Composition and orientation dependence of phase configuration and dielectric constant tunability in poled Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$–PbTiO$_3$ single crystals

Composition and orientation dependence of phase configuration and dielectric constant tunability in poled Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$–PbTiO$_3$ single crystals

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Abstract

The composition and orientation dependence of the room temperature piezoelectric constant d_{33} and the dielectric constant tunability was investigated in poled single crystals of $(1 - x)$Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$–xPbTiO$_3$ (PMN–PT) with x varying from 0.24 to 0.38. The temperature, frequency, orientation and composition dependence of the dielectric constant in the poled crystals shows that domain configurations and phase transitions in the poled crystals strongly depend on both composition and orientation. Poled polydomain crystals near the morphotropic phase boundary, especially for $\langle 001 \rangle$-poled 0.70PMN–0.30PT crystals with a critical composition for the relaxor state, possess a large piezoelectric constant $d_{33} = 2210$ pC N^{-1} and a high dielectric constant tunability of 40.6% (at a dc bias of 1 kV mm^{-1}). The large tunability of ε_r in PMN–PT crystals is expected to be the most promising candidate for potential applications in continuously adjustable capacitors and dielectric amplifiers.

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 the ferroelectric rhombohedral (FE$_r$) and tetragonal (FE$_t$) phases, have promising potential for applications in transducers, sensors and actuators due to their ultra-high 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]. They also have the potential benefit to be used in electro-optical technology due to their high electro-optical coefficients [5, 6]. The origins of their excellent performance have

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been attributed to the polarization rotation induced by the external electric field [7]. However, the role of possible metastable ferroelectric monoclinic (FE$_m$) and ferroelectric orthorhombic (FE$_o$) phases has also been emphasized [8–12].

At room temperature, the MPB of the $(1 - x)$Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$–xPbTiO$_3$ system is at about $x = 0.34$. For compositions with $x \geqslant 0.35$, the crystal structure is tetragonal *4mm*, while for those with $x \leqslant 0.33$, the crystal symmetry is rhombohedral *3m* [13]. However, recently a larger width of the MPB region $(0.30 < x < 0.35)$ has been proposed by Guo *et al* [11, 12] for $\langle 001 \rangle$ and $\langle 011 \rangle$ oriented PMN–PT crystals on the basis of two abnormal regions of the dielectric and piezoelectric properties. It is known that crystal composition, crystallographic orientation, electric field, and temperature all have strong influence on the phase transition and effective materials properties of PMN–PT single crystals [1–13]. The purpose of this paper is to understand the phase structure and the dielectric nonlinearity behaviour in a series of poled PMN–PT single crystals with different orientations by investigating their dielectric response under a dc bias.

2. Experiment

The $(1-x)$PMN–xPT single crystals used in this work were grown using a modified Bridgman technique with nominal compositions $x = 0.24, 0.30, 0.33$ and 0.38, respectively [14]. Various crystals oriented along the $\langle 001 \rangle$, $\langle 011 \rangle$ and $\langle 111 \rangle$ directions were prepared with dimensions of about $5 \times 5 \times 1$ mm^3, and they were coated with silver electrodes. It was reported that the segregation behaviour during the growth results in a variation of the PbTiO$_3$ (PT) content along the longitudinal direction of a boule, so the compositions of $(1 - x)$PMN–xPT crystals were determined by measurement of the dielectric maximum temperature (T_m) in our experiments. The samples were poled in silicon oil under an applied field of 10 kV cm^{-1} for 15 min near the dielectric maximum temperature (T_m) and cooled down to room temperature. The piezoelectric coefficients (d_{33}) were measured by a Berlincount-type quasistatic meter at about 55 Hz. The dielectric properties of the poled crystals were measured using an HP4194A impedance analyser at frequencies of 100 Hz, 1 kHz and 10 kHz in the temperature range between 25 and 230 °C at a constant heating rate of 1 °C min^{-1}.

The dielectric response under a dc bias was measured by a multi-frequency LCR Meter (Model SR720 of Stanford Research Systems) at a frequency of 10 kHz while the crystal was placed in silicone oil. The applied dc bias varied from 0 to 1000 V mm^{-1}. The dc bias was applied on the samples in the same direction as the poling field in order to prevent the occurrence of polarization reversal. Each time the dc bias was applied, a waiting time of 100 s was imposed before measuring the dielectric constant.

