified Sawyer–Tower bridge using a sinusoidal type drive field with a frequency of 1 Hz and an amplitude of 20 kV cm^{-1} in the temperature range between 25 and 110 °C.

3. Results and discussions

3.1. Dielectric and discharging current measurements

3.1.1. Bias field effect in the ⟨001⟩ direction. Figures 1 and 2 show the dc bias and temperature dependence of relative permittivity ε_r of the ⟨001⟩-oriented 0.62PMN–0.38PT single crystal upon heating and cooling, respectively. Under zero bias, the permittivity reaches the maximum at a temperature T_m of ∼175 °C upon heating and ∼165 °C upon cooling; the ferroelectric phase transition between the FE_t and paraelectric cubic phases takes place near T_m. The phase transition temperature T_m is very different during the cooling cycles and during the heating cycles, which should mainly be ascribed to a thermal hysteresis of a first order transition [8, 17]. With further increasing dc bias, the dielectric peak T_m shifts towards higher temperature. Under zero bias, the frequency dispersion behaviour of permittivity could hardly be observed in the 0.62PMN–0.38PT single crystal during the whole heating and cooling, indicating the property of a macrodomain state.

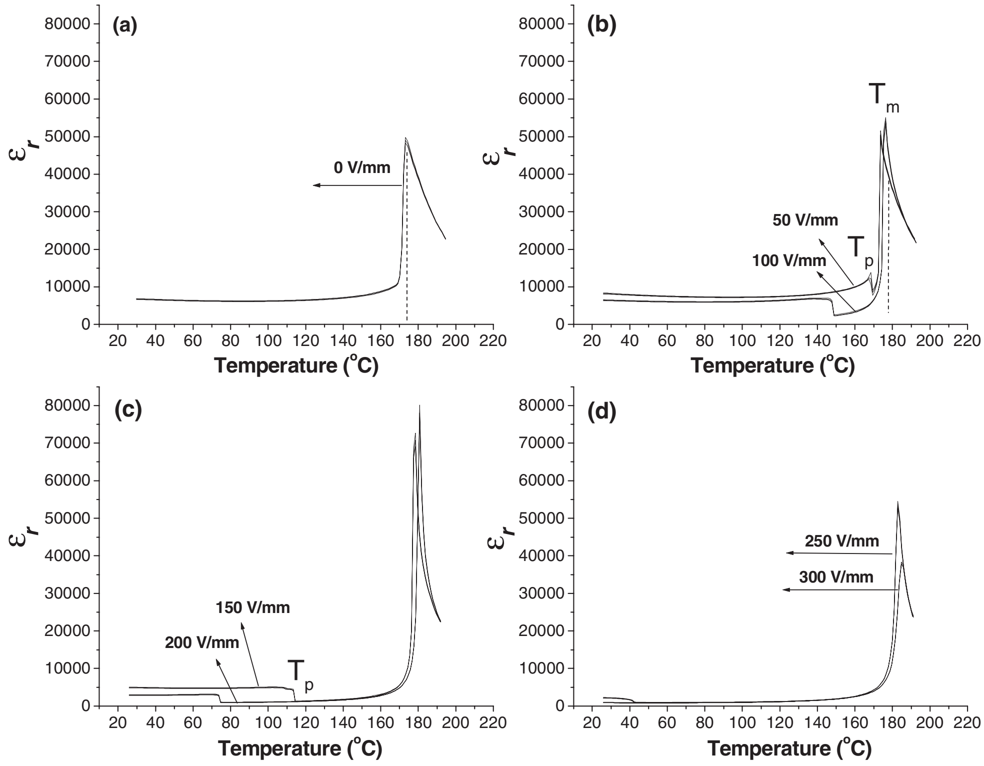

Figure 1. Temperature and dc bias dependence of the dielectric constant in the ⟨001⟩-oriented 0.62PMN–0.38PT single crystal measured at frequencies of 100 Hz, 1 and 10 kHz in the heating runs.

