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Effect of a bias field on the dielectric properties of $0.69Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.31PbTiO_3$ single crystals with different orientations

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Abstract
The microdomain–macrodomain transformations and phase transitions in $0.69Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.31PbTiO_3$ single crystals were investigated by measuring the temperature dependence of relative permittivity as a function of crystal orientation and applied dc bias. A rhombohedral–tetragonal phase transition in the original crystal has been confirmed by powder x-ray diffraction at temperatures from 25 to 180 °C. The results show that microdomain relaxor ferroelectric states in the original crystals could be transformed to macrodomain ferroelectric states by applying a dc bias along any of the ⟨111⟩, ⟨011⟩ and ⟨001⟩ directions. It is also proposed that an electric field applied along the ⟨011⟩ or ⟨001⟩ direction could induce an orthorhombic or a monoclinic ferroelectric phase, respectively, between the rhombohedral and tetragonal ferroelectric phases in an intermediate temperature range.

1. Introduction

Relaxor-based single crystals of $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ (PMN–PT) have promising potential for applications in transducers, sensors and actuators due to their ultra-high electromechanical coupling factors ($k_{33} > 94\%$), high piezoelectric coefficients ($d_{33} > 2500$ pC N^{-1}) and high strain levels up to 1.7% [1, 2]. They also have potential benefit in electro-optical technology due to their high electro-optical coefficients [3, 4]. Efforts are focused on the composition close to the morphotropic phase boundary (MPB) between the ferroelectric rhombohedral (FE_r) and ferroelectric tetragonal (FE_t) phases and on the ⟨001⟩ directions. The origins of their excellent performance have been attributed to the polarization

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rotation under external electric field [5]. However, the roles of possible metastable ferroelectric monoclinic (FE_m) and ferroelectric orthorhombic (FE_o) phases have also been emphasized [6–12]. Furthermore, the quenched random fields in the ferroelectric microdomain relaxor state [13, 14] have been suggested [15, 16] as facilitators for the formation of metastable phases.

In PMN–PT single crystals, the MPB compositions have a molar content of PT close to 0.33 [17, 18]. The 0.69PMN–0.31PT single crystal has a composition near the MPB. In this paper, powder x-ray diffraction (XRD) of the single crystal will be used to confirm its crystal symmetry. Pure PMN is a typical ferroelectric relaxor [13, 14]. Studies of the ferroelectric domain state in relaxors have been performed through the investigation of the biased dielectric property in lead lanthanum zirconate titanate (PLZT 8:65:35) [19] and lead magnesium niobate PMN [20]. In those studies, the characteristic temperatures T_d and T_f are observed. T_f corresponds to the microdomain–macrodomain transformation in the heating process under a dc bias. T_d refers to the decay of macrodomain states to microdomain states in the heating process or the building up of the macrodomain states from the microdomain states in the cooling process under a dc bias. The microdomain state shows frequency dispersion in the relative permittivity spectra and the dispersion behaviour disappears when the microdomain state is transformed to a macrodomain state by an external electric field. Thus the transformations between microdomain states and macrodomain states as well as the temperatures T_f and T_d could be easily determined. PMN–PT is a relaxor-based material. In this paper, the *in situ* observation of the biased dielectric property of 0.69PMN–0.31PT single crystals in both heating and cooling processes will be presented to investigate the dependence of its domain states and phase structures on crystal orientation, dc bias and temperature.

2. Experiment

The 0.69PMN–0.31PT single crystal was grown by the modified Bridgman technique [18, 21]. Powder XRD of the as-grown single crystal was performed from 25 to 180 °C using Cu Kα radiation (Siemens, Bruker D8 Advance XRD system). A detailed peak evolution as a function of temperature was made from measurements over a small temperature interval in a 2-theta (2θ) range of 44.5°–45.5° for the (002) peak. The XRD data were analysed using the commercial software EVA (Siemens Bruker) by stripping out the Kα-2 peaks. The reason that we have chosen the (002) peak instead of higher angle peaks (although they give better resolution) is that it has greater intensity than the higher angle ones. Peak evolution around a 2θ of 45° is rather obvious therefore no deconvolution or profile analysis were applied.