3. Results and discussions

3.1. Dielectric and phase transition behaviour of poled PMN–PT single crystals

The dielectric constants ε_r as a function of temperature and frequency (0.1, 1 and 10 kHz) for $\langle 001 \rangle$-, $\langle 011 \rangle$- and $\langle 111 \rangle$-poled PMN–PT single crystals with different compositions, respectively, are presented in figures 1(a)–(c). For the poled 0.76PMN–0.24PT single crystals, whether in the $\langle 001 \rangle$, $\langle 011 \rangle$ or $\langle 111 \rangle$ direction, each one shows two peaks T_d (∼85 °C) and T_m (∼110 °C); the ferroelectric phase transition between the FE$_t$ and the paraelectric cubic phases takes place near T_m. The absence of frequency dispersion of relative permittivity in the temperature range between 25 °C and T_d indicates a macrodomain ferroelectric state in the poled crystals, which has been built up by the poling field. However, some frequency
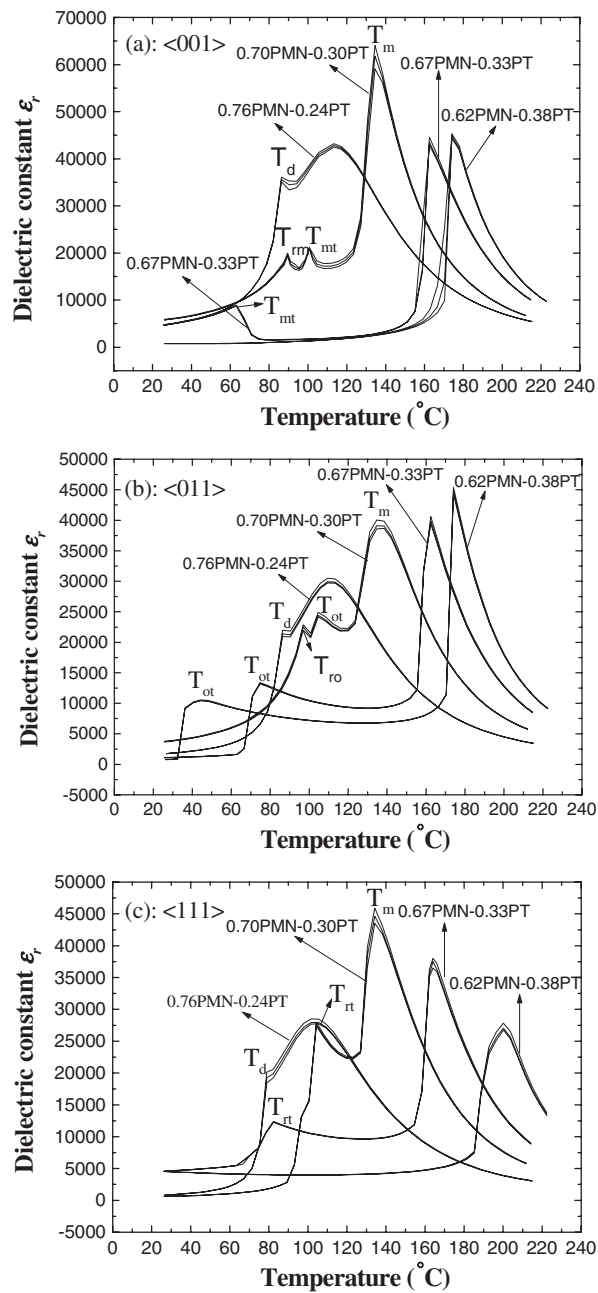
Figure 1. The composition and temperature dependence of the dielectric constant (100 Hz, 1 kHz and 10 kHz) in poled $(1 - x)$PMN–xPT crystals with a probing field applied along (a) $\langle 001 \rangle$, (b) $\langle 011 \rangle$ and (c) $\langle 111 \rangle$, respectively.

dispersion of the permittivity for the temperature range between T_d and T_m is observed, indicating a microdomain relaxor state. T_d is usually considered to be related to the decay of the macrodomain state into a microdomain state in the heating process, and is similar to

Table 1. Summary of the room-temperature phase structure, domain state, room temperature piezoelectric constant d_{33} and dielectric constant tunability at a dc bias of 1 kV mm^{-1} in poled $(1-x)$PMN–xPT single crystals.