Upon heating under a dc bias of 50 V mm^{-1}, a small dielectric peak T_p (∼167 °C) can be induced. When the bias increases to 100 V mm^{-1}, the peak becomes a lower-temperature dielectric shoulder T_p (∼145 °C) and the dielectric constant ε_r sharply decreases, as shown in figure 1(b). When the bias further increases, the dielectric shoulder T_p shifts towards lower temperatures. When the bias increases to 300 V mm^{-1}, the shoulder T_p is not observed in the range of testing temperatures. We think that the dielectric shoulder T_p appearance is related to the single-domain states of the crystal. The tetragonal 0.62PMN–0.38PT crystal has statistically six possible polarization orientations along the pseudocubic ⟨001⟩ under zero bias [15]. Under bias fields, at the temperature T_p, the bias can overcome the coercive field and induce all six polar vectors to align along ⟨001⟩ E-field direction, and a single-domain configuration can form in the crystal, which causes a sharp decrease of the dielectric constant ε_r and induces the dielectric shoulder T_p. When the bias gradually increases, the single-domain configuration can be induced at lower temperature, so the T_p peak gradually shifts towards lower temperature.

The relative permittivity (0.1, 1 and 10 kHz) and discharging current density as a function of temperature are shown in figure 3 for the ⟨001⟩-poled crystal. Only a normal FE_t to cubic ferroelectric phase transition occurs at T_m. During the heating of the poled crystal, due to no bias field keeping the single-domain configuration stable, when temperature increases to adjacent T_m, the poled ferroelectric macrodomains aligned along ⟨001⟩ direction become unstable and decay to the microdomain state, which results in frequency dispersion behaviour. When the temperature increases to T_m, the disappearance of the microdomains and depolarization of the

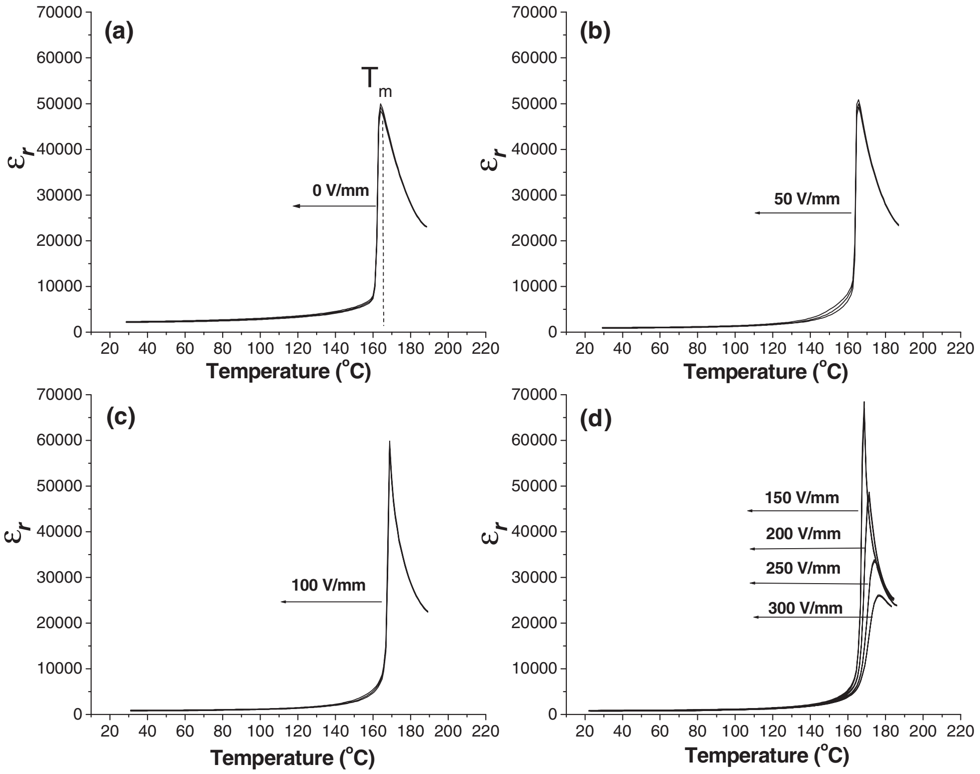

Figure 2. Temperature and dc bias dependence of dielectric constant in the ⟨001⟩-oriented 0.62PMN–0.38PT single crystal measured at frequencies of 100 Hz, 1 and 10 kHz in the cooling runs.

crystal induce a large discharging peak. In the biased cooling run, as presented in figure 2(b), under a small dc bias such as 50 V mm^{-1}, the frequency dispersion behaviour can also be observed near T_m on the low-temperature side due to the appearance of the microdomains before the macrodomain formation. When the bias increases to 150 V mm^{-1}, the frequency dispersion behaviour disappears due to the bias field removing the influence of heating actuation and directly inducing ferroelectric macrodomain formation. Thus there are different effects in the heating and cooling runs under the same dc bias.