From as-grown single crystal, various crystals oriented along the $\langle 111\rangle$, $\langle 011\rangle$ and $\langle 001\rangle$ directions were prepared with size ~5 mm × 5 mm × 1 mm and silver electrodes. The temperature dependence of the relative permittivity under different dc biases was measured by a multi-frequency LCR Meter (Model SR720 of Stanford Research Systems) at frequencies of 100 Hz, 1 kHz and 10 kHz. The applied dc bias field ranges from 0 to 300 V mm^{-1}. The testing temperature range was 20–250 °C. The temperature change rate was 1 °C min^{-1} in the heating process and -1 °C min^{-1} in the cooling process. Each time before the dc bias was applied, the crystals were thermally depoled by heating up to 240 °C.

3. Results and discussion

3.1. Powder XRD characterization

The powder XRD patterns in figure 1 show a perovskite structure in the as-grown 0.69PMN–0.31PT single crystal at temperatures from 25 to 180 °C. Further detailed measurement of the

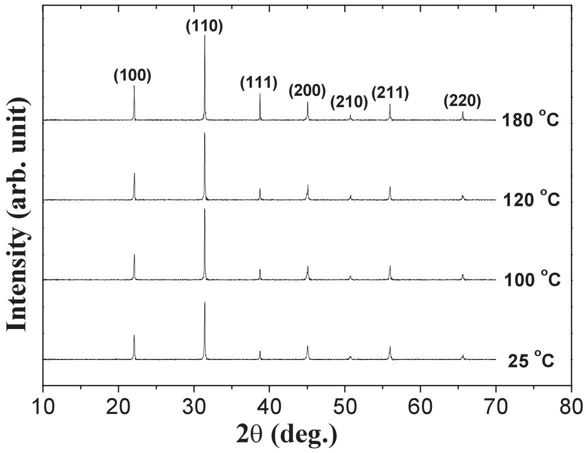

Figure 1. Temperature dependence of the powder XRD patterns of the as-grown 0.69PMN–0.31PT single crystal with 2θ in the range of 10°–70°.

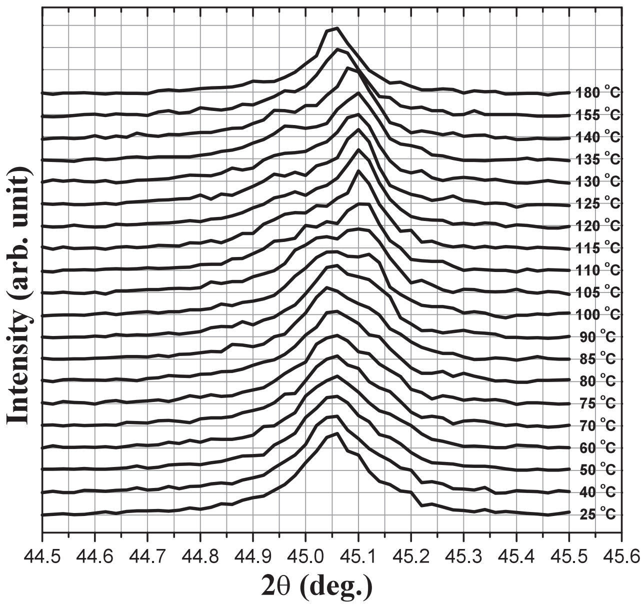

Figure 2. Temperature dependence of the powder XRD patterns of the as-grown 0.69PMN–0.31PT single crystal with 2θ in the range of 44.5°–45.5°.

(200) peak is shown in figure 2. At temperatures from 25 to 80 °C, the (200) peaks have a 2θ value of 45.06°, which indicates an FE_r phase structure. At 85 °C, an additional shoulder appears on the right of the lower temperature peak. At 100 °C, the shoulder evolves to a peak at 45.12° with the same intensity as the peak at 45.06°. The two peaks correspond to the (200) and (002) peak, respectively, of the FE_t phase. With increasing temperature, the left (002) peak devolves to a shoulder joining the right (200) peak. At 115 °C, the right (200) peak shifts to 45.10°. At 140 °C, the right (200) peak begins to shift to the left. Then at 180 °C, only one (200) peak exists at 45.06°.