Composition x	Crystal orientation	Phase structure	Domain state	$\varepsilon_r(0)$ 10 kHz	d_{33} (pC N^{-1})	ε_r tunability (%) 1 kV mm^{-1}, 10 kHz
0.24	⟨001⟩	FE$_r$	Polydomain	3995	770	25.9
0.30	⟨001⟩	FE$_r$	Polydomain	5210	2210	40.6
0.33	⟨001⟩	FE$_m$	Polydomain	3167	1870	34.2
0.38	⟨001⟩	FE$_t$	Monodomain	828	400	20.7
0.24	⟨011⟩	FE$_r$	Polydomain	1679	350	26.3
0.30	⟨011⟩	FE$_r$	Polydomain	3770	1100	35.1
0.33	⟨011⟩	FE$_o$	Monodomain	849	260	32.4
0.38	⟨011⟩	FE$_o$	Monodomain	996	300	30.8
0.24	⟨111⟩	FE$_r$	Monodomain	867	100	18.7
0.30	⟨111⟩	FE$_r$	Monodomain	608	100	14.8
0.33	⟨111⟩	FE$_r$ and FE$_t$	Polydomain	4409	550	73.4
0.38	⟨111⟩	FE$_t$	Polydomain	5679	500	25.3

the characteristic temperature T_d in relaxors containing lanthanum zirconate titanate (PLZT 8:65:35) and PMN [15, 16]. In ⟨001⟩-poled 0.7PMN–0.3PT crystals, as shown in figure 1(a), two small permittivity peaks can be observed at T_{rm} and T_{mt}, respectively. The first small peak T_{rm} coincides with a transition from the FE$_r$ state to an FE$_m$ state, while the second small peak indicates the transition from the FE$_m$ to an FE$_t$ state [11, 12]. Similarly, for ⟨011⟩-poled 0.7PMN–0.3PT crystals, there are also two small permittivity peaks at T_{ro} and T_{ot}, respectively, an orthorhombic ferroelectric (FE$_o$) phase being intermediate between the lower temperature FE$_r$ phase and the higher temperature FE$_t$ phase, similar to the result of ⟨011⟩-poled 0.67PMN–0.33PT in [9].

It has been reported that a dominant FE$_m$ phase can be induced by a large poling field applied along the ⟨001⟩ direction in PMN–PT single crystals with compositions near the MPB at room temperature [11, 17]. This has been used to interpret the origin of the excellent piezoelectric property of the single crystals. Here we speculate that in the ⟨001⟩-poled 0.67PMN–0.33PT crystal, whose composition is close to the MPB, a stable FE$_m$ phase induced by the ⟨001⟩-applied poling field should exist at room temperature. As the temperature increases, the FE$_m$ phase forms into the higher temperature FE$_t$ phase near the small peak T_{mt} ($\sim$62 °C). However, for ⟨011⟩-poled 0.67PMN–0.33PT and tetragonal 0.62PMN–0.38PT crystals, the poling along the non-polar ⟨011⟩ direction gives rise to a much smaller dielectric constant of $\sim$800 and piezoelectric constant of $\sim$300 pC N^{-1}, which coincide with those in the induced FE$_o$ phase from ⟨011⟩-poled PMNT crystals near the MPB [9, 11]. This indicates that the poling field along the ⟨011⟩ direction can induce a stable monodomain orthorhombic ferroelectric phase, whose spontaneous polarization is along the ⟨011⟩ direction. As the temperature increases, at the dielectric shoulder T_{ot}, the FE$_o$ phase also forms into the higher temperature FE$_t$ phase. For ⟨111⟩-poled 0.70PMN–0.30PT and 0.67PMN–0.33PT crystals, a dielectric phase-transition peak T_{rt} between the FE$_r$ and FE$_t$ phases is observed. Even for poled 0.67PMN–0.38PT tetragonal crystals, near the dielectric peak T_m corresponding to the FE$_t$-cubic phase transition, the frequency dispersion behaviour of the permittivity is still observed.

The measured piezoelectric constants d_{33} of the poled crystals are summarized in table 1. For ⟨001⟩-oriented crystals near the MPB, the metastable phases and the polarization rotation have been emphasized to be capable to enhance the piezoelectric properties [7–12].
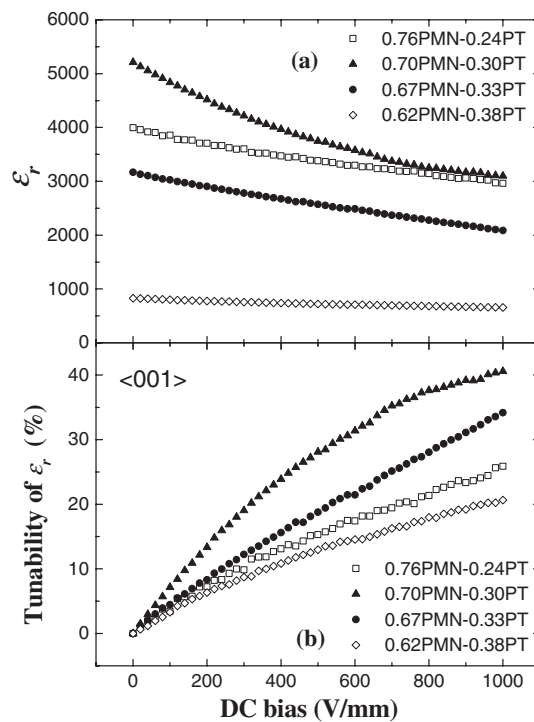
Figure 2. The dc bias and composition dependence of (a) the dielectric constant ε_r and (b) the tunability of ε_r in $\langle 001 \rangle$-poled $(1 - x)$PMN–xPT crystals measured at a frequency of 10 kHz.

