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# Domain Configuration and Ferroelectric Related Properties of the $(110)_{cub}$ Cuts of Relaxor-Based $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ Single Crystals

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Domain configuration and ferroelectric related properties of $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ were investigated as a function of applied electric field for the $(110)_{cub}$ cuts. It was found that a single domain orthorhombic state could be achieved by applying an electric field along the direction $\langle 110\rangle_{cub}$, but the state after removing the electric field strongly depends on the composition and electric field. A qualitative analysis revealed that a slight variation in composition near morphotropic phase boundaries or in an electric field has a significant influence on domain configuration and piezoelectricity for the $(110)_{cub}$ cuts in $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$. [DOI: 10.1143/JJAP.41.1451]

KEYWORDS: lead magnesium niobate titanate, engineered domain configuration, piezoelectric coefficient, *in situ* domain observation, electric-field-induced phase transition

## 1. Introduction

A new generation of single-crystal materials such as $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3$–$xPbTiO_3$ (PMNT) and $(1-x)Pb(Zn_{1/3}Nb_{2/3})O_3$–$xPbTiO_3$ (PZNT) have revealed piezoelectric properties markedly superior to those of conventional $Pb(Zr,Ti)O_3$ (PZT) ceramics,[1–4] which have been widely used in ultrasonic transducers and strain actuators. $\langle 001\rangle_{cub}$-oriented single crystals of PMNT and PZNT in the rhombohedral phase at the compositions near their morphotropic phase boundaries (MPBs) have been reported to possess ultrahigh piezoelectric response ($k_{33} \sim 94\%$, $d_{33} \sim 2500$ pC/N) and large electric field strain values (1.7%).[1–6] The large electrically induced strain is considered to originate in an induced phase transition.[6] The term "engineered domain configuration" has been coined to describe ferroelectric crystals with high piezoelectric coefficients ($d_{33}$) and low hysteresis strain behavior, which have been poled by the application of an electric field along one of the possible polar axes of the crystal other than the zero-field polar axis,[6] creating a set of domains in which the polarizations are oriented such that their angles with respect to the poling direction are minimized. The number of such equivalent domains depends on the symmetry of the zero-field state and the direction of the applied field. As for $\langle 110\rangle_{cub}$ poled rhombohedral 3m crystals, there are two domains with two equivalent polar vectors along the [111] and $[\bar{1}\bar{1}1]$ directions.

Recently, a field-induced ferroelectric orthorhombic ($FE_o$) phase and high piezoelectric coefficients ($d_{33} \sim 1600$ pC/N) were observed for the $(110)_{cub}$ cuts in PMNT single crystals near the MPB.[7,8] Thus it is of some scientific interest to determine the range of phases existing under applied fields and it is of significant technological interest to determine the strain changes at the transitions and identify regions in which high piezoelectric coefficients can be found.

Our objective in this article is to report the dependence of domain configuration and ferroelectric related properties on composition and electric field for the $(110)_{cub}$ cuts of PMNT single crystals near the MPB.

## 2. Experimental

PMNT 68/32 crystals were grown directly from the melt by a modified Bridgman technique. Optically, PMNT 68/32 single crystals were light yellow in color. The details of preparation of PMNT single crystals and their characterization have been described elsewhere.[9,10] Single crystal plates were oriented along the $\langle 110\rangle_{cub}$ crystallographic axis as determined using an X-ray diffractometer.

For electrical characterization, plate samples with a thickness of 0.7 mm were used. Silver paste was painted on the crystal surfaces and fired at 550°C for 30 min. The samples were poled in silicon oil under an applied field of 10 kV/cm at room temperature. Dielectric properties were measured using a HP4192A impedance analyzer from room temperature to 200°C at 1 kHz, and piezoelectric constant $d_{33}$ was measured by a Berlincourt-type quasistatic meter at about 55 Hz. Electric-field-induced strain measurements were performed using a linear variable differential transducer (LVDT), which was operated at a drive frequency of 0.1 Hz and maximum applied field strength of 15 kV/cm.

In order to confirm the phase, observation of ferroelectric domain configurations under a polarizing microscope was carried out. Samples were mirror-polished to a thickness of less than 0.2 mm, and for *in situ* domain observation under DC-bias conditions, samples were prepared by polishing to a size of approximately $0.2 \times 1.5 \times 6$ mm$^3$. Their top and bottom surfaces ($1.5 \times 6$ mm$^2$) were also mirror-polished. Gold electrodes were sputtered on both sides ($0.2 \times 6$ mm$^2$), and the distance between electrodes was around 1.5 mm along the $\langle 110\rangle$ direction. Domain configuration was observed using a crossed-Nicols prism under a polarization microscope. DC-bias exposure was carried out along the $\langle 110\rangle$ direction, normal to the incident polarized light, using a high-voltage DC amplifier.

