Dielectric behavior and phase transition in [111]-oriented PIN-PMN-PT single crystals under dc bias

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Temperature and electric field dependences of the dielectric behavior and phase transition for [111]-oriented 0.23PIN-0.52PMN-0.25PT (PIN-PMN-0.25PT) and 0.24PIN-0.43PMN-0.33PT (PIN-PMN-0.33PT) single crystals were investigated over a temperature range from -100°C to 250°C using field-heating (FH) dielectric measurements. The transition phenomenon from ferroelectric microdomain to macrodomain was found in rhombohedra (R) phase region in the single crystals under dc bias. This transition temperature T_f of micro-to-macrodomain is sensitive to dc bias and move quickly to lower temperature with increasing dc bias. The phase transition temperatures in the two single crystals shift toward high temperature and the dielectric permittivities at the phase transition temperature decrease with increasing dc bias. Especially, the phase transition peaks are gradually broad in PIN-PMN-0.33PT single crystal with the increasing dc bias. Effects of dc bias on the dielectric behavior and phase transition in PIN-PMN-PT single crystals are discussed.

Keywords: PIN-PMN-PT single crystal; electric field; phase transition; dielectric.

1. Introduction

The relaxor-based single crystal $\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3\text{-Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (PIN-PMN-PT) with morphotropic phase boundary (MPB) composition have excellent piezoelectric properties of $d_{33} \sim 2000 \text{ pC/N}$ and $k_{33} \sim 95\%$, meanwhile the depoling temperature is higher $20\text{--}30^{\circ}\text{C}$ than that of binary $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (PMN-PT) single crystal. Due to these merits, many studies have been carried out on the relationship between piezoelectric properties and MPB compositions.^{1–3} For PMN-PT single crystals, the dielectric properties and phase transition characteristics under dc bias were systematically studied.^{4–7} It was found that the appearance/stability of the intermediate phases is strongly dependent on the direction and strength of the electric field and the orientation of the crystal.⁴ For PMN-PT single crystal with MPB composition, the intermediate M and O phases can be induced during the field heating process for both the [110]- and [001]-oriented crystals but not for the [111]-oriented crystals. For 0.76PMN-0.24PT single crystal with composition far away from MPB, the diffusion index under dc bias along [001], [011] and [111] direction was closely related with the value, not the direction, of dc bias.⁸ Comparing to PMN-PT single crystals, the dielectric properties and phase transition characteristics of PIN-PMN-PT single crystal under dc bias will

possibly be more complicated than that in PMN-PT single crystals due to multiple B site ions.

Owing to the inevitable compositional segregation in the PIN-PMN-PT crystal growth process, the composition along the crystal growth direction is also different,⁹ resulting in variation of dielectric properties and phase transition characteristics. In this paper, the dielectric behavior and phase transition characteristics of [111]-oriented 0.23PIN-0.52PMN-0.25PT (PIN-PMN-0.25PT, R phase composition) and 0.24PIN-0.43PMN-0.33PT (PIN-PMN-0.33PT, MPB composition) single crystals under different electric fields along [111] direction were characterized over a broad temperature range from -100°C to 250°C . The microdomain to macrodomain transition was found, which would lead to a good understanding of the dielectric behavior of the ternary single crystal.

2. Experimental Procedure

PIN-PMN-PT single crystal was grown by a modified Bridgman method. The composition of the single crystals were analyzed by an electron probe X-ray microanalyzer (EPMA, JEOL JXA-8230 superprobe).¹⁰ [111]-oriented PIN-PMN-0.25PT and PIN-PMN-0.33PT single crystals of

size of $5 \times 5 \times 0.5 \text{ mm}^3$ were chosen for dielectric measurements. Silver electrodes were fired on both faces of the samples at 600°C for 25 min. Dielectric measurements were performed at frequencies of 0.1, 1, 10 and 100 kHz, respectively, over a temperature range from -100°C to 250°C with a heating rate of $2^\circ\text{C}\cdot\text{min}$ by using an automated system where a computer was employed to control a Delta temperature box, an HP4284A LCR meter, and a high voltage generator (Model PS350/5000V-25W, Stanford research system, INC.). The dielectric properties of the samples were measured using field-heating (FH) process, in which the sample was heated under a constant dc bias along [111] direction. The dc bias was from 0 to $5 \text{ kV}\cdot\text{cm}^{-1}$. To eliminate the influence of the sample history on the results, all the samples were annealed at 400°C for 2 h prior to the dielectric measurements.

