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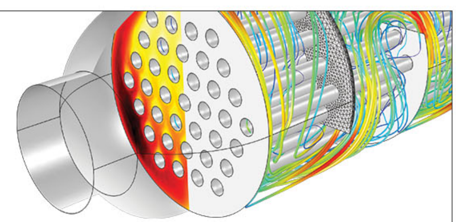

# Monoclinic $M_C$ vs orthorhombic in [001] and [110] electric-field-cooled $Pb(Mg_{1/3}Nb_{2/3}O_3)-35\%PbTiO_3$ Crystals

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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*. [DOI: 10.1063/1.2175497]

Relaxor ferroelectric based morphotropic phase boundary crystals, such as $(1-x)Pb(Mg_{1/3}Nb_{2/3}O_3)-xPbTiO_3$ (PMN−$x$%PT) and $(1-x)Pb(Zn_{1/3}Nb_{2/3}O_3)-xPbTiO_3$ (PZN-x%PT), have attracted much interest as high performance piezoelectric actuator and transducer materials.[1] 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 $Pb(Zr_xTi_{1-x})O_3$.[2–4] 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[5–7] for $31\% \leq x \leq 37\%$. In addition, a monoclinic $M_C$ phase has been observed for (001) field cooled (FC) in PMN-30%PT,[8] whereas the ZFC state was R.

An orthorhombic (O) phase (*Bmm*2) has also been reported to be induced by a field applied along [001] in PZN−$x$%PT for $8 \leq x \leq 10$.[9,10] This O phase is the limiting case of the monoclinic $M_C$ structure: in the limit of $a_M = c_M$ and $\beta > 90°$, 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 $a_O = 2a_M \sin(\beta/2)$, $c_O = 2a_M \cos(\beta/2)$, and $b_O = b_M$.[6,11] Dielectric property studies of PMN–33%PT crystals with E//[110] have reported an intermittently present mestastable orthorhombic phase over a narrow temperature range. Polarized light microscopy indicated that this evasive phase was a single domain orthorhombic one.[12] In addition, the P-E and $\epsilon$-E behaviors of ZFC PMN-30%PT[13] 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 $3\times3\times3$ 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 $T_c \sim 435$ K, was cut along the pseudocubic $(110)/(1\bar{1}0)/(001)$ planes, and was polished to 0.25 $\mu$m. 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 $\mu$m. 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 (H0L) 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 rlu) $a^* = 1.560$ 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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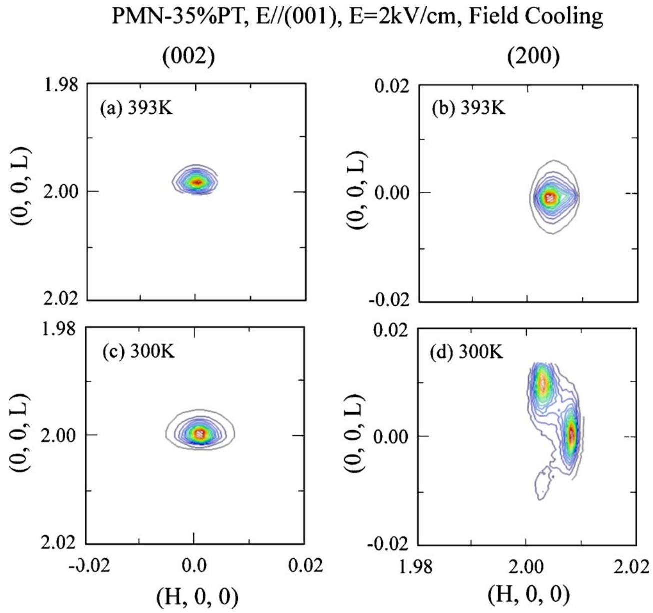


FIG. 1. (Color online) Mesh scans taken around (002) and (200) reflections of PMN-35%PT with E=2 kV/cm applied along [001] at 393 and 300 K in the FC condition.

