Monoclinic M C vs orthorhombic in [001] and [110] electric-field-cooled Pb(Mg_{1/3}Nb_{2/3}O_3)-35\%PbTiO_3 Crystals

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Monoclinic $M_C$ vs orthorhombic in [001] and [110] electric-field-cooled Pb(Mg$_{1/3}$Nb$_{2/3}$O$_3$)$-35\%$PbTiO$_3$ Crystals

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Structural phase transformations in Pb(Mg$_{1/3}$Nb$_{2/3}$O$_3$)$-35\%$PbTiO$_3$ crystals with an electric field (E) applied along [110] and [001] directions have been performed by x-ray diffraction. In the field-cooling process, a phase transformation sequence of Cubic(C) → Tetragonal(T) → Orthorhombic(O) was found for E//[110]; whereas a sequence of C → T → monoclinic($M_C$) was found for E//[001]. Our results establish that the stability of $M_C$ relative to O (or limiting $M_C$) is altered by the direction along which E is applied. © 2006 American Institute of Physics.

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Relaxor ferroelectric based morphotropic phase boundary crystals, such as (1−x)Pb(Mg$_{1/3}$Nb$_{2/3}$O$_3$)$-x\%$PbTiO$_3$ (PMN−x% PT) and (1−x)Pb(Zn$_{1/3}$Nb$_{2/3}$O$_3$)$-x\%$PbTiO$_3$ (PZN-x% PT), have attracted much interest as high performance piezoelectric actuator and transducer materials. An important breakthrough in understanding the structural origin of these high electromechanical properties was the discovery of ferroelectric monoclinic (M) phases bridging the R and T ones, as first reported for PbTiO$_3$.$^1$ The monoclinic $M_A$ phase ($Cm$) has a unique $b_m$ axis along the [110] direction, and a unit cell that is doubled with respect to the primitive cubic one which is rotated 45° about the $c$ axis; whereas, the monoclinic $M_C$ ($Pm$) has a unique $b_m$ axis along the [010] direction. Both neutron and x-ray powder diffraction measurements have revealed the existence of a $M_C$ phase ($c_M\neq a_M$) in zero-field-cooled (ZFC) PMN−x% PT$^2-5$ for 31% ≤ x ≤ 37%. In addition, a monoclinic $M_C$ phase has been observed for (001) field cooled (FC) in PMN-30%PT,$^6$ whereas the ZFC state was R.

An orthorhombic (O) phase (Bmm2) has also been reported to be induced by a field applied along [001] in PZN−x% PT for 8 ≤ x ≤ 10.$^9,10$ This O phase is the limiting case of the monoclinic $M_C$ structure: in the limit of $a_M=c_M$ and $\beta>90^\circ$, the crystal symmetry becomes O, and the polarization is then fixed to the [110] direction. This O structure has a doubled unit cell, consisting of two $M_C$ primitive cells, with lattice parameters of $a_O=2a_M$, $c_O=2c_M$, $\sin(\beta/2)$, and $b_O=b_{Mf}\,6,11$ Dielectric property studies of PMN−33%PT crystals with E//[110] have reported an intermittently present metastable orthorhombic phase over a narrow temperature range. Polarized light microscopy indicated that this evasive phase was a single domain orthorhombic one.$^{1,2}$ In addition, the P-E and $\varepsilon$-E behaviors of ZFC PMN-30%PT$^3$ crystals with E along [110] have been reported, upon which was conjectured a field-induced O phase at room temperature. However, structural studies have not yet established the presence of a ferroelectric O phase in PMN−x%PT, either for E//[001] or E//[110].

In this investigation, we have studied the phase stability of PMN−35%PT crystals for both E//[001] and E//[110] by high-resolution x-ray diffraction (XRD). Our results establish a $M_C$ phase on [001] field cooling, but an O phase (or limiting $M_C$) on [110] field cooling. Single crystals of PMN−35%PT with dimension of 3×3×3 mm$^3$ were obtained from HC Materials (Urbana, IL), and were grown by a top-seeded modified Bridgman method. The PMN−35%PT cube, carefully chosen with $T_C\sim435$ K, was cut along the pseudocubic (110)/(110)/(001) planes, and was polished to 0.25 μm. All measurements were performed on the same specimen and consisted of two steps. The first was to apply an electric field along the [001] direction and the second was to apply an electric field along [110]. Gold electrodes were successively deposited on one pair of opposite (001) and (110) faces of the cube. The XRD studies were performed using a Philips MPD high-resolution system equipped with a two bounce hybrid monochromator, an open three-circle Eulerian cradle, and a doomed hot stage. A Ge (220)-cut crystal was used as an analyzer, which had an angular resolution of 0.0068°. The x-ray wavelength was that of Cu $K\alpha=1.5406$ Å, and the x-ray generator operated at 45 kV and 40 mA. The penetration depth in the samples was on the order of 10 μm. In our diffraction studies, we have performed mesh scans around the (002) Bragg reflection in the (HHL) zone, defined by the [110] and [001] vectors; the (220) and (2-20) reflections in the scattering zone defined by the [110] and [1-10] vectors; and (200) in the (HOL) zone, defined by the [100] and [001] vectors. Each measurement cycle was begun by heating up to 550 K to depole the crystal, and measurements subsequently taken on cooling. In this study, we choose the reciprocal lattice unit (or 1 rhu) $a^* = 1.560$ Å$^{-1}$ ($a=2\pi/a^*=4.027$ Å). All mesh scans of (001) and (110) PMN-35%PT shown in this study were plotted in reference to this reciprocal unit.