3.1.2. Bias field effect in the ⟨011⟩ direction. Figures 4 and 5 show the temperature and dc bias dependence of the relative permittivity of the ⟨011⟩-oriented 0.62PMN–0.38PT single crystal upon heating and cooling, respectively. In the biased heating run, under a bias field of 50 V mm^{-1}, the characteristic temperature T_p appears and the dielectric constant abruptly increases, which indicates spontaneous polarization in FE_t phases aligned along the ⟨001⟩ direction adjacent ⟨011⟩. When the bias gradually increases, the T_p peak gradually shifts towards lower temperature and the relative permittivity ε_r at room temperature can still reach ∼5300, as shown in figure 4(c). When the bias increases to 300 V mm^{-1}, the relative permittivity ε_r at room temperature sharply deceases to ∼700, indicating an orthorhombic ferroelectric (FE_o) phase which is induced by the ⟨011⟩-applied dc bias [9–11]. When the temperature increases, the ferroelectric phase transition between the FE_o and FE_t phases takes place near the dielectric peak T_{ot} (50 °C).

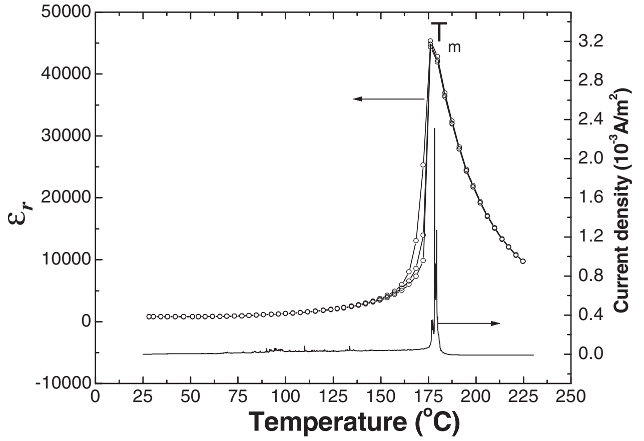

Figure 3. Temperature dependence of dielectric constant (100 Hz, 1 and 10 kHz) and TSDC density in the ⟨001⟩-oriented 0.62PMN–0.38PT single crystal.

In the biased cooling run, as presented in figure 5, when the bias gradually increases to 300 V mm^{-1}, the peak T_{ot} (∼40 °C) is very obvious and the relative permittivity ε_r at room temperature is ∼700, showing a stable orthorhombic ferroelectric phase.

DC bias field influences on T_m and T_p of the ⟨001⟩ and ⟨011⟩ oriented 0.62PMN–0.38PT single crystals in the heating runs are generalized in figure 6. For the ⟨001⟩ and ⟨011⟩ oriented 0.62PMN–0.38PT single crystals, when DC bias field increases, T_m gradually shifts towards the higher temperature while T_p sharply decreases. However, the $T_p(E)$ curve seems quasi linear in ⟨001⟩ samples which is not the case in ⟨001⟩ ones. These variations are like the coercive field versus the temperature. It would be interesting to explain them quantitatively; further work is needed. Here it should be noted that the segregation behaviour during the growth resulted in a variation of $PbTiO_3$ (PT) along the longitudinal direction of a boule, so the variation of PT content can influence the field-induced phase and transition temperature.