The above result shows that only an FE_r phase exists at a temperature below 85 °C. In the temperature range between 85 and 110 °C, the FE_r and FE_t phases coexist. At temperatures from 115 to 135 °C, mainly the FE_t phase exists. In the temperature range of 135–155 °C, the FE_t phase and the paraelectric cubic phase coexist. At temperatures above 155 °C, such as 180 °C, only a cubic phase exists.

3.2. Biased dielectric property on heating and on cooling

3.2.1. Bias field effect in the ⟨111⟩ direction. Figures 3 and 4 show the dc bias and temperature dependence of relative permittivity ε_r of the ⟨111⟩-oriented 0.69PMN–0.31PT single crystal upon heating and cooling, respectively. Under zero bias, the permittivity reaches the maximum at a temperature T_m of ∼131 °C upon heating and ∼125 °C upon cooling. In accordance with our XRD results, the ferroelectric phase transition between the FE_t and paraelectric cubic phases takes place near T_m. Upon heating, the permittivity shoulder at ∼112 °C shows the formation of the FE_t phase, which has been confirmed in the XRD patterns in figure 2. However, upon cooling, the permittivity shoulder does not appear. But the peak width at half maximum of the phase transition permittivity peak reaches ∼48 °C, much broader than that of ∼34 °C upon heating. This thermal hysteresis shows that the cubic–FE_t and the FE_t–FE_r phase transition peaks have become sufficiently close on cooling as not to be resolvable as separate permittivity peaks. The frequency dispersion of permittivity is obvious in the phase transitions, indicating the existence of microdomain relaxor states in both the FE_r and FE_t phases.

Upon heating under a dc bias of 50 V mm^{-1}, a microdomain–macrodomain transformation is induced at a T_f of ∼60 °C in the FE_r phase, as determined by the frequency dispersion behaviour shown in figure 3(b). Then, at a temperature T_{rd} of ∼100 °C, the induced FE_r macrodomain state decays back to a microdomain state, which is similar to the T_d phenomenon in PLZT [19]. At a T_{rt} of ∼106 °C, a microdomain FE_r–microdomain FE_t phase transition takes place, as shown by the T_{rt} peak in figure 3(b). Higher dc bias shifts T_f towards a lower temperature. So the T_f peak is not observed in the testing temperature range under higher dc bias, as shown in figures 3(c) and (d). It could be seen that an electric field larger than 100 V mm^{-1} could induce a macrodomain state in the FE_r phase at room temperature. Under a dc bias larger than 150 V mm^{-1}, the T_{rd} coincides with the T_{rt}. With increasing dc bias, the T_{rt} and T_m peaks both shift towards higher temperatures, indicating the dc bias applied along the ⟨111⟩ direction tends to make the FE_r phase more stable. It is because the FE_r phase has a spontaneous polarization also along the ⟨111⟩ direction.

Upon cooling under a dc bias of 50 V mm^{-1}, the T_{rd} shoulder at ∼80 °C and the T_{rt} peak at ∼90 °C are both reproduced. The transformation takes place in the sequence of cubic phase, microdomain FE_t phase, microdomain FE_r phase and macrodomain FE_r phase. Once the macrodomain FE_r phase forms, it continues to exist down to lower temperatures. So the T_f is not reproduced. Under a dc bias of 100 and 150 V mm^{-1}, the T_{rd} coincides with the T_{rt}. A microdomain FE_t–macrodomain FE_r phase transition takes place at T_{rt}. The T_{rt} peak decays to a shoulder joining the T_m peak under a 150 V mm^{-1} bias. Under a dc bias higher than 200 V mm^{-1}, frequency dispersion behaviour could only be observed at temperatures near T_m. In this case, the cubic phase-microdomain FE_t phase transition may take place simultaneously with the FE_t microdomain–macrodomain transformation. Then at a lower temperature, a macrodomain FE_t–macrodomain FE_r phase transition takes place.