## 3. Results and Discussion

Observation of ferroelectric domain configurations confirmed that the phase of PMNT 68/32 is actually a mixture of the rhombohedral ferroelectric ($FE_r$) and monoclinic ferroelectric ($FE_m$) phases due to segregation during the growth of PMNT single crystals. The details have been described elsewhere.[7]

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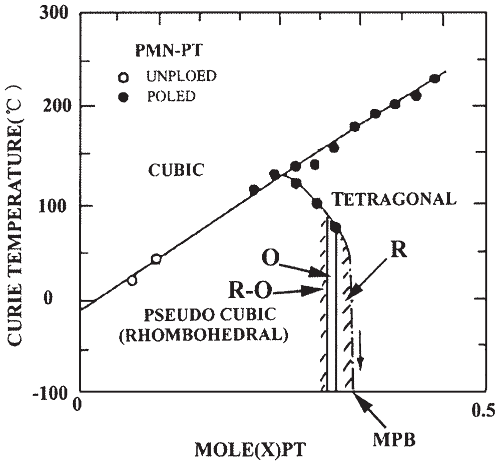

Fig. 1. Universal phase diagram of $(1-x)$ PMN–$x$PT at low temperature.

In PMNT, the Curie temperature ($T_c$) is sensitive to the content of $PbTiO_3$ (PT), thus the content of PT in the samples is determined qualitatively by measurement of $T_c$ in our experiment.[7)] It can be divided into three composition regions (denoted by "R–O", "O" and "R" regions hereafter) according to the differences in domain configuration and ferroelectric related properties (Fig. 1).

Figure 2 shows strain *VS* electric-field curves of a $\langle 110\rangle_{cub}$-oriented PMNT crystal measured using a bipolar electric field with 0.1 Hz frequency at room temperature. This measurement was performed under mechanically "free" conditions. It should be noted that these curves were obtained not in the first cycle of electric-field exposure, but after the second cycle. The shape of the $\varepsilon$–$E$ curve can be separated into three types based on the composition.

Figure 2(a) shows the strain *VS* electric-field curve of a crystal in an "R–O" composition region. Two discontinuous changes, which suggest the occurrence of electric-field-induced phase transition, and lower hysteretic strain *VS* electric-field behavior, were observed. *In-situ* observation was carried out under electric fields from 0 to 10 kV/cm. At 4 kV/cm, some $FE_o$ regions appeared partially, and a monodomain $FE_o$ state was obtained after applying an electric field of more than 5 kV/cm. When the electric field decreased to 2.5 kV/cm, it was observed that most of the region exhibits the $FE_o$ state, but some $FE_r$ (or $FE_m$) domains were also found [Figs. 3(a)–3(c)]. The above results revealed that two phase transitions occurred at 4 kVcm ($FE_r \rightarrow FE_o$) and 2.5 kV/cm ($FE_o \rightarrow FE_r$), and thus resulted in the discontinuous change as shown in Fig. 2(a). The $d_{33}$ of a polydomain $FE_o$ and $FE_r$ (or $FE_m$) state can reach a maximum of 1600 pC/N.

Figure 2(b) shows the strain *VS* electric-field curve of a crystal in a narrow "O" composition region near the MPB. A discontinuous change and strong hysteretic effects were observed, as can be observed from the difference between the forward and reverse switching fields. *In-situ* observations of domains under an applied electric field revealed that a small field (<3–4 kV/cm) can induce a polydomain orthorhombic ferroelectric ($FE_o$) and $FE_r$ (or $FE_m$) state with $d_{33}$ of 1600 pC/N, but a field higher than 4–5 kV/cm can induce a monodomain $FE_o$ state with $d_{33}$ of 300 pC/N, which can remain constant even after removal of the electric field.