Correspondingly, these crystals with x as 0.3 and 0.33 have a piezoelectric constant that is larger than 1500 pC N^{-1}, as shown in table 1. However, for the poled crystals with a monodomain state, their piezoelectric constants are much lower than 400 pC N^{-1}. But here it should be noted that the largest piezoelectric constant d_{33} of 2210 pC N^{-1} is found in the $\langle 001 \rangle$-oriented crystal with the critical composition x of 0.30 for the relaxor state.

3.2. Dielectric constant tunability under dc bias

Figures 2(a) and (b) show the dc bias and composition dependence of the dielectric constant ε_r and of the tunability of ε_r, respectively, for $\langle 001 \rangle$-poled crystals measured under various dc bias at room temperature. The tunability of ε_r at the dc bias of E_b is defined as $[\varepsilon_r(0) - \varepsilon_r(E_b)] \times 100\%/\varepsilon_r(0)$, where $\varepsilon_r(0)$ and $\varepsilon_r(E_b)$ are the dielectric constant ε_r at zero dc bias and at a bias of E_b, respectively. The data of $\varepsilon_r(0)$ and of the tunability of ε_r at the bias of 1 kV mm^{-1} in the $\langle 001 \rangle$-poled crystals are also listed in table 1. The results also reveal the largest tunability of ε_r, with a large value of 40.6% at a dc bias of only 1 kV mm^{-1}, in the 0.70PMN–0.30PT crystal with a critical composition for the relaxor state, while also a large dielectric tunability (34.2%) occurs in a $\langle 001 \rangle$-poled 0.67PMN–0.33PT crystal. The largest dielectric tunability reflects the most significant structure adaptivity of the engineered domain configuration, in which the applied electric field easily induces large lattice distortion with compensating strain in the polar domain equivalent being symmetrically distributed along $\langle 001 \rangle$ [1]. However, it should not be excluded that the applied electric field should also induce a polarization rotation from $\langle 111 \rangle$ to $\langle 001 \rangle$ in an advantageous path through metastable phases in
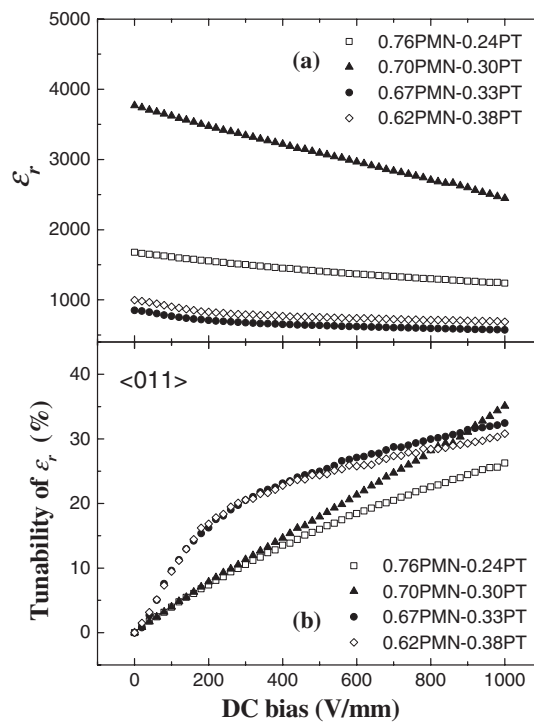
Figure 3. The dc bias and composition dependence of (a) the dielectric constant ε_r and (b) the tunability of ε_r in $\langle 011 \rangle$-poled $(1 - x)$PMN–xPT crystals measured at a frequency of 10 kHz.

the 0.70PMN–0.30PT crystal also with a MPB composition, which also produces high structure adaptivity [7]. In both cases, we believe that the critical relaxor state plays an important role, as shown by the largest susceptibility of the 0.70PMN–0.30PT crystal. Thus the relaxor state contributes greatly to the sensitive engineered domain configuration and polarization rotation through metastable phases under an electric field, and resultantly contributes greatly to structure adaptivity, piezoelectric susceptibility and dielectric constant tunability.