3.2.2. Bias field effect in the ⟨011⟩ direction. Figures 5 and 6 show the temperature and dc bias dependence of relative permittivity in the ⟨011⟩-oriented 0.69PMN–0.31PT single crystal upon heating and cooling, respectively. Under a higher dc bias of larger than 150 V mm^{-1},

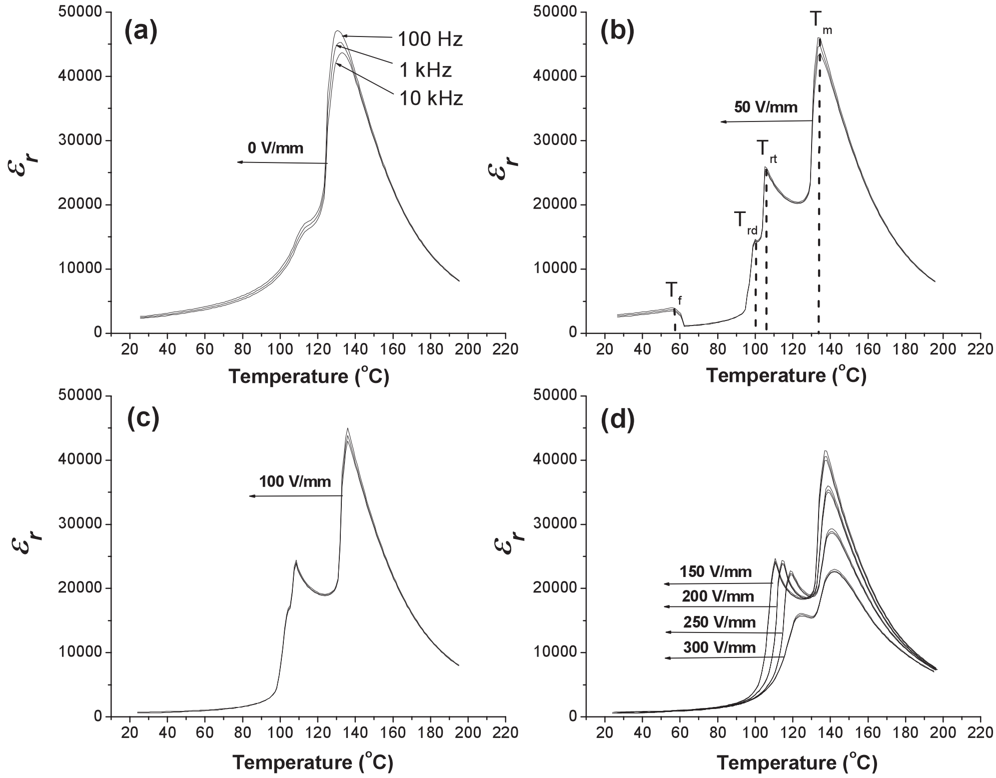

Figure 3. Temperature and dc bias dependence of relative permittivity in the ⟨111⟩-oriented 0.69PMN–0.31PT single crystal measured at frequencies of 100 Hz, 1 and 10 kHz in the heating runs. (The note on the arrow indicates the value of applied dc bias.)

three dielectric peaks appear in both the heating and cooling runs. The temperature range between the temperatures T_{ro} and T_{ot}, as indicated in figures 5 and 6, becomes broader with increasing dc bias. The bias was applied along the ⟨011⟩ direction. So here it is proposed that an orthorhombic ferroelectric (FE_o) phase is induced by the ⟨011⟩-applied dc bias at temperatures from T_{ro} to T_{ot} between the lower temperature FE_r phase and the higher temperature FE_t phase. The FE_o phase has a polar direction also along the ⟨011⟩ direction. Thus the higher the ⟨011⟩-applied dc bias, the broader the T_{ro}–T_{ot} temperature range. It has also been reported that a small poling field leaves an FE_o phase between the FE_r and FE_t phases in the ⟨011⟩-oriented 0.67PMN–0.33PT single crystal [10].

