Field-induced polarization rotation in (001)-cut $Pb(Mg_{1/3}Nb_{2/3})_{0.76}Ti_{0.24}O_3$

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Polarization rotation of field-induced phase transformations was observed by means of a polarizing microscope on a (001)-cut single crystal $Pb(Mg_{1/3}Nb_{2/3})_{0.76}Ti_{0.24}O_3$ (PMNT24%) at room temperature with an electric field applied along the [001] direction. A hysteresis loop was also measured for comparison. As the electric field increases, polarizations of rhombohedral R domains rotate toward the [001] tetragonal T_{001} phase through M_A-type monoclinic distortions, i.e., $R \rightarrow M_A \rightarrow T_{001}$. The crystal cannot entirely reach the T_{001} phase as the field approaches 44 kV/cm. In addition, spotlike domains that perhaps correspond to M_B-type monoclinic or triclinic phases were also observed. This field-induced phase transformation is strongly irreversible.

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A morphotropic phase boundary (MPB) between rhombohedral (R) and tetragonal (T) phases originally was proposed in relaxor-based ferroelectric (FE) crystals $Pb(Mg_{1/3}Nb_{2/3})_{1-x}Ti_xO_3$ (PMNTx) and $Pb(Zn_{1/3}Nb_{2/3})_{1-x}Ti_xO_3$ (PZNTx) for $0.28 \leqslant x \leqslant 0.36$ and $x < 0.15$, respectively.[1,2] However, monoclinic (M) and orthorhombic (O) phases have been reported in both PMNT and PZNT systems, which depend strongly on Ti concentration, temperature range, strength of the external electric (E) field, and crystallographic orientation.[3–13] Compositional heterogeneities (or spatial phase segregation) are also commonly observed in these materials, especially for compounds near the MPB.

An almost certainly monoclinic phase was induced by the E field applied along ⟨001⟩ in a PZNT8% single crystal, as observed with *in situ* x-ray diffraction.[4] A metastable orthorhombic FE phase (between R and T phases) was proposed in PZNT8% crystals oriented along ⟨001⟩, ⟨110⟩, and ⟨111⟩ from E-field-dependent polarization results.[5] By synchrotron x-ray diffraction with the E field applied along the [001] direction, various polarization rotation paths of R-M_A-M_C-T and R-M_A-T were proposed in PZNT8% and PZNT4.5% crystals, respectively.[6] An O phase was observed in PZNTx for $x=8\%$, $x=9\%$, and 10% after a prior E-field application along [001].[7]

With a prior E field poling along a (011)-cut PMNT33% crystal, an extra O phase between R and T phases was claimed from the dielectric result.[8] From polarization results, an E-field-induced transformation from ⟨111⟩ R to ⟨110⟩ O phase through M_B-type M distortion, i.e., R-M_B-O, was proposed on a (110)-cut PMNT30% crystal.[9] Based on synchrotron results, an M_A-type M phase was observed in a (001)-cut PMNT35% single crystal previously poled under an E field of 43 kV/cm.[10] However, unpoled and weakly poled PMNT35% samples exhibit an average R symmetry.[10] Irreversible field-induced phase transformations through M_A-type monoclinic distortions, i.e., $R \rightarrow M_A \rightarrow T \rightarrow M_A \rightarrow R_{111}$ were observed in a (111)-cut PMNT33% single crystal.[11] An M_C-type M phase has so far been reported in PMNT only for powder and ceramic samples.[12–14] It is important to note that the effect of M_A-type polarization rotation will be largely cancelled in randomly oriented ceramics.[15]

It is believed that polarization rotation through monoclinic distortions plays an important role in high piezoelectric performance in the PMNT system. However, the correlation between polarization rotation and other parameters, such as crystal orientation, titanium (Ti) content, and the strength of the E field, is still not clear. Particularly, the effect of an electric field on a PMNT crystal has not been extensively studied. How the R-T transformation via M_A-, M_B-, or M_C-type monoclinic distortions takes place under an E field is not well understood.[16] In this paper E-field-induced domain structures were investigated on a (001)-cut PMNT24% single crystal, which has a rhombohedral (R) phase[1] at room temperature.

The lead magnesium niobate-lead titanate crystal PMNT24% was grown using a modified Bridgman method. The sample was cut perpendicular to the ⟨001⟩ direction. Transparent conductive films of ITO (indium tin oxide) were deposited on sample surfaces by RF (radio frequency) sputtering and the sample thickness is about 45 μm. The experimental configuration is illustrated in Ref. 3. A dc external electric field was applied to the sample along the [001] direction. The domain structures were observed by using a Nikon E600POL polarizing microscope with a 0°/90° crossed polarizer/analyzer (P/A) pair. All pictures presented in Fig. 1 were observed with the P/A pair at 45° with regard to the [110] direction, except the inset of Fig. 1(a) which was observed with the P/A pair at 0°. "N" indicates the area of the electrode boundary.