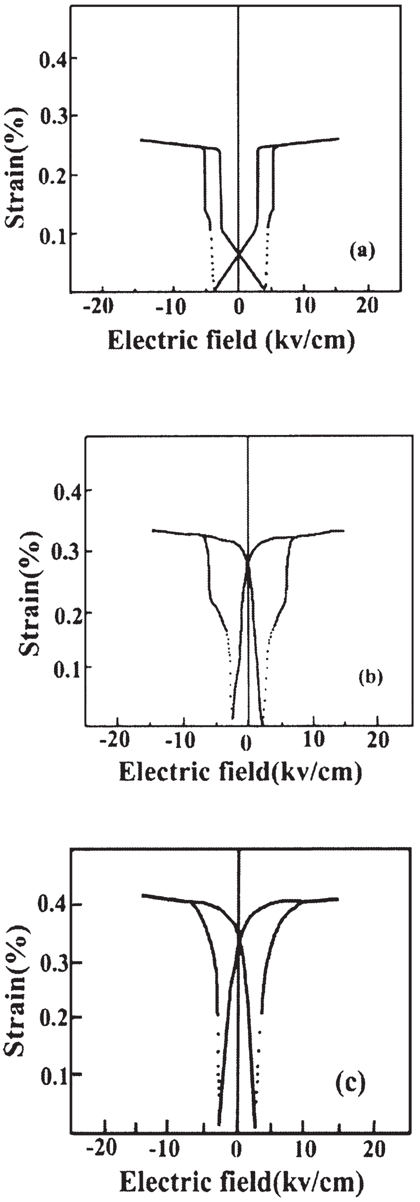

Fig. 2. Strain *VS* electric-field curves for $\langle 110\rangle_{cub}$-oriented PMNT crystal under bipolar electric field below 15 kV/cm with 0.1 Hz frequency at room temperature: (a) for crystal in an "R–O" composition region, (b) for crystal in a narrow "O" composition region, (c) for crystal in a "R" composition region.

Figure 2(c) shows the strain *VS* electric-field curve of a crystal in an "R" composition region. A continuous change and large hysteresis were observed. *In-situ* observation showed that a monodomain $FE_o$ state can also achieved under these conditions. But after removing the electric field, the sample showed a mainly polydomain $FE_r$ (or $FE_m$) state with $d_{33}$ of 300 pC/N [Figs. 3(d)–3(e)]. These results unambiguously demonstrate the presence of a fully polarizable, fully deformable $FE_o$ state, as indicated by Viehland[11)] for the $\langle 110\rangle$-oriented PZNT 92/8 crystal.

It was evident shown that the $FE_o$ phase could be induced, but was metastable with respect to the rhombohedral ferroelectric phase. These results are consistent with the phenomenological predication of Amin *et al.*[12)] They observed that a $FE_o$ phase was always present as a metastable state in PZT. On the rhombohedral side of the