Figure 7 presents the relative permittivity and discharging current density as a function of temperature for the ⟨011⟩-poled crystal. After poling, different from the ⟨001⟩-oriented crystal (figure 3), an additional dielectric anomaly peak takes place at T_{ot} of ∼38°. The discharging current of the poled crystal also shows two discharging peaks at T_{ot} and T_m, respectively. The discharging current peak value at T_{ot} is even much larger than that at T_m, indicating an abrupt structural transformation related to a large polarization change occuring at T_{ot}. It can be concluded that the poling field induces another phase other than the tetragonal phase to be stable at temperatures below T_{ot}.

It should be noted that for the ⟨111⟩-oriented 0.62PMN–0.38PT crystals, still only a simple dielectric and discharging peak occur at T_m. In the biased heating and cooling runs, this is a consequence of engineered-domain stability [15].

Table 1 shows the orientation dependence of the relative permittivity and piezoelectric constant measured at room temperature. The poling along the ⟨001⟩ direction of the tetragonal phase builds up a monodomain state from the original polydomain state and gives rise to a much smaller dielectric constant of 790 and piezoelectric constant of 400 pC N^{-1}. The poling along the non-polar ⟨111⟩ direction of the tetragonal phase gives a much higher dielectric constant of 4540 and piezoelectric constant of 450 pC N^{-1} due to an engineered domain structure [9, 16]. However, the poling along the non-polar ⟨011⟩ direction of the tetragonal phase gives rise to an even smaller dielectric constant of 770 and piezoelectric constant of 300 pC N^{-1}. This

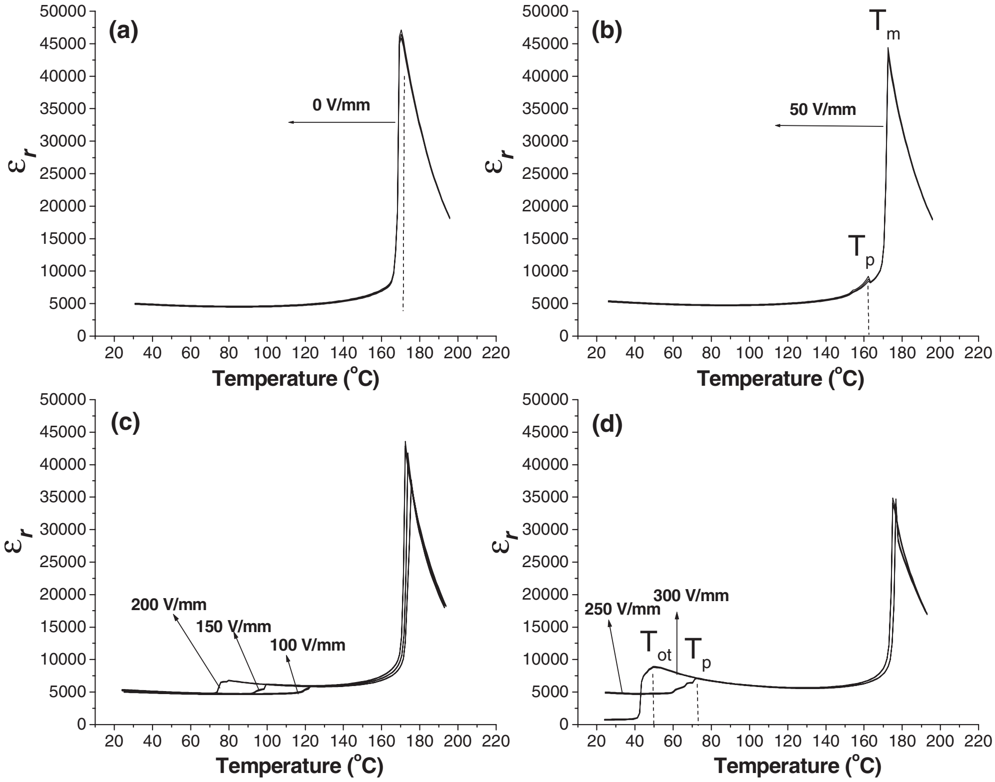

Figure 4. Temperature and dc bias dependence of dielectric constant in the ⟨011⟩-oriented 0.62PMN–0.38PT single crystal measured at frequencies of 100 Hz, 1 and 10 kHz in the heating runs.

Table 1. Orientation dependence of relative permittivity ε_r and piezoelectric constant d_{33} of the 0.62PMN–0.38PT single crystals measured at room temperature.