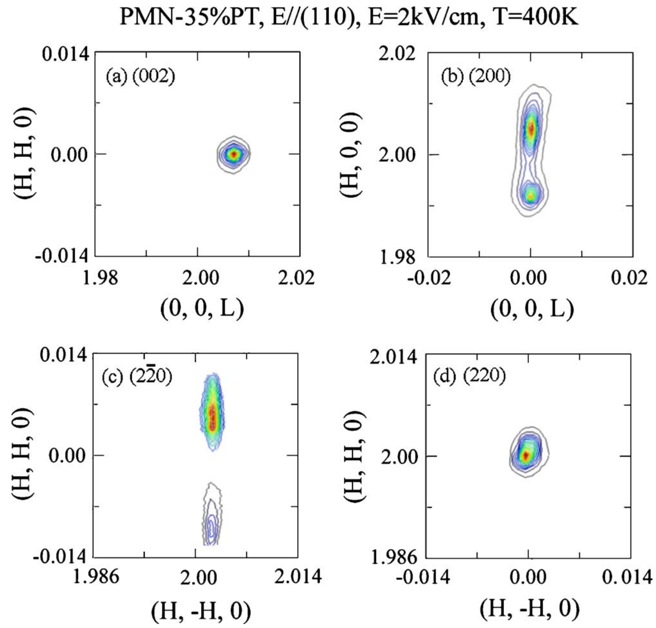


FIG. 2. (Color online) Mesh scans taken around (002), (200), (2$\bar{2}$0), and (220) reflections of PMN-35%PT with E=2 kV/cm applied along [110] at 400 K in the FC condition.

(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 $M_C$ 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 (2$\bar{2}$0) 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 (2$\bar{2}$0) mesh scan [see Fig. 2(c)] splits into two peaks along the transverse direction, but remains as a single peak for the (220) scan [see Fig. 2(d)]. Accordingly, for (2$\bar{2}$0) 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), (2$\bar{2}$0), 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 $a_O=5.7055$ Å,

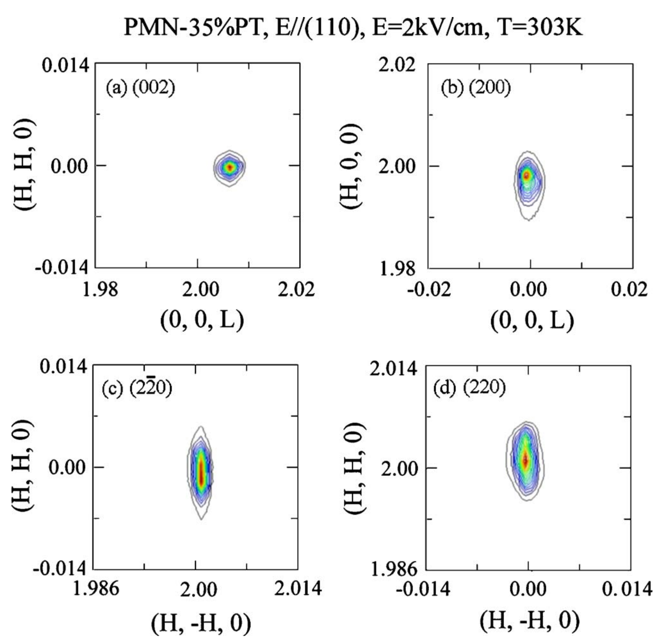


FIG. 3. (Color online) Mesh scans taken around (002), (200), (2$\bar{2}$0), and (220) reflections of PMN-35%PT with E=2 kV/cm applied along [110] at 303 K in the FC condition.

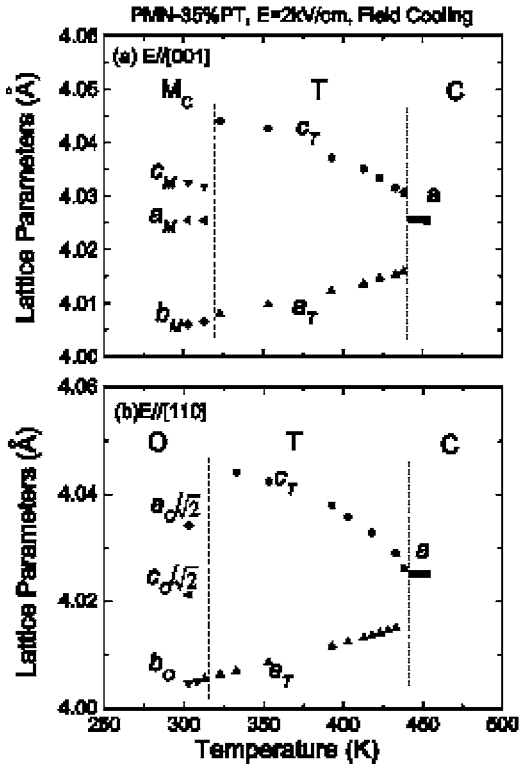


FIG. 4. Temperature dependence of lattice parameters for PMN-35%PT with (a) E=1 kV/cm applied along [001]; and (b) E=2 kV/cm applied along [110].

$c_O$=5.6870 Å, and $b_o$=4.0050 Å, where $a_o$ was extracted from the (220) reflection, $c_o$ from the $(2\bar{2}0)$, 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 Å, $b_M$=4.005 Å, and $\beta$=90.186°.

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→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→O transformations, whereas the values of $a_M$ ($a_O/\sqrt{2}$) and $c_M$ ($c_O/\sqrt{2}$) exhibit sharp decreases at the $T \rightarrow M_C$ (T→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→T→O for FE//[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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