In the biased heating run, the room temperature FE_r phase has a macrodomain state when the dc bias is larger than 100 V mm^{-1}, under which the T_f is pushed to below 20 °C. Under the 50 V mm^{-1} bias, the T_f peak and the T_{ro} peak join to form a broad peak. The frequency dispersion of permittivity could not be observed between T_{ro} and T_{ot}, showing that a macrodomain FE_o phase is stabilized by the ⟨011⟩-applied dc bias.

In the biased cooling run, the T_f is not reproduced. The dielectric peak at a temperature T_{od}, as indicated in figure 6(b), occurs under dc biases of 50 and 100 V mm^{-1}. In this case, the microdomain FE_t–microdomain FE_o phase transition occurs at T_{ot} and, subsequently, an FE_o microdomain–macrodomain transformation occurs at T_{od}.

It is also noted that in both biased heating and biased cooling runs, some degree of frequency dispersion of permittivity is observed near the FE_o–FE_t phase transition temperature

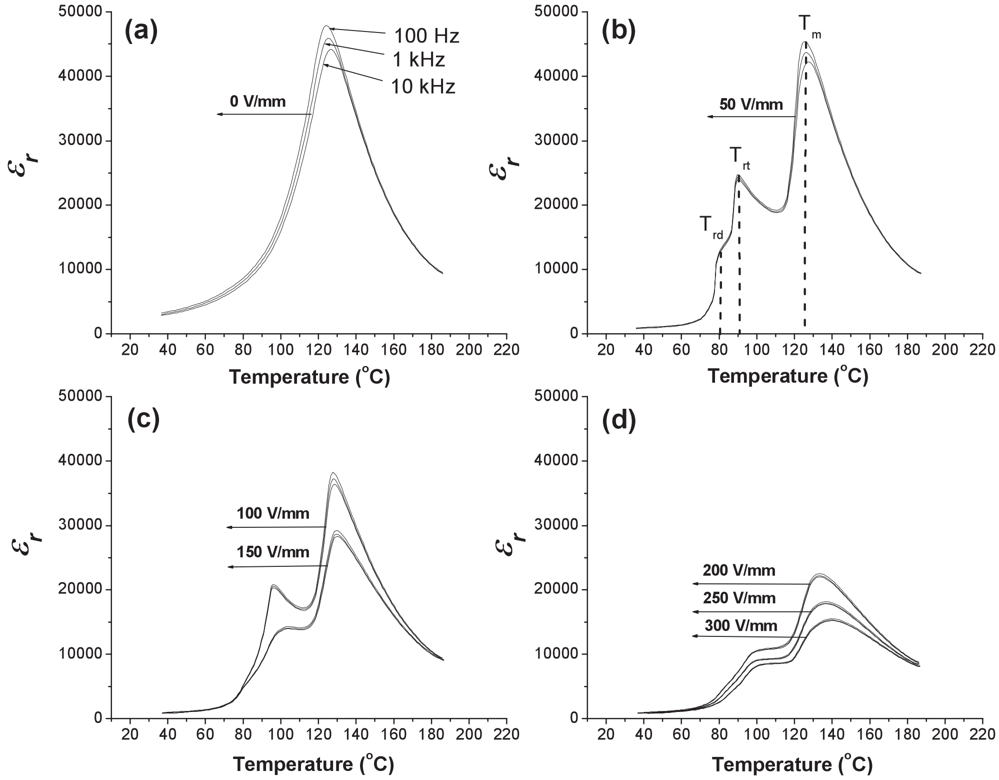

Figure 4. Temperature and dc bias dependence of relative permittivity in the ⟨111⟩-oriented 0.69PMN–0.31PT single crystal measured at frequencies of 100 Hz, 1 and 10 kHz in the cooling runs. (The note on the arrow indicates the value of applied dc bias.)

T_{ot} under higher dc bias, as seen in both figures 5 and 6. It may be possible that the FE_o–FE_t phase transition takes place through a metastable disordered microdomain FE_m M_C phase under higher electric field applied along the ⟨011⟩ direction [22].

