Monoclinic M_B phase and phase instability in $[110]$ field cooled $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ -4.5% PbTiO_3 single crystals

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(Received 11 May 2009; accepted 14 July 2009; published online 5 August 2009)

We report the finding of a monoclinic M_B phase in $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ -4.5% PbTiO_3 single crystals. High precision x-ray diffraction investigations of $[110]$ field cooled crystals have shown a transformation sequence of cubic(C) $\rightarrow$ tetragonal(T) $\rightarrow$ orthorhombic(O) $\rightarrow$ monoclinic(M_B), which is different from that previously reported [A.-E. Renault *et al.*, J. Appl. Phys. **97**, 044105 (2005)]. Beginning in the zero-field-cooled condition at 383 K, a rhombohedral (R) $\rightarrow M_B \rightarrow O$ sequence was observed with increasing field. Coexisting M_B and O phases were then found upon removal of field, which fully transformed to M_B on cooling to room temperature. © 2009 American Institute of Physics. [DOI: 10.1063/1.3200230]

Relaxor ferroelectric single crystals, such as $(1-x)\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3}\text{O}_3)$ - $x\text{PbTiO}_3$ (PZN- $x\%$ PT) and $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3}\text{O}_3)$ - $x\text{PbTiO}_3$ (PMN- $x\%$ PT), have attracted much interest as high-performance piezoelectric actuator and transducer materials.¹ It has been reported that the high-electromechanical properties are due to monoclinic (M) phases bridging the R and T ones induced by an applied electric field (E),^{1,2} as first reported for $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$.³⁻⁵ Subsequently, various ferroelectric M phases in oriented PZN- $x\%$ PT (Ref. 6–8) and PMN- $x\%$ PT (Refs. 9–12) crystals have been found by x-ray diffraction (XRD) and neutron diffraction. The monoclinic symmetry allows the polarization vector to be unconstrained within a plane, rather than constricted to a particular crystallographic axis as for higher symmetry R , T , or orthorhombic (O) phases. According to the polarization rotation theory,¹³ the high-electromechanical properties of ferroelectric monoclinic phases are due to the rotation of the polarization vector within the symmetry-allowed plane. More explicitly, it is the strong interaction between the lattice dynamics and the acoustic phonons which caused the instability of ferroelectric monoclinic phases.¹⁴

For PZN-4.5%PT at room temperature, the R phase has been reported to reversibly transform into an O one when a large E field was applied along the $[\bar{1}01]$ orientation.¹⁵ A study of $[\bar{1}01]$ crystals in the field cooling (FC) condition then demonstrated a $C \rightarrow T \rightarrow O \rightarrow R$ transformation sequence.¹⁶ However, the intermediate O phase might not transform directly to R as there is a bridging monoclinic (M_B) phase between R and O .^{11,17} Here, we have established the structural transformation sequence of PZN-4.5%PT crystals with $E // [110]$. XRD studies have unambiguously shown a phase sequence of $C \rightarrow T \rightarrow O \rightarrow M_B$ on field cooling, which is different from results in prior reports.^{16,18} We find that there is a $R \rightarrow M_B \rightarrow O$ sequence with increasing field beginning from the zero-field-cooled condition at 383 K, and that there is coexisting M_B and O phases upon removal of E , which fully transform to M_B on cooling to room temperature.

Single crystals of PZN-4.5%PT with dimensions of $2 \times 2 \times 2 \text{ mm}^3$ were oriented along the $(\bar{1}\bar{1}1)/(110)/(\bar{1}12)$ planes, and gold electrodes were deposited on one pair of opposite (110) faces. The XRD studies were performed using a Philips MPD high-resolution system. The x-ray penetration depth in the samples was on the order of $10 \mu\text{m}$. In our diffraction studies, we have performed mesh scans around the (002), (220), ($2\bar{2}0$), and (200) zones. Each measurement cycle was begun by heating up to 473 K to depole the crystal, and measurements were subsequently taken on cooling. At 473 K, the lattice constant was $a=4.0572 \text{ \AA}$; correspondingly, the reciprocal lattice unit (or 1 rlu) was defined to be $a^*=2\pi/a=1.548 \text{ \AA}^{-1}$. All mesh scans with E applied along $[110]$ shown in this study were plotted in reference to this reciprocal unit.

At 460 K under $E=1 \text{ kV/cm}$, the mesh scans (data not shown) and lattice parameters reveal that the structure is cubic. Figures 1(a)–1(d) show mesh scans taken around the (002), (200), ($2\bar{2}0$), and (220) zones when the sample was cooled under E to 413 K, respectively. The (002) reflection had only a single sharp peak. The lattice constant was $4.05 \text{ \AA}$. However, the (200) reflection split into two peaks along the longitudinal direction and the lattice parameters were determined to be $a=4.051 \text{ \AA}$ and $c=4.062 \text{ \AA}$. The (220) mesh scan splits along the transverse direction, whereas the ($2\bar{2}0$) scan displayed only a single peak. This evidences that PZN-4.5%PT has a tetragonal lattice, in which the polarization is constrained to $[100]$ and $[010]$ directions for a and b domains.

As the temperature was further decreased, the longitudinal splitting in the (200) mesh scan disappeared near 393 K. Figures 2(a)–2(d) show mesh scans taken around the (002), (200), ($2\bar{2}0$), and (220) zones at 383 K. Only a single domain was observed, indicating the presence of a well-developed single domain state throughout the entire crystal. The structure of this phase was determined to be the O one, where the polarization is fixed along the $[110]$ direction. The lattice parameters of this O phase were calculated from the mesh scans to be $a_O=5.739 \text{ \AA}$, $b_O=5.734 \text{ \AA}$, and $c_O=4.046 \text{ \AA}$.