	ε_r (before poling)	ε_r (after poling)	d_{33} (pC N^{-1})
⟨011⟩	5390	770	300
⟨001⟩	6690	790	400
⟨111⟩	3440	4540	450

indicates that the poling field along the ⟨011⟩ direction induces a monodomain orthorhombic (FE_o) ferroelectric phase, whose spontaneous polarization is along the ⟨011⟩ direction. In the induced FE_o phase from the rhombohedral 0.67PMN–0.33PT single crystal, the monodomain FE_o state has a similar piezoelectric constant of 250 pC N^{-1} and dielectric constant of 880 [9].

3.2. *P–E* loop measurements

Figures 8 and 9 show the P–E results of the crystals in a temperature range between 25 and 110 °C. In figure 8(a) are shown single P–E loops measured along the ⟨011⟩, ⟨001⟩ and the ⟨111⟩ directions at 25 °C. The P–E loop measured along the ⟨001⟩ direction shows clearly the fully polarizable tetragonal state with a saturation polarization (at $E = 20$ kV cm^{-1}) of

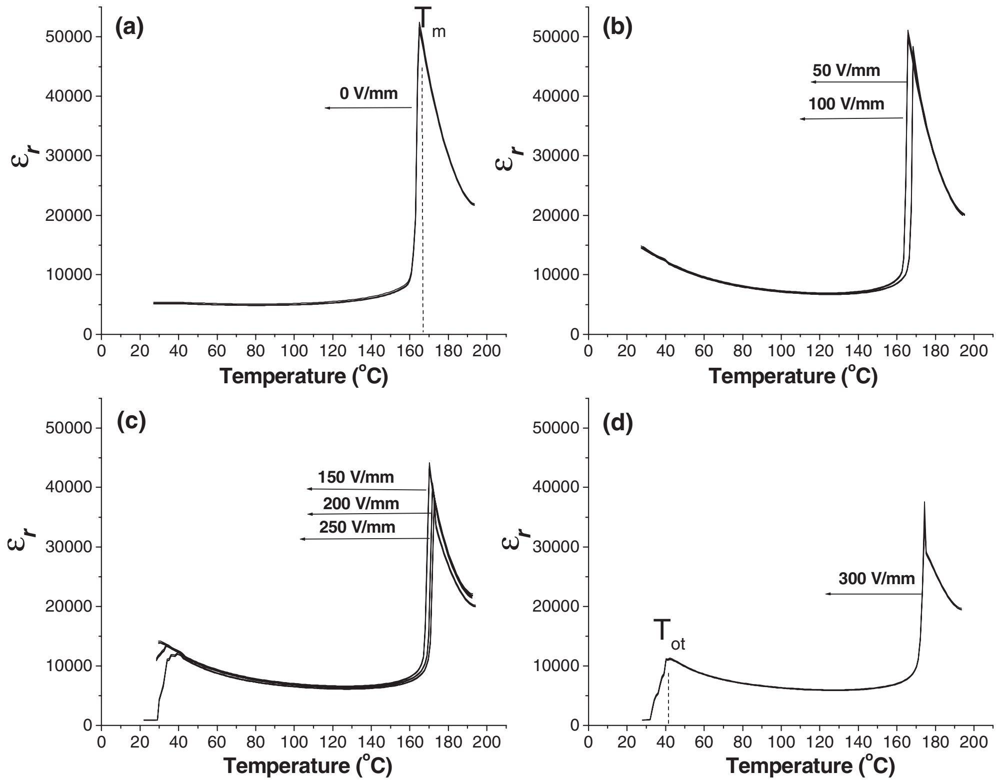

Figure 5. Temperature and dc bias dependence of dielectric constant in the ⟨011⟩-oriented 0.62PMN–0.38PT single crystal measured at frequencies of 100 Hz, 1 and 10 kHz in the cooling runs.