The propagation direction $\vec{k}$ of the polychromatic "white" light is along [001] for this work. The most information is

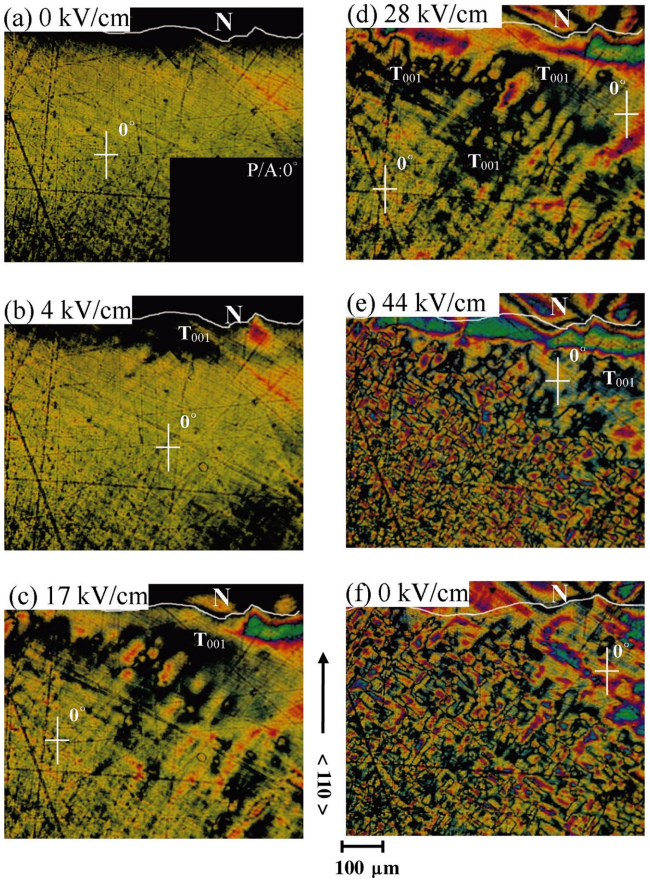

FIG. 1. (Color) E-field dependent domain structures observed at room temperature.

obtained from an observation of optical extinction, which occurs if all the following conditions are satisfied: (1) there must be no optical activity for the direction $\vec{k}$, (2) either $\vec{k}$ must lie along an optical axis, or if $\vec{k}$ is not along an optical axis, the incident $\vec{E}$ must lie along one of the two perpendicular axes in the plane perpendicular to $\vec{k}$ for which the optical-frequency permittivity is maximum or minimum. For uniaxial symmetries, such as R and T phases, the optical axis is known from structural symmetry. A clear mathematical analysis for the general extinction problem, including biaxial symmetries such as O and M, appears in Sommerfeld[17] and Hartshorne *et al.*[18]

Distortion to phases of lower symmetry (monoclinic or triclinic) allows **P** to vary continuously during the distortion. The T and R phases have uniaxial strain tensors with principal axes and polarization **P** along $\langle 001\rangle$ and $\langle 111\rangle$, respectively. For the O phase observed in perovskites, the strain tensor is biaxial, with principal axes (for one example) along $[101]$, $[10\bar{1}]$, and $[010]$ and **P** along $\pm[101]$ or $\pm[10\bar{1}]$. Monoclinic cell strain tensors are biaxial, with one principal axis along $\langle 001\rangle$ or $\langle 110\rangle$, and the other two axes and **P** in arbitrary directions perpendicular to that axis. The $\langle 001\rangle$ case corresponds to the cell based on the primitive unit cell ($Z=1$) for the cubic phase, while the $\langle 110\rangle$ case corresponds to the cell based on the double-size orthorhombic cell ($Z=2$).