3.2.3. Bias field effect in the ⟨001⟩ direction. Figures 7 and 8 show the dc bias and temperature dependence of relative permittivity in the ⟨001⟩-oriented 0.69PMN–0.31PT single crystal in the heating and cooling runs, respectively. For clarity, only the data measured at frequencies of 1 and 10 kHz are presented.

In the biased heating run using a dc bias value of 50 V mm^{-1}, a microdomain FE_r–macrodomain FE_t phase transition occurs at ~96 °C, below which the frequency dispersion of permittivity is evident as shown in figure 7. At T_m, the macrodomain FE_t–paraelectric cubic phase transition occurs. It could be seen that the ⟨001⟩-applied dc bias stabilizes the macrodomain FE_t phase, whose polar direction is along the ⟨001⟩ direction. Under a higher dc bias, the frequency dispersion could not be observed below T_m, However, two broad lower temperature dielectric anomaly peaks appear at T_{rm} and T_{mt}. With increasing dc bias, both the T_{rm} and T_{mt} peaks shift to lower temperatures. Clearly, the ⟨001⟩-applied dc bias extends the temperature range between T_{mt} and T_m, in which exists the macrodomain FE_t phase. Correspondingly, the T_{rm} decreases, below which exists the macrodomain FE_r phase.

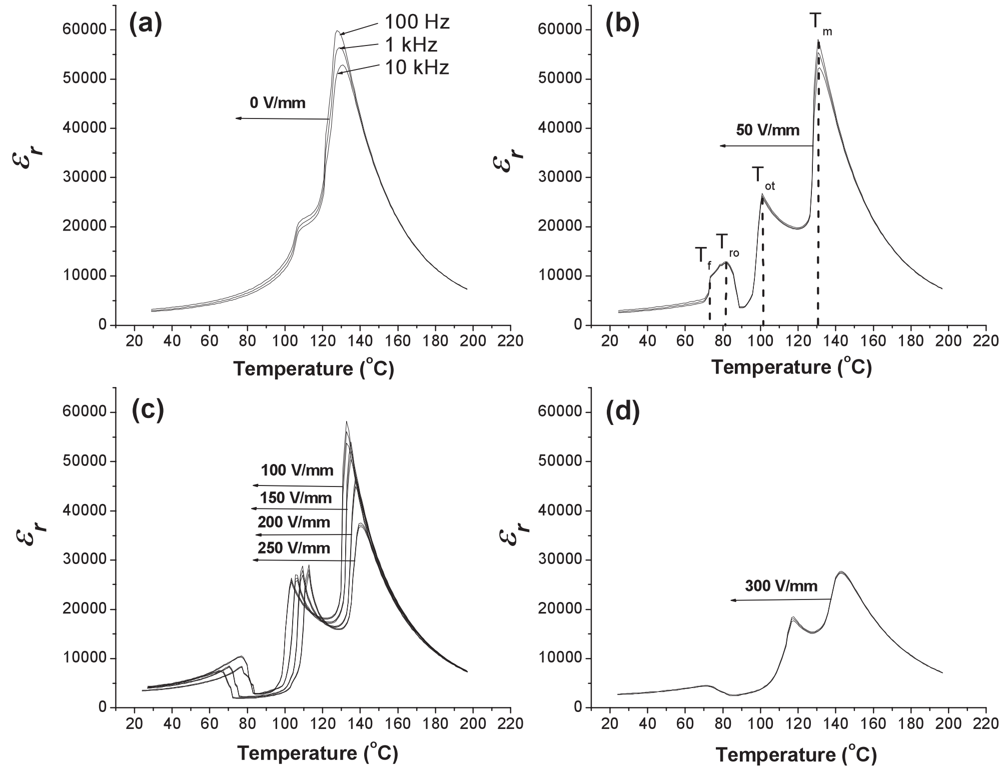

Figure 5. Temperature and dc bias dependence of relative permittivity in the ⟨011⟩-oriented 0.69PMN–0.31PT single crystal measured at frequencies of 100 Hz, 1 kHz and 10 kHz in the heating runs. (The note on the arrow indicates the value of applied dc bias.)

