

## Observation of domain texture in poled $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ – $\text{PbTiO}_3$ crystals

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## Observation of domain texture in poled $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ crystals

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Mapping of domain distributions under constant Bragg conditions has been performed on poled  $(0.7)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-}0.3\text{PbTiO}_3$  crystals. Studies were done on crystals of cubic geometry, where each cube face was oriented along a  $\langle 001 \rangle_c$ . Multiple domains with monoclinic limiting symmetry (angle  $\sim 173^\circ\text{-}176^\circ$ ) were observed on all three  $(001)_c$  faces. Perpendicular to the poling direction, domain modulations were observed by a splitting of each variant. © 2002 American Institute of Physics. [DOI: 10.1063/1.1519352]

X-ray diffraction (XRD) investigations of oriented  $(0.7)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-}0.3\text{PbTiO}_3$  (PMN-PT) and PZN-PT crystals have demonstrated the presence of monoclinic ( $\text{FE}_m$ ) ferroelectric states, sandwiched between the ferroelectric rhombohedral  $\text{FE}_r$  and tetragonal  $\text{FE}_t$  phases, close to the morphotropic phase boundary.<sup>1-4</sup> Most XRD investigations have been performed either on polycrystalline specimens, or along the  $(001)_c$  or  $(011)_c$  faces on poled single crystals. However, twinning complicates analysis of diffraction data. Twin domains mix symmetries at their boundaries, in addition boundaries tilt with respect to each other to achieve the strain invariant condition. The domain structure of  $\text{PbTiO}_3$  and  $\text{LaAlO}_3$  crystals has previously been studied by diffraction under constant Bragg conditions, i.e.,  $\omega$ - $\phi$  (omega-phi) and  $\phi$ - $\psi$  (phi-psi) scans.<sup>5</sup> It was shown that it was possible to separate domain contributions due to spatial variations in the diffraction intensity around the  $\phi$  axis.

Using transmission electron microscopy, PMN-PT has been shown to possess a high density of microtwins on the nanometer scale that is strongly dependent upon changes in PT content and aliovalent substituents.<sup>6,7</sup> Clearly, in the case of microtwinning or clusters, complications in the analysis of XRD data become very significant. For example, microtwinning of two long and thin  $\text{FE}_t$  or  $\text{FE}_r$  variants on the micrometer scale would result in orthorhombic or monoclinic limiting symmetry.<sup>8</sup>

The purpose of this study was to systematically investigate the domain structure of PMN-PT single crystals by diffraction under constant Bragg conditions. Poled cubical specimens have been studied, in which all three faces have been oriented parallel to different  $(001)_c$  planes. Accordingly, the domain structure and distribution can be investigated both parallel and perpendicular to the poling field. The results demonstrate the presence of high twin densities within the poled condition which have a short lateral correlation length perpendicular to the poling direction, and which are tilted and also tiled with respect to each other. The domain-averaged or limiting symmetry is monoclinic.

A Philips high resolution x-ray diffractometer equipped with an open Eulerian cradle was used in this investigation. PMN-PT crystals were grown by a flux method, and were obtained from HC Materials (Urbana, IL). Cubical crystals of

dimensions  $5 \times 5 \times 5 \text{ mm}^3$  were cut. Each face of the cube was oriented along a  $\langle 001 \rangle_c$  and were poled along one of the  $\langle 001 \rangle_c$ , denoted as  $[001]_c$ . Specimens of composition  $0.7\text{PMN}\text{-}0.3\text{PT}$  were investigated. Previous x-ray investigations have shown that surface damage is a problem in Pb-based perovskites, due to a small x-ray penetration depth ( $\mu\text{m}$  range).<sup>1-4,9</sup> To reduce the surface damage, all faces of every cube were polished to a  $0.25 \mu\text{m}$  finish. Polishing resulted in dramatic sharpening of the diffraction peaks. Figure 1 shows a blowup of a line scan taken from this cube. In this figure, the peak width at half maximum can be seen to be 262 s or 4.3 min. This peak width is close to 3 min obtained by higher energy x-ray sources.<sup>1-4,9</sup>

All three  $\langle 001 \rangle_c$  faces of the PMN-PT cubes were investigated by  $\psi$ - $\phi$  and  $\omega$ - $\phi$  scans. The term  $\psi$  is the angular position of the sample surface normal in the direction perpendicular to the diffraction plane, whereas  $\phi$  is the rotation angle perpendicular to the plane of diffraction. To probe texture symmetry, a  $\psi$ - $\phi$  scan performs a series of coupled rotations about the two axes perpendicular to  $\omega/2\theta$  (omega-2theta), while maintaining a constant  $2\theta$ .<sup>10</sup> This gives the integration volume of reciprocal space on a plane perpendicular to the plane of diffraction. Rotation of this perpendicular plane gives the 3D spatial distribution of the diffraction intensity (or texture) at constant Bragg conditions.