Figures 3(a) and (b) show the dc bias and composition dependence of the dielectric constant ε_r and tunability of ε_r for $\langle 011 \rangle$-poled crystals, respectively, measured under various dc bias at room temperature. Similarly, the $\langle 011 \rangle$-poled polydomain 0.70PMN–0.30PT crystal also has the largest dielectric tunability (35.1%) at a bias of 1 kV cm^{-1}, which may be attributed to the induced FE$_r$–FE$_o$ phase transition.

For the $\langle 111 \rangle$-poled 0.67PMN–0.33PT crystal, as presented in figures 4(a) and (b), the largest ε_r tunability (73.4%) can be obtained at the 1 kV mm^{-1} bias (the dielectric constant can also reach 4409 pC N^{-1} under zero field, as shown in table 1). Due to the compositional complexity near the MPB, the FE$_r$ and FE$_t$ phases may form a manifold of coexisting phases in the $\langle 111 \rangle$-poled 0.67PMN–0.33PT crystal. Under a $\langle 111 \rangle$-oriented electric field, the FE$_t$ to FE$_r$ phase transition, i.e. the induced polarization rotation from the $\langle 100 \rangle$ to the $\langle 111 \rangle$ direction, results in a large ε_r tunability.

It should also be noted that the properties of the poled crystals with polydomain state, whose piezoelectric constant and dielectric tunability are much larger than the corresponding ones with monodomain state, are presented in table 1.
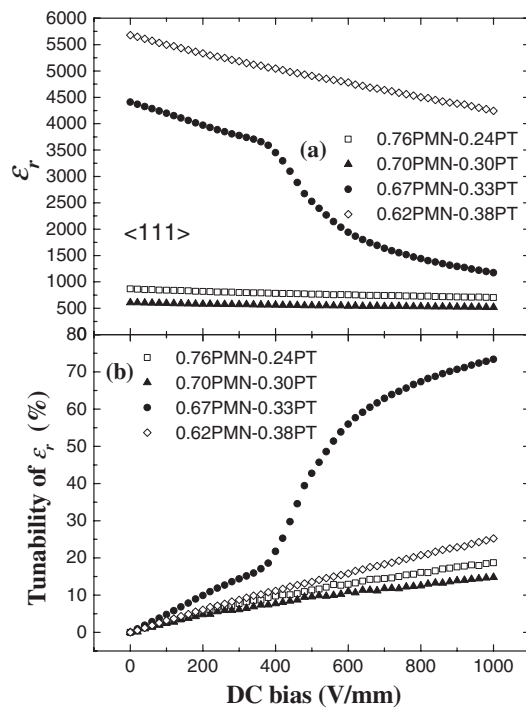
Figure 4. The dc bias and composition dependence of (a) the dielectric constant ε_r and (b) the tunability of ε_r in $\langle 111 \rangle$-poled $(1 - x)$PMN–xPT crystals measured at a frequency of 10 kHz.

4. Conclusions

In summary, in poled PMN–PT single crystals, the dielectric and piezoelectric properties strongly depend on composition and orientation. Different phase configurations and phase transitions can occur during temperature versus dielectric constant measurements. For poled $(1 - x)$PMN–xPbT crystals with x varying from 0.24 to 0.38, whether $\langle 001 \rangle$, $\langle 011 \rangle$ or $\langle 111 \rangle$, frequency dispersion of the permittivity cannot be observed near room temperature, indicating a macrodomain state after poling. An examination of the dependence of the dielectric tunability on phase structure, domain state, composition and orientation was also performed. For the $\langle 001 \rangle$ and $\langle 011 \rangle$ directions, the poled 0.70PMN–0.30PT crystals have the highest piezoelectric coefficients ($d_{33} = 2210$ pC N^{-1}) and dielectric constant tunability (40.6%), a consequence of engineered domain configuration and polarization rotation under electric field, while high ε_r tunability can also be obtained in $\langle 001 \rangle$- and $\langle 011 \rangle$-poled 0.67PMN–0.33PT crystals near the MPB. However, for the $\langle 111 \rangle$ direction, the largest ε_r tunability can reach 73.4% in the poled 0.67PMN–0.33PT crystal at 1 kV mm^{-1} bias. To summarize, the poled crystals with polydomain state have piezoelectric constants and dielectric tunabilities much larger than the corresponding monodomain state. The large tunability of ε_r in PMN–PT crystals may give the promise of potential applications in continuous adjustable capacitors and dielectric amplifiers.

Acknowledgments

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