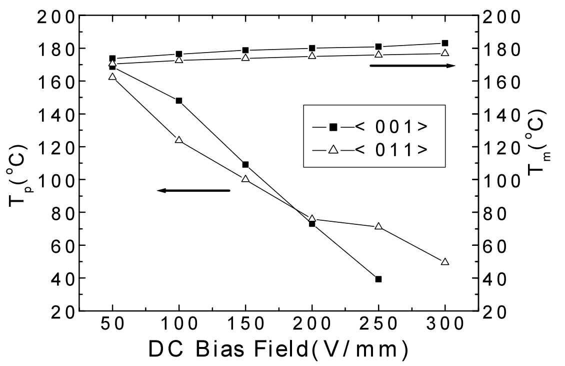

Figure 6. dc bias field influence on T_m and T_p of the ⟨001⟩ and ⟨011⟩ oriented 0.62PMN–0.38PT single crystals in the heating runs.

38.1 $\mu C\ cm^{-2}$ and remnant polarization P_r of ∼36.8 $\mu C\ cm^{-2}$. For the non-polar ⟨111⟩ direction, the saturation polarization and P_r are much smaller (32.2 and 23.0 $\mu C\ cm^{-2}$, respectively). However, the sinusoidal drive electric field applied along the ⟨011⟩ direction induces a square P–E loop with much higher saturation polarization of 42.7 $\mu C\ cm^{-2}$ and P_r of 40.2 $\mu C\ cm^{-2}$. The results demonstrate clearly the presence of a fully polarizable and

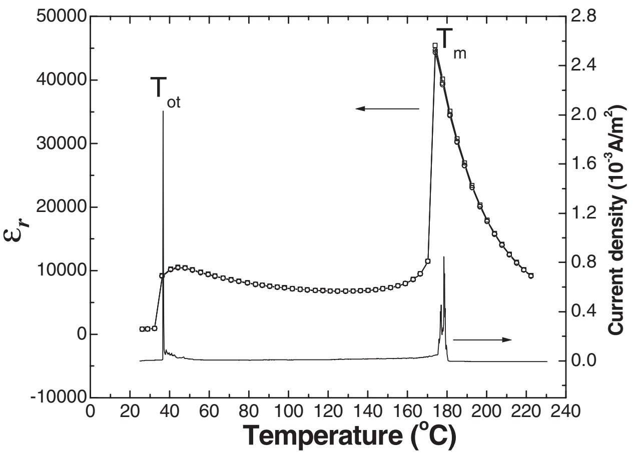

Figure 7. Temperature dependence of dielectric constant (100 Hz, 1 and 10 kHz) and TSDC density in the ⟨011⟩-oriented 0.62PMN–0.38PT single crystal.

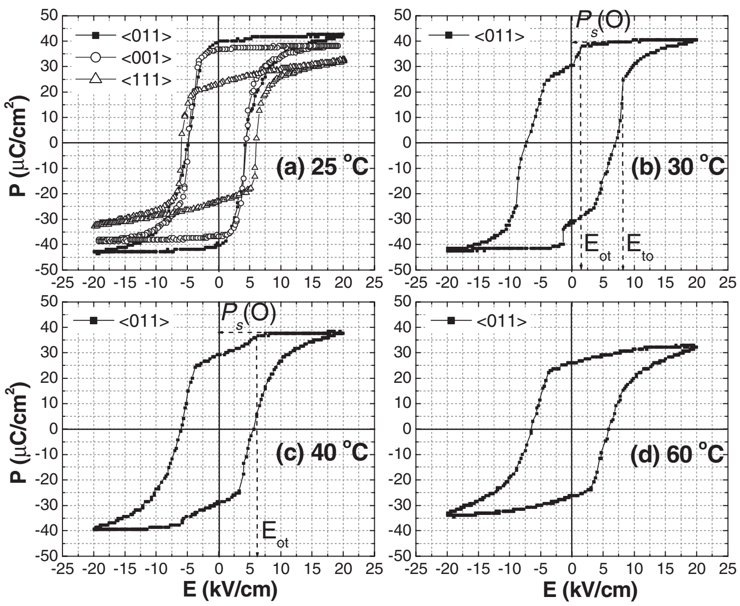

Figure 8. P–E loop patterns of the 0.62PMN–0.38PT single crystals as a function of orientation and temperature.

deformable orthorhombic ferroelectric state, which is induced by the drive electric field applied along the ⟨011⟩ direction.