3. Results and Discussion

Temperature dependence of dielectric permittivity (ϵ') at 0.1, 1, 10, and 100 kHz and loss ($\tan \delta$) at 1 kHz for [111]-oriented PIN-PMN-0.25PT single crystal under dc bias of 0, 1, 2, 3 and $4 \text{ kV}\cdot\text{cm}^{-1}$ is shown in Figs. 1(a)–1(e), respectively. As shown in Fig. 1(a), without dc bias, the obvious dielectric permittivity frequency dependence can be seen near $T_m \sim 150^\circ\text{C}$ (peak I) with $\Delta T_{\text{dispersion}} (= T_{m,100 \text{ kHz}} - T_{m,0.1 \text{ kHz}}) = 8.4^\circ\text{C}$. The $\tan \delta$ is found to remain substantially unchanged with a value of 0.06 in the range from room temperature to 110°C , and increases to a maximum value of 0.09 near 135°C , which is determined to be the phase transition of rhombohedral (R) to Cubic (C) phase.¹¹ It is noted that the loss peaks around 0°C for all samples are related to water vapor during the measurement process.

Under dc bias of $1 \text{ kV}\cdot\text{cm}^{-1}$, the peak labeled T_f observed near 50°C is found, which is a new phenomenon heretofore unobserved in PIN-PMN-PT system. Below T_f , the dielectric permittivity frequency dispersion is shown in inset of Fig. 1(b). When the temperature is once over T_f , ϵ' and $\tan \delta$ have clear step-like decrease from ~ 2450 to ~ 900 and from ~ 0.063 to ~ 0.016 at 1 kHz, respectively, and the frequency dispersion of ϵ' almost disappears, as shown in Fig. 1(b). By increasing the temperature further, a sharp dielectric peak A can be clearly seen near 125°C , and the temperature corresponding to which is nearly independent of frequency and the dielectric peak values decrease with increasing frequency. The dielectric permittivity frequency dispersion near $T_m \sim 150^\circ\text{C}$ (peak I) is also evident with $\Delta T_{\text{dispersion}} = 8.3^\circ\text{C}$ and disappear above $\sim 160^\circ\text{C}$. The dielectric permittivity peak actually reflects two processes: one is the phase transition R-to-C (peak A) and the other is the ferroelectric relaxor process (peak I). It means that the phase transition and relaxor process could be split under small dc bias.

The dielectric anomaly at temperature T_f is assumed to be the micro-macro domain transition.¹² When the temperature is below T_f , the polar region and part of microdomains with arbitrary polarization direction exist. The thermal energy is not sufficient to overcome the barrier of dipole reversion, resulting in evident dielectric dispersion. Thermal energy overcomes the barrier of dipole reversion when the temperature is above T_f . So the dipoles in microdomains are arranged along the direction of dc bias resulting in the rapid reduction of dielectric dispersion and dielectric loss in Fig. 1(b).

Similarly to $1 \text{ kV}\cdot\text{cm}^{-1}$, T_f is also observed around 0°C , -30°C , -50°C when dc bias is 2, 3 and $4 \text{ kV}\cdot\text{cm}^{-1}$, respectively, as shown in Figs. 1(c)–1(e). With the increase of dc bias, T_f clearly moves to lower temperature. It can also be found that T_f is sensitive to dc bias. When dc bias is increased, the dynamics of micro-domains reconstruction is accelerated and the thermal energy needed to overcome the barriers of dipole's reversion in microdomain decreases. Therefore, the transition temperature of microdomain to macrodomain moves to lower temperature.

Compared to Fig. 1(b), the dielectric peak A is found to disappear or move to higher temperature and merge together with T_m under dc bias of $2 \text{ kV}\cdot\text{cm}^{-1}$, as shown in Fig. 1(c). The dielectric dispersion at T_m is also evident with $\Delta T_{\text{dispersion}} = 11.8^\circ\text{C}$. With the further increase of dc bias, dielectric dispersion around T_m decreases greatly with $\Delta T_{\text{dispersion}} = 3.4^\circ\text{C}$ and 1.8°C when dc bias increases to $3 \text{ kV}\cdot\text{cm}^{-1}$ (Fig. 1(d)) and $4 \text{ kV}\cdot\text{cm}^{-1}$ (Fig. 1(e)). Dielectric dispersion $\Delta T_{\text{dispersion}}$ also decreases with increase of dc bias for enhancement of orientation of dc bias on macrodomain.