Figures 2(a)-2(c) show  $\psi$ - $\phi$  scans taken from the various  $(001)_c$  faces for 70/30. The data in the figures show two preferred orientations on the  $(001)_c$  of all three faces. These

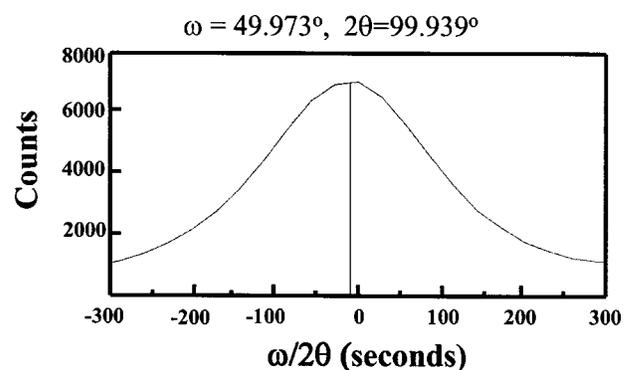


FIG. 1. Line scan take from using this system from a PMN-PT crystal polished to  $0.25 \mu\text{m}$ .

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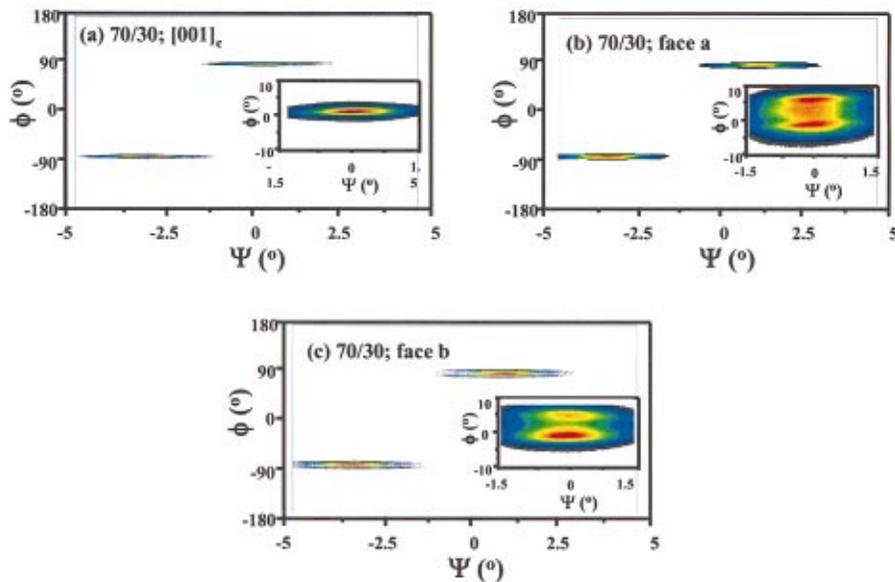


FIG. 2. (Color) The  $\phi$ - $\psi$  scans for 70/30 taken along various crystallographic axes that were either parallel or perpendicular to the poling direction. (a)  $(001)_c$ , which was parallel, (b)  $(100)_c$  which was perpendicular, and (c)  $(010)_c$  which was also perpendicular. The insets show a blowup of one of the domain peaks.

two preferred orientations are rotated in  $\phi$  by  $174^\circ$ – $176^\circ$ , and are tilted in  $\psi$  by  $3^\circ$ – $4^\circ$  with respect to each other. The  $\phi$  rotation demonstrates the presence of a rotation on the surface of all  $(001)_c$  faces, both parallel and perpendicular to the poling direction. This rotation has monoclinic symmetry, as  $\phi$  is noticeable less than  $180^\circ$ . This demonstrates that the  $c$  axis is not confined to the  $[001]_c$ , as previously reported.<sup>7</sup> Rather, the results unambiguously demonstrate the presence of two domain states whose  $c$  axes are slightly tilted away from the  $[001]_c$ . This is directly revealed from the symmetry in the diffraction intensity of the  $\psi$ - $\phi$  scan. Detailed investigations of a number of crystals demonstrated that the principle commonality of poled PMN–PT crystals over a range of PT contents was this domain-averaged monoclinic limiting symmetry, in addition to  $a \sim b \sim c$ . Neumann's law will require that the property tensor matrices for a poled cube have monoclinic (point group) symmetry.<sup>11</sup>

The inset of Figs. 2(a)–2(c) shows an enhancement in scale of one of the domains. Along the poling direction, Fig. 2(a) reveals a single peak. This peak was very sharp, demonstrating that the domains are quite uniform along this di-

rection. However, perpendicular to the poling direction, the insets of Figs. 2(b) and 2(c) reveal a splitting of each domain state along  $\phi$  by a few degrees. These peaks were broad, demonstrating that the domains are quite nonuniform along this direction. The splitting of the  $\psi$ - $\phi$  scans was different along the two different perpendicular faces. A triplet splitting can be seen in Fig. 2(b), whereas a doublet splitting can be seen in Fig. 2(c). These results demonstrate the presence of an