Upon heating, the P–E loops for the ⟨001⟩ and ⟨111⟩ crystals keep a similar shape as that at 25 °C. But their corresponding values of saturation and remnant polarization decrease, as shown in figure 9. However, for the ⟨011⟩ direction, the remnant polarization at 30 °C decreases abruptly to a value between that for the ⟨001⟩ direction and that for the ⟨111⟩ direction, and then keeps the trend subsequently upon heating. But the triple-like P–E loops in the temperature range between 30 and 55 °C still show much higher saturation polarization

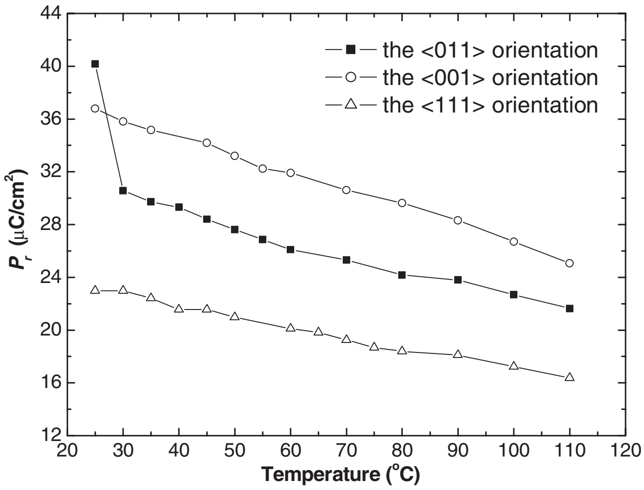

Figure 9. Temperature and orientation dependence of the remnant polarization P_r in the 0.62PMN–0.38PT single crystals.

as shown in figures 8(b) and (c). These triple-like loops reveal the field induced tetragonal–metastable orthorhombic phase transition. By the intercept on the polarization axis of the extrapolation of the linear extremum of the loop through the saturation polarization point, as shown in figures 8(b) and (c), we obtain the spontaneous polarization P_s(O) of the metastable orthorhombic phase, which could be only stabilized by a large drive electric field. P_s(O) is 39.6 and 37.7 μC cm^{-2} at 30 and 45 °C, respectively. At 30 °C, a field larger than the E_{to} of 8.2 kV cm^{-1} could transform the tetragonal phase to the orthorhombic phase. Once the orthorhombic phase is established, it could be stabilized until the electric field is below E_{ot} of 1.4 kV cm^{-1}. The induced FE_o state becomes unstable and re-transforms to the FE_t phase under a smaller electric field than E_{ot}.

It can be seen clearly that the induced orthorhombic phase becomes unstable with increasing temperature. At 25 °C, the induced orthorhombic phase exists in a stable state even after the removal of the drive electric field, and as a result gives a single square P–E loop of the FE_o phase. Upon heating to 45 °C, E_{ot} increases to a higher value of 6.2 kV cm^{-1}. At temperatures above 60 °C, no FE_o state could be induced by the drive electric field with an amplitude of 20 kV cm^{-1}, and only a single P–E loop of the tetragonal phase appears. This result is consistent with the dielectric and discharging current result, which shows that the FE_o phase, induced by the poling field at room temperature, becomes unstable and re-transforms to the tetragonal phase at ∼36 °C.

4. Conclusions

In summary, our investigation has shown that 0.62PMN–0.38PT single crystals have been a macrodomain state in the ferroelectric phase at zero bias, indicating a normal ferroelectric. Both the domain states and phase structures could be modified by an applied external electric field combined with different thermal history. The effect of the external bias field strongly depends on the crystal orientation. The results illustrate that an electric field, applied along the ⟨001⟩ and ⟨011⟩ directions of the original tetragonal 0.62PMN–0.38PT single crystal, could induce a dielectric shoulder T_p or an orthorhombic ferroelectric (FE_o) phase. The stability of the induced FE_o phase decreases with increasing temperature and it finally re-transforms to the more stable tetragonal phase at higher temperatures. However, for the ⟨111⟩-oriented tetragonal crystals, the appearance of only a single dielectric and discharging peak T_m can be ascribed to engineered-domain stability.

Acknowledgments

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