Comparing to PIN-PMN-0.25PT single crystal with R phase, the ϵ' - T curve under dc bias for PIN-PMN-0.33PT single crystal with MPB composition is more complicated, as seen in Fig. 2. Only one dielectric peak (peak I) near 194°C is found with weak dielectric permittivity frequency dispersion of $\Delta T_{\text{dispersion}} = 0.9^\circ\text{C}$ under $0 \text{ kV}\cdot\text{cm}^{-1}$ dc bias, as shown in Fig. 2(a). The dielectric permittivity frequency dispersion of PIN-PMN-PT single crystal reduces with the increase of PT content, comparing to Figs. 1(a) and 2(a). As dc bias increases to $1 \text{ kV}\cdot\text{cm}^{-1}$ (Fig. 2(b)), Peak I splits into two peaks and the corresponding temperatures are 186°C and 191°C , respectively. The dielectric peak around 186°C is found to be sharper than the peak around 191°C . The shape of dielectric peak I is similar to the “ λ -like” dielectric-permittivity peak in [111]-oriented 0.68PMN-0.32PT single crystal under electric fields.⁴ A peak at 186°C is corresponding to the transition of tetragonal (T) phase to Cubic (C) phase. The peak position is independent of frequency, and the peak value decreases with increase of frequency. Another peak at 191°C is corresponding to the ferroelectric relaxor process with $\Delta T_{\text{dispersion}} = 1.7^\circ\text{C}$. On the lower temperature side of peak I, peak II at 130°C is found to be related to R-to-T phase transition. The dielectric loss double peaks corresponding to

Fig. 1. Temperature dependence of dielectric permittivity at 0.1, 1, 10 and 100 kHz and loss at 1 kHz for PIN-PMN-0.25PT single crystal during FH with different dc biases: (a) $0 \text{ kV} \cdot \text{cm}^{-1}$, (b) $1 \text{ kV} \cdot \text{cm}^{-1}$, (c) $2 \text{ kV} \cdot \text{cm}^{-1}$, (d) $3 \text{ kV} \cdot \text{cm}^{-1}$ and (e) $4 \text{ kV} \cdot \text{cm}^{-1}$.

peak II can be clearly seen, and the loss peak on the lower temperature side may be related to the phase transition of R to O, the loss peak on the higher temperature side may be related to the phase transition of O to T.¹³ Therefore, the phase

transition sequence for [111]-oriented PIN-PMN-0.33PT single crystal under dc bias during heating process may be $R \rightarrow O \rightarrow T \rightarrow C$. However, the temperature region of O phase is very narrow.

Fig. 2. Temperature dependence of dielectric permittivity at 0.1, 1, 10 and 100 kHz and loss at 1 kHz for PIN-PMN-0.33PT single crystal during FH with different dc biases: (a) $0 \text{ kV} \cdot \text{cm}^{-1}$, (b) $1 \text{ kV} \cdot \text{cm}^{-1}$, (c) $2 \text{ kV} \cdot \text{cm}^{-1}$, (d) $3 \text{ kV} \cdot \text{cm}^{-1}$, (e) $4 \text{ kV} \cdot \text{cm}^{-1}$ and (f) $5 \text{ kV} \cdot \text{cm}^{-1}$.

An interesting phenomenon similar to Fig. 1 is found around the temperature of 70°C (T_f), below which dielectric permittivity is dependent on frequency, and above which dielectric permittivity is nearly independent of frequency, as

can be clearly seen in the insets of Fig. 2(b). When the temperature increases over $T_f \sim 70^\circ\text{C}$, dielectric permittivity and loss at 1 kHz decrease quickly from ~ 2938 to ~ 868 and from ~ 0.040 to ~ 0.012 , respectively. Under dc bias of

Fig. 3. Temperature dependence of dielectric permittivity at 1 kHz during heating process under dc biases for [111] single crystal with different compositions: (a) PIN-PMN-0.25PT and (b) PIN-PMN-0.33PT.

$1 \text{ kV} \cdot \text{cm}^{-1}$, the change of dielectric properties around 70°C is similar to that around 50°C for PIN-PMN-0.25PT single crystal.

With the increase of dc bias, peak I and peak II move to higher temperature, while T_f moves to lower temperature, as can be seen in Figs. 2(c)–2(f). When dc bias increases to $5 \text{ kV} \cdot \text{cm}^{-1}$, peak II and peak II are broad, and move to 212.7°C and 166.3°C , with dielectric permittivity of 14,700 and 10,200, respectively, along with T_f moving to -57°C .