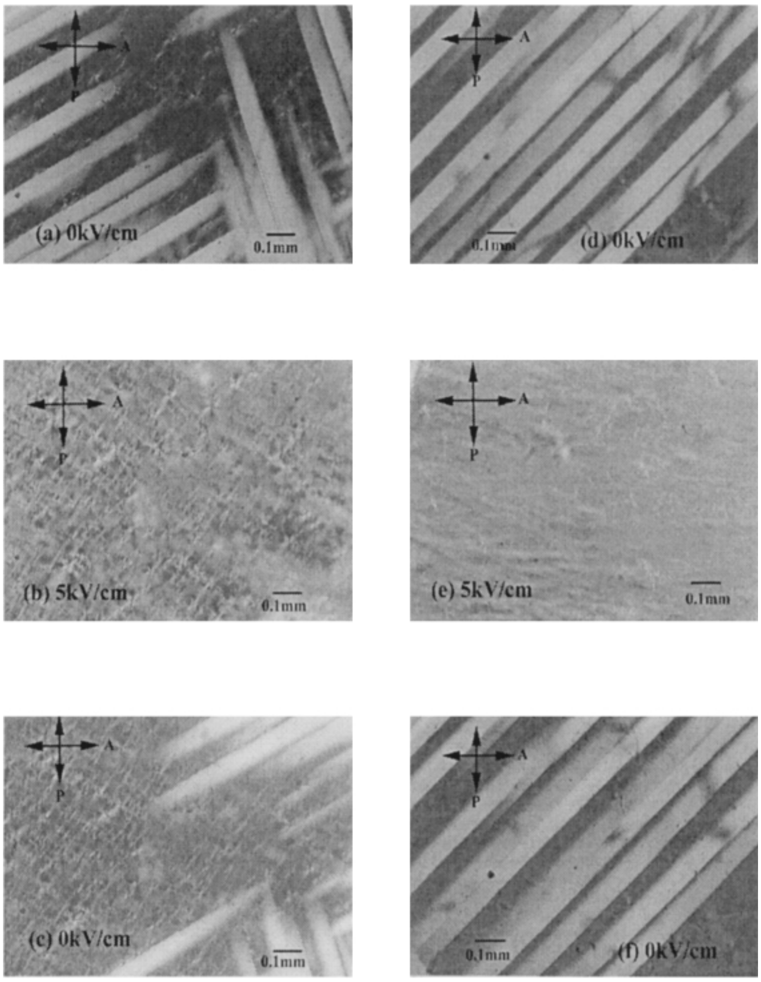

Fig. 3. *In-situ* domain observations under electric field in $\langle 110\rangle_{\mathrm{cub}}$-oriented PMNT crystal: (a), (b) and (c) for crystal in an ‘‘R–O’’ composition region; (d), (e) and (f) for crystal in a ‘‘R’’ composition region.

MPB, it was higher in free energy ($\Delta G$) than the rhombohedral phase, but lower than the tetragonal ones. We propose that this is similar to the case of PMNT. The stability of the $\mathrm{FE_o}$ state should result from the difference $\Delta G$ between the $\mathrm{FE_r}$ (or $\mathrm{FE_m}$) and $\mathrm{FE_o}$ phases, which is sensitive to the composition. The difference $\Delta G$ between $\mathrm{FE_r}$ (or $\mathrm{FE_m}$) and $\mathrm{FE_o}$ phases in the ‘‘R–O’’ composition region should be much less than that the case of in the ‘‘R’’ composition region; a monodomain orthorhombic ferroelectric phase can be held in PMNT that is closest in $\Delta G$ to the rhombohedral phase.

The higher piezoelectric coefficient and lower hysteretic strain *VS* electric-field behavior have been attribute to the term ‘‘engineered domain configuration’’ which is expected to possess three features for piezoelectric performance:[13)] (1) low hysteretic strain *VS* electric-field behavior owing to inhibition of domain wall motion, (2) higher piezoelectric coefficient along the non-polar direction along the polar direction and (3) change macroscopic symmetry in crystals with engineered domain configuration. Therefore, it is evident that the engineered domain configuration of the $(110)_{\mathrm{cub}}$ cuts of rhombohedral PMNT 68/32 crystals significantly depends on the composition and electric field. Anomalously high piezoelectric coefficient and lower hysteretic strain *VS* electric-field behavior were only found in the compositions, in which two equivalent energy states, i.e., the rhombohedral (monoclinic) and orthorhombic phases can coexist.

On the other hand, although the piezoelectric coefficient $d_{33} > 1600\,\mathrm{pC/N}$ was determined in Fig. 2(a), the maximum strain value of 0.42% was obtained in Fig. 2(c). This is consistent with the report of Yoon and Lee,[14)] who proposed that the strain value is dependent on the domain switching, piezoelectric constant, polarization, and applied electric field. Therefore, the strain in this work is maximized at a composition near the MPB.

## 4. Conclusions

Domain configuration and ferroelectric related properties of PMNT 68/32 crystals were investigated as a function of electric field applied to the $(110)_{\mathrm{cub}}$ cuts. For crystals in a narrow ‘‘O’’ composition region near the MPB or in an ‘‘R’’ composition region, when a bipolar electric field was applied along the $\langle 110\rangle_{\mathrm{cub}}$ direction, the strain *VS* electric field curve showed a large hysteresis. *In-situ* domain observation revealed that this large hysteresis was caused by a monodomain orthorhombic state with $d_{33}$ of $300\,\mathrm{pC/N}$, which can either hold or significantly recover to $\mathrm{FE_r}$ (or $\mathrm{FE_m}$) state after removal of the electric field. For crystals in an ‘‘R–O’’ composition region, low hysteretic strain *VS* electric field behavior was observed. *In-situ* domain observation revealed that this low hysteresis resulted from a relatively stable domain configuration ($FE_o$ and $FE_r$ phases coexisting) with $d_{33}$ of 1600 pC/N, which suggests the formation of the engineered domain configuration of the $(110)_{cub}$ cuts of a rhombohedral PMNT 68/32 crystals. Therefore, it is confirmed that the engineered domain configuration of the $(110)_{cub}$ cuts of rhombohedral PMNT 68/32 crystals significantly depends on the composition and electric field.

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