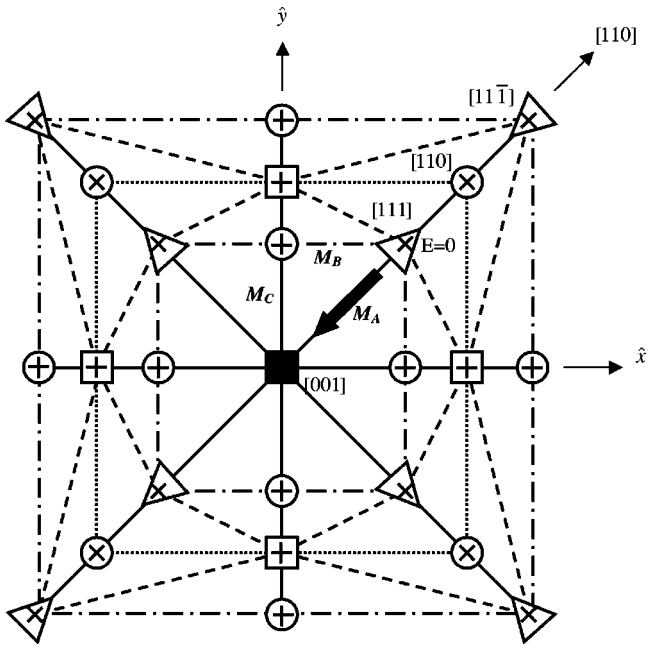

FIG. 2. Relation between the optical extinction orientations corresponding to polarizations for various phases and domains, projected on the (001) plane.

Figure 2 shows the (001)-cut projection (with all four sides folded out) of relations among the various phases and corresponding polarizations for the primitive unit cell ($Z=1$) and double-size orthorhombic cell ($Z=2$). A square indicates the directions of tetragonal polarization vectors **P**. A triangle indicates directions for rhombohedral **P**'s. A circle indicates directions for orthorhombic **P**'s. Solid, dashed-dotted, and dashed lines indicate directions that polarizations can take for monoclinic cells based on the double-size ($Z=2$) orthorhombic cell. Dotted lines alternate between squares and circles, indicating directions that polarizations can take for monoclinic cells based on the simple ($Z=1$) cubic cell. Any polarization whose direction does not correspond to one of the three symbol types or four types of lines results from a triclinic cell.

Domains that are optically inactive for $\vec{k}$ along $[001]$ will have extinction for the optical electric field along the radial and circumferential axes, indicated by solid crossed lines inside the symbols. Solid lines between some symbols indicate no shift in extinction directions away from those in symbols connected by these lines. Lines for the remaining $Z=2$ (dashed and dashed-dotted) and all $Z=1$ (dotted) M polarization directions indicate a shift in the extinction direction away from the radial and circumferential axes. The central "black" square indicates total optical extinction for any optical field direction.

The M_C cell **P** lies between two adjacent T and O **P** vectors. The M_A cell has **P** between two adjacent T and R **P** vectors, whereas the M_B cell has **P** between two adjacent R and O **P** vectors. The M_A and M_B "phases" in our opinion should be called a single phase whose cell is based on the $Z=2$ orthorhombic cell. Most higher-symmetry phases (O,

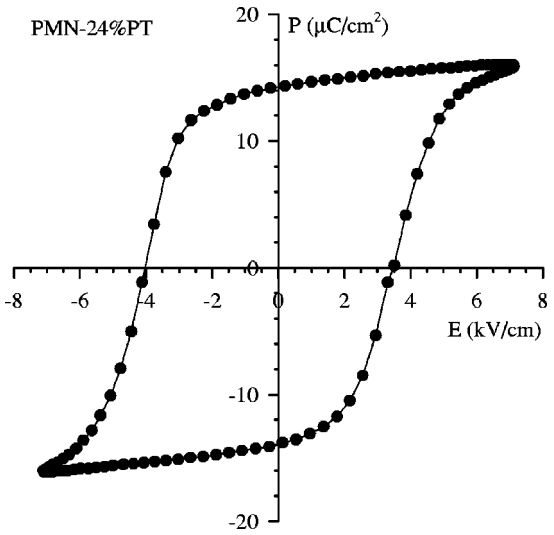

FIG. 3. Hysteresis loop of polarization vs E field obtained at room temperature.

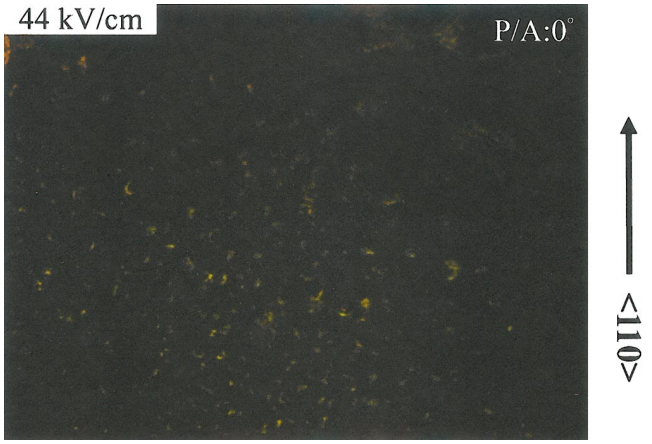

FIG. 4. (Color) Domain structures observed at $E=44$ kV/cm with the 0°/90° P/A axis along the [110] direction.