Another interesting phenomenon can be found in dielectric loss corresponding to peak II under dc bias of $2 \text{ kV} \cdot \text{cm}^{-1}$ with only one peak in Fig. 2(c), unlike the double loss peaks in Fig. 2(b). The double loss peaks corresponding to peak II reappear when the dc bias further increases to $3 \text{ kV} \cdot \text{cm}^{-1}$, and disappear under $5 \text{ kV} \cdot \text{cm}^{-1}$. It can be known that the loss peak on the lower temperature side may be related to the phase

transition of R to O, the loss peak on the higher temperature side may be related to the phase transition of O to T. Therefore, it can be speculated that the dielectric loss peaks related to peak II is sensitive to dc bias, that is, O phase is unstable and sensitive to dc bias in [111]-oriented PIN-PMN-PT single crystal.

Temperature dependence of dielectric permittivity at 1 kHz under different dc bias for PIN-PMN-0.25PT and PIN-PMN-0.33PT single crystals is shown in Figs. 3(a) and 3(b), respectively. It can be seen that the ϵ' -T curve for PIN-PMN-0.33PT single crystal in Fig. 3(b) is more complicated than that for PIN-PMN-0.25PT single crystal in Fig. 3(a). Dielectric peak II in Fig. 3(b), related to phase transition of R to T, is found to move to higher temperature with the increase of dc bias. For PIN-PMN-0.33PT existed in the MPB of PIN-PMN-PT system, determined from previous works,¹⁰ multiphase coexist with nearly the same free energy and the T phase can be easily induced by combined effect of dc bias and temperature. For 24PIN-PMN-32PT single crystals with MPB compositions, dc bias can also stabilize the R phase under large signal stress-strain.¹⁴ As PIN-PMN-0.33PT single crystal at low temperature belongs to rhombohedral phase with spontaneous polarization [111] direction, dc bias applied along [111] direction can increase the R phase stability, and then expand the temperature range where R phase exists, making the phase transition temperature of R to T move to higher temperature.

The transition temperature T_f of ferroelectric microdomain to macrodomain for [111]-oriented PIN-PMN-PT single crystal moves to lower temperature with the increase of dc bias whether the PT content is low or high, as shown in Fig. 4. It is also found that T_f for [111]-oriented PIN-PMN-0.33PT single crystal is higher than that for PIN-PMN-0.25PT single crystal under the same dc bias, except $2 \text{ kV} \cdot \text{cm}^{-1}$. We carried out the same dielectric measurements on [111]-oriented PMN-0.32PT single crystal. But T_f was not found.⁴ Although the reason for T_f is not clear, T_f depends on the composition of the single crystal and the strength of the electric field.

Fig. 4. T_f as a function of dc bias for [111]-oriented PIN-PMN-PT single.

Fig. 5. The dc bias dependence of the dielectric permittivity at 1 kHz for [111]-oriented crystals at room temperature.

The dc bias dependence of the dielectric permittivity at 1 kHz for [111]-oriented crystals with different compositions at room temperature are depicted in Fig. 5. It is found that dielectric permittivity of these two crystals under $0 \text{ kV} \cdot \text{cm}^{-1}$ are nearly same with the value of ~ 2000 . When dc bias increase to $1 \text{ kV} \cdot \text{cm}^{-1}$, dielectric permittivity increase slightly to ~ 2100 and then decrease quickly to ~ 500 under dc bias of $2 \text{ kV} \cdot \text{cm}^{-1}$. When the dc bias is more than $2 \text{ kV} \cdot \text{cm}^{-1}$, the dielectric permittivity is essentially unchanged. It is well known that the dielectric permittivity of PIN-PMN-PT crystal along the spontaneous polarization [111] direction is less than that along other direction. Part of the ferroelectric domains is arranged along the direction of dc bias when dc bias is not so high enough. As dc bias along [111] direction is over $2 \text{ kV} \cdot \text{cm}^{-1}$, ferroelectric domains are arranged almost along electric field, resulting in the significant reduction of dielectric permittivity.

4. Conclusion

The dielectric behavior and phase transition induced by electric field and temperature for [111]-oriented PIN-PMN-0.25PT and PIN-PMN-0.33PT single crystals were investigated. The transition temperatures T_f of ferroelectric microdomain to macrodomain in R phase region is found. T_f depends on the composition of the single crystal and the strength of the electric field. For [111]-oriented PIN-PMN-0.25PT single crystal, the phase transition temperature of R-to-C increases and the dielectric permittivity decreases at phase transition peaks with increasing dc bias. In PIN-PMN-0.33PT single crystal, T phase and O phase can be induced by combined effect of dc bias and temperature. The O phase is unstable and sensitive to dc bias. The phase transition path is $R \rightarrow (\text{or } O) \rightarrow T \rightarrow C$. The phase transition temperatures move to high temperature and the phase transition peaks of T-to-C were clearly broad with the increasing dc bias.

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