Upon further decrease in the temperature to 363 K, the (002) mesh scan was found to split along the transverse di-

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FIG. 1. (Color online) Mesh scans of (002), (200), ($\bar{2}\bar{2}0$), and (220) of PZN-4.5%PT with $E=1$ kV/cm applied along [110] at 413 K in the FC condition.

rection, revealing yet another phase transition. Figures 3(a)–3(d) show (002), (200), ($\bar{2}\bar{2}0$), and (220) scans taken at 338 K. The (002) reflection split into two peaks, whereas the other three mesh scans remained as a single peak. This is a signature of the monoclinic M_A/M_B phase. Then, the lattice parameters were calculated to be $a_M/\sqrt{2}=4.057$ Å, $b_M/\sqrt{2}=4.054$ Å, and $c_M=4.054$ Å. Please note that the orthorhombic (O) and monoclinic (M_B) unit cells are rotated by 45°

FIG. 2. (Color online) Mesh scans of (002), (200), ($\bar{2}\bar{2}0$), and (220) of PZN-4.5%PT with $E=1$ kV/cm applied along [110] at 383 K in the FC condition.

FIG. 3. (Color online) Mesh scans of (002), (200), ($\bar{2}\bar{2}0$), and (220) of PZN-4.5%PT with $E=1$ kV/cm applied along [110] at 338 K in the FC condition.

along the c -axis from the original cubic unit cell. This means that below 363 K, a [110] FC can no longer sustain a single-domain O phase whose polarization is fixed along the [110] direction. Rather, a transition to a polydomain monoclinic phase occurs. The fact $a_M/\sqrt{2} > c_M$ confirms that this monoclinic phase is the M_B one, which bridges $O \rightarrow R$. Cao *et al.*¹¹ previously reported such a M_B phase for PMN-30%PT. Now we confirm that it is a universal behavior observed also for PZN- x %PT. This prior work also revealed a $R \rightarrow M_B \rightarrow O$ phase transformational sequence with increasing E beginning in the zero-field-cooling (ZFC) condition.¹⁷ It is relevant to note that this sequence is consistent with the thermodynamic theory of Vanderbilt and Cohen.¹⁹ Our results show PZN-4.5%PT has an intermediate state that is different from the ground state observed in the ZFC condition. This intermediate state is due to the constraint imposed by $E//[110]$.

The lattice parameters and tilt angle ($\beta-90^\circ$) of [110] field-cooled PZN-4.5%PT under $E=1$ kV/cm are plotted as a function of temperature in Fig. 4. At 443 K, a sharp change in the lattice parameters occurred, corresponding to the $C \rightarrow T$ transition. The lattice constants (a_T) c_T gradually decreased (increased) as the temperature was decreased, until a sudden drop near 393 K. On further cooling below 363 K, a transformation to a M_B phase was observed and a monoclinic tilt angle of $\beta-90^\circ \approx 0.09^\circ$ was found.

The field dependence of the structure was then investigated at 383 K, beginning from the ZFC condition. The crystal was first heated to 473 K, and subsequently cooled under zero field. The (002) and (220) XRD mesh scans were obtained at various dc biases (data not shown). The (002) scans were taken under fields of $E=0, 1.5$, and 2.5 kV/cm, respectively. For $E=0$ kV/cm, only a single broad peak was found in the (002) scan, although a longitudinal splitting was observed in the (220) scan (data not shown). These results show that the R phase is stable in the ZFC condition, with a

FIG. 4. (Color online) Temperature dependence of lattice constants and tilt angle of monoclinic phase for PZN-4.5%PT with $E=1$ kV/cm along [110].

lattice parameter of $a_R=4.058$ Å. Upon applying a field of 0.5 kV/cm, a peak splitting was found to develop along the transverse direction in the (002) reflection (data not given), whereas the (220) scan only showed a single peak (data not given). When the electric field was further increased to 1.5 kV/cm, the peak splitting of the (002) reflection became very obvious. These features are signatures of the monoclinic M_B/M_A phase. The lattice parameters c_{M_B} and a_{M_B} , extracted from the (002) and (220) reflections, show that $a_{M_B}/\sqrt{2} > c_{M_B}$. Our results are different from a previous report in which a direct $R \rightarrow O$ phase transformation was observed in the FC condition.¹⁵

Upon removal of E , a M_C phase was observed (data was not shown). However, instead coexisting M_B and O phases were confirmed by calculating the d -spacings of the “ M_C ” phase, and comparing them to those for M_B and O . In so doing, we found that the values of the (002) d -spacing were equal to the ones for M_B and O , respectively. This phase coexistence was found to persist for a long time period after removal of E at 383 K. These results demonstrate that a volume fraction of the O phase transforms to M_B immediately after removal of E , however some persists as O . Furthermore, on cooling to 303 K, the (002) mesh scan revealed a two-fold peak splitting, which is the signature of M_B . These findings indicate that the M_B phase is the ground-state condition for (110) crystals.

In summary, for an E applied along the [110] direction, the phase transformation sequence of PZN-4.5%PT was found to be $C \rightarrow T \rightarrow O \rightarrow M_B$ in the FC state. Beginning in the ZFC state at 383 K, the R ground state further reversibly transforms into the O phase with increasing E , via an intermediate M_B one. Upon removal of E , a partial recovery of M_B occurs from the O phase. This mixture of M_B and O indicates that the remaining field is not sufficient to fix the polarization along [110]. Once established after removal of E , the M_B phase persists on cooling to room temperature at which point the crystal completely transforms into M_B .

We would like to gratefully acknowledge financial support from the Office of Naval Research under Grant Nos. N00014-06-1-0204 and MURI N00014-06-1-0530. One of the authors also would like to thank the financial support from the China Scholarship Council. We would like to acknowledge the useful discussion with G.Y. Xu.

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