In the biased cooling run as shown in figure 8, there are also two broad permittivity peaks at T_{rm} and T_{mt}, respectively. Both the T_{rm} and T_{mt} peaks shift to lower temperatures with increasing dc bias.

It could be seen that a different phase is induced in the temperature range between T_{rm} and T_{mt} in both the biased heating and biased cooling runs. Both the T_{rm} and T_{mt} peaks are broad, which implies the coexistence of the FE_r, FE_t and the induced phase in a broad temperature range.

It has been reported that a dominant monoclinic ferroelectric (FE_m) phase could be induced by a large poling field applied along the ⟨001⟩ direction in 0.92PZN–0.08PT and 0.65PMN–0.35PT single crystals at room temperature [23, 24]. This has been used to interpret the origin of the excellent piezoelectric property of the single crystals. So here it is speculated that in the 0.69PMN–0.31PT single crystal, an FE_m phase was induced by the ⟨001⟩-applied dc bias between the FE_r and the FE_t phases in the temperature range between T_{rm} and T_{mt}. The broad T_{rm} and T_{mt} peaks reflect that the FE_m, FE_r and FE_t phases coexist in a broad temperature range. With increasing dc bias, both T_{rm} and T_{mt} shift towards room temperature. Also both the T_{rm} and the T_{mt} peaks become broader. So it is expected that a further increase in the electric field applied along the ⟨001⟩ direction may induce a dominant FE_m phase at room temperature, which gives rise to the excellent room temperature piezoelectric properties in the 0.69PMN–0.31PT single crystal.

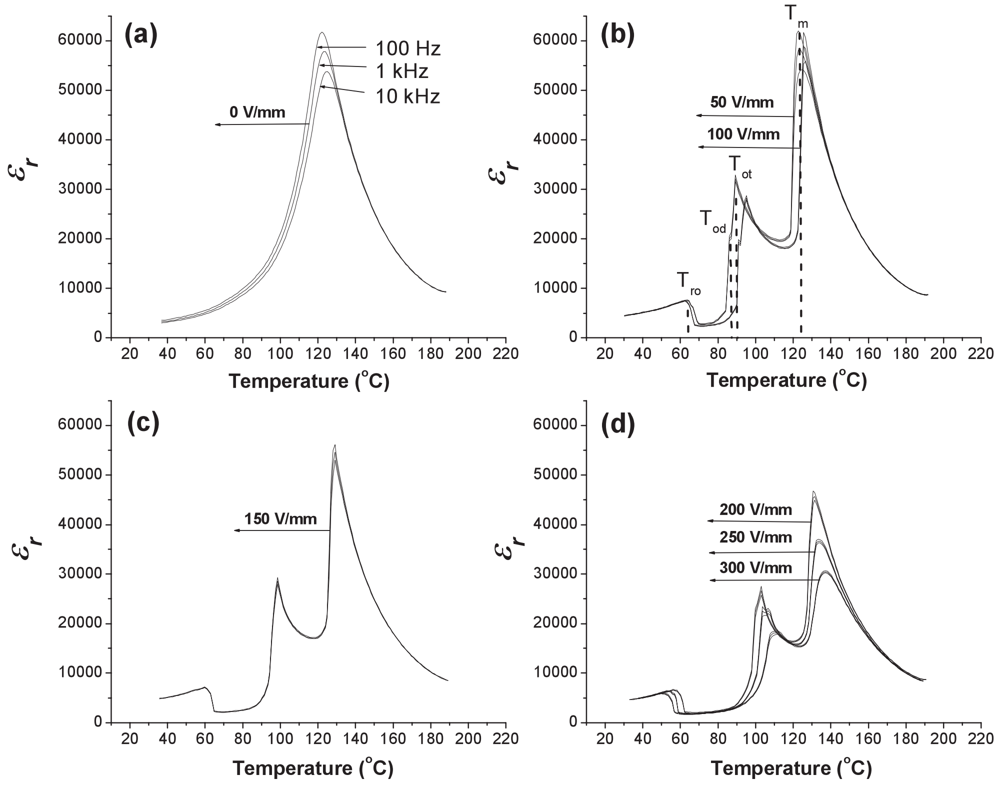

Figure 6. Temperature and dc bias dependence of relative permittivity in the ⟨011⟩-oriented 0.69PMN–0.31PT single crystal measured at frequencies of 100 Hz, 1 kHz and 10 kHz in the cooling runs. (The note on the arrow indicates the value of applied dc bias.)