R, or T) with nearby polarization **P** directions are related directly by monoclinic phases. For instance, rotation of polarization **P** from the R-domain [111] direction to the T-domain [001] direction can proceed by means of a monoclinic M_A cell with the highest-symmetry principal axis b_m along [110].

As shown in Fig. 1(a), at $E=0$ kV/cm, for this crystal which had been annealed above T_c, the whole domain matrix exhibits extinction for a P/A axis along the [110] direction. Hereafter, the extinction angle corresponds to the angle between one of the P/A pair axes and the [110] direction as indicated in Fig. 1. When observing the (001)-cut sample along the [001] direction between a crossed P/A pair, as shown in Fig. 2, the extinction angle is 0° (or 90°) for all R domains. Thus, domains in PMNT24% crystal are certainly rhombohedral at $E=0$ kV/cm. One notes that four of the 12 O domain types would give the same extinction angle of 0° as R domains. However, there is no evidence for the O phase in PMNT24% at zero E field. If O domains exist in the sample, extinction would be twice as likely to be seen at an angle of 45°, as shown in Fig. 2. However, it was not found at 45° as evidenced in Fig. 1(a).

With an increasing E field, the domain matrix begins to exhibit change near $E=4$ kV/cm as shown in Fig. 1(b). This is consistent with the coercive field $E_C \sim 3.8$ kV/cm as shown in Fig. 3. As indicated by T_{001} in Fig. 1(b), some domains near $E=4$ kV/cm show extinction at all P/A angles, indicating a T phase with polarization along the [001] direction. The T_{001} domain corresponds to the black square in Fig. 2. Except for the T_{001} domains, the rest of the domain matrix exhibits an R phase with extinction at 0°. As the field increases, the T_{001} phases gradually expand in the domain matrix. Above $E \sim 30$ kV/cm, as illustrated in Fig. 1(e), the T_{001} phase rapidly spreads into the domain matrix and forms networklike [001] tetragonal domain chains, indicating a long-range order of the [001] tetragonal phase. Except for the networklike T_{001} domains, most domains have extinction angle at 0°. However, for $E \geqslant 30$ kV/cm spotlike domains that do not exhibit extinction at 0° appear in the domain matrix as shown in Fig. 4. These spotlike domains exhibit extinction at angles within a few degrees of 20°. Upon a decreasing E field, as shown in Fig. 1(f), domains exhibit very different structures compared with domains while increasing the E field, showing a hysteretic poling process in agreement with the hysteresis loop shown in Fig. 3. Note that the polarizing microscope results aid in interpreting the hysteresis loop in Fig. 3. The loop appears saturated, so one might think that as the field along [001] is reversed, a single [001] domain is switched into a single $[00\bar{1}]$ domain. Alternatively, one might think that the crystal converts from the four rhombohedral domains with a positive polarization component along [001] to the four domains with a negative component along [001]. From the polarizing microscope pictures in Fig. 1 it is apparent that the hysteresis loop results from incomplete switching.

What is the rotation path of domain polarizations as the E field increases? When observing the (001)-cut sample between a crossed P/A pair, as shown in Fig. 2, polarizations of the M_A-type monoclinic phases would exhibit extinction along the ⟨110⟩ direction, which is at the P/A angle of 0° or 90°. Thus, above ~4 kV/cm, R domains most likely undergo M_A-type distortions and turn toward T_{001} domains, i.e., $R \rightarrow M_A \rightarrow T_{001}$ as indicated by the solid black arrow in Fig. 2. Note that the polarization rotation path of R-M_A-T was also proposed in a rhombohedral PZNT4.5% crystal at room temperature by synchrotron x-ray diffraction with the E field applied along the [001] direction.[6] From free energy calculations under the E field application,[15] Fu *et al.* proposed that the polarization rotation path R-M_A-T is energetically favorable in $BaTiO_3$.

On the other hand, the polarizations of the domains that cannot reach extinction at all P/A angles near $E=44$ kV/cm, but do have extinction at 0° as shown in Fig. 1(e), must lie on the M_A path between R ($E=0$) and the T_{001} phases which corresponds to the total optical extinction. While applying an E field along [111] on a (111)-cut PMNT33% crystal, a total optical extinction associated with

the [111] R domain was easily induced near $E = 12$ kV/cm.[11] It indicates that the [001] direction is not a preferred polar direction for the PMNT24% crystal at room temperature. In addition, spotlike domains as shown in the inset of Fig. 1(e), which exhibit extinction at angles within a few degrees of 20°, perhaps correspond to M_B-type monoclinic or triclinic phases.

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