Figure 1 shows mesh scans taken around the (002) and (200) reflections for [001] FC PMN−35%PT at various temperatures for E=2 kV/cm. At 475 K (data not shown), the (002) and (200) mesh scans did not exhibit splitting, and it was found that $c=a$. Thus, it is clear that the lattice has cubic symmetry. As the temperature was decreased, the (002) and

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(200) mesh scans both exhibited one peak; but an elongation of the lattice constant $c_T$ and a contraction of $a_T$ were clearly observed, as shown in Fig. 1(a) and 1(b) at $T=393$ K. This indicates that the crystal transforms into a $T$ structure. Upon further decreasing temperature, a second transition to a $M_T$ phase was found, as shown in Figs. 1(c) and 1(d) at 300 K. The (200) peak split into three reflections, (200) twin peaks and one (020) single peak; whereas, the (002) remained as a single reflection.

We also studied the temperature dependence of the lattice parameters for a PMN-35%PT crystal in the [110] field-cooled condition. Relative to [001] FC PMN-35%PT, [110] field cooling results in a more complicated domain configuration. This is because [001] field cooling fixes the prototype $c$ axis, whereas [110] field cooling only fixes the crystallographic [110] direction. To obtain a more comprehensive understanding, we then measured field cooling mesh scans about the (002), (200), (220) and (220) reflections for a $E//[[110]$ of 2 kV/cm. Figures 2(a)–2(d) show mesh scans at 400 K taken around these four directions, respectively. The (002) reflection [see Fig. 2(a)] only has a single sharp peak. The lattice constant extracted from it was 4.0119 Å. However, the (200) reflection [see Fig. 2(b)] was split into two peaks along the longitudinal direction, with the lattice parameters of $a=4.0122$ Å and $c=4.0361$ Å. The [110] field cooling constrains the polarization in the $T$ phase to the (001) plane. The $a_T$ lattice parameter is then derived from the (002), whereas $c_T$ is obtained from the (200) reflection. Since [110] field cooling fixes the [110] crystallographic orientations, the (220) mesh scan [see Fig. 2(c)] splits into two peaks along the transverse direction, but remains as a single peak for the (220) scan [see Fig. 2(d)]. Accordingly, for (220) mesh scan, $a$ and $b$ twinning in the (001) plane is only seen along the transverse (220) direction. Our results in Fig. 2 evidence a tetragonal lattice, with 90° domain formation only in the (001) plane, whose polarization is constrained along the [100] and [010] direction.

As the temperature was further decreased on [110] field cooling, the longitudinal splitting in the (200) mesh scan disappeared near 308 K, indicating another phase transformation. Figures 3(a)–3(d) show mesh scans at 303 K within this phase field that were taken about the (002), (200), (220), and (220) reflections, respectively. Only a single domain was observed in each of these scans, indicating the presence of a well-developed single domain state throughout the entire crystal. The structure of this phase was determined to be orthorhombic, where the polarization is fixed to the [110]. The lattice parameters of this orthorhombic phase were determined from these mesh scans to be $a_T=5.7055$ Å,
$c_O = 5.6870 \, \text{Å}$, and $b_O = 4.0050 \, \text{Å}$, where $a_o$ was extracted from the $(220)$ reflection, $c_o$ from the $(\overline{2}0\overline{2})$, and $b_o$ from the $(002)$. This O structure has an equivalent limiting $M_C$ primitive cell with the corresponding lattice parameters of $a_M = c_M = 4.0279 \, \text{Å}$, $b_M = 4.005 \, \text{Å}$, and $\beta = 90.18^\circ$.

Figure 4 shows the temperature dependence of the lattice constants for (a) an $E//[001]$ of 2 kV/cm and (b) an $E//[110]$ of 2 kV/cm. The results for the two orientations are identical except in the low temperature region, where $[001]$ field cooling results in $M_C$, whereas $[110]$ field cooling results in O. The lattice constant $c_T$ ($a_T$) gradually increased (decreased) as the temperature decreased and suddenly dropped near 308 K. At lower temperatures, $[001]$ field cooling resulted in a $T \rightarrow M_C$ transformation, whereas $[110]$ field cooling results in a $T \rightarrow O$. It is worth noting that the values of $b_M$ and $b_O$ were both continuous with $a_T$ at their respective $T \rightarrow M_C$ and $T \rightarrow O$ transformations, whereas the values of $a_M$ ($a_T/\sqrt{2}$) and $c_M$ ($c_T/\sqrt{2}$) exhibit sharp decreases at the $T \rightarrow M_C$ ($T \rightarrow O$) transformation relative to $c_T$. In addition, we found the O phase to be stable on removal of $E//[110]$, and correspondingly the $M_C$ to be stable on removal of $E//[001]$. This illustrates a subtle yet important difference between the ground state of these two field-cooled conditions.

In summary, the sequence of $[001]$ and $[110]$ electric field cooled PMN-35%PT crystals was $C \rightarrow T \rightarrow M_C$ for $E//[001]$, but $C \rightarrow T \rightarrow O$ for $E//[110]$, respectively. Our results establish that the stability of $M_C$ relative to O (or limiting $M_C$) is altered by the direction along which E is applied.

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![FIG. 4. Temperature dependence of lattice parameters for PMN-35%PT with (a) $E=1 \, \text{kV/cm}$ applied along [001]; and (b) $E=2 \, \text{kV/cm}$ applied along [110].](image-url)