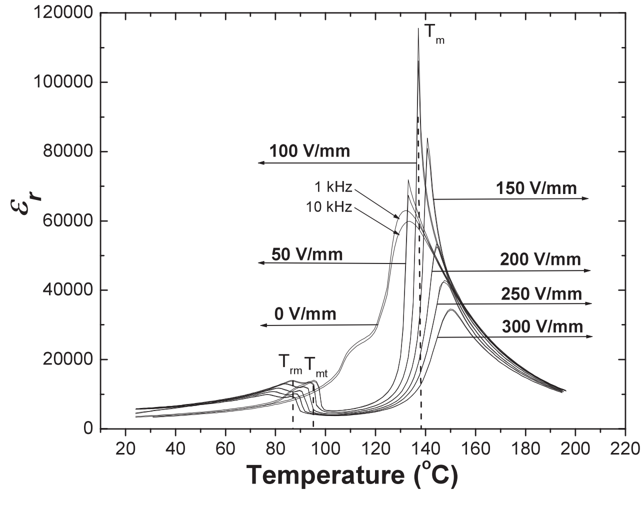

Figure 7. Temperature and dc bias dependence of relative permittivity in the ⟨001⟩-oriented 0.69PMN–0.31PT single crystal measured at frequencies of 1 and 10 kHz in the heating runs. (The note on the arrow indicates the value of applied dc bias.)

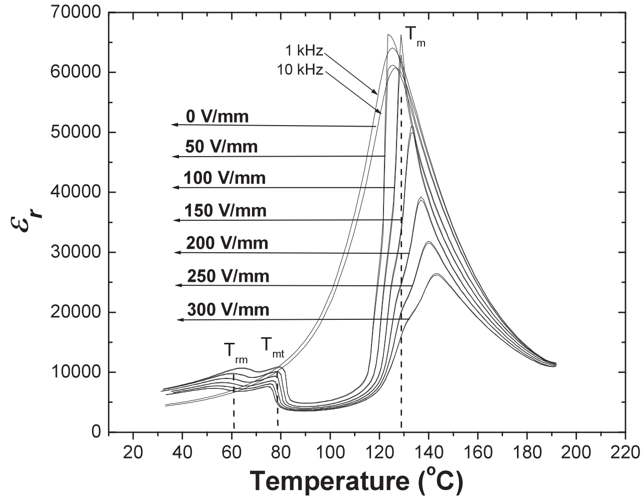

Figure 8. Temperature and dc bias dependence of relative permittivity in the ⟨001⟩-oriented 0.69PMN–0.31PT single crystal measured at frequencies of 1 and 10 kHz in the cooling runs. (The note on the arrow indicates the value of applied dc bias.)

4. Summary

In conclusion, our investigation has shown that the 0.69PMN–0.31PT single crystal has a microdomain FE_r–microdomain FE_t phase transition in the ferroelectric phase at zero bias. 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 ⟨111⟩-applied bias field could affect the domain state, i.e., the microdomain state or the macrodomain state, and phase transition temperatures. However, the electric field applied along the ⟨011⟩ or ⟨001⟩ direction could also induce an FE_o or an FE_m phase, respectively, between the FE_r and FE_t phases in the intermediate temperature range. It is also speculated that an electric field with appropriate value applied on the ⟨001⟩-oriented 0.69PMN–0.31PT single crystal could induce a dominant FE_m phase at room temperature and produce excellent room temperature piezoelectric properties.

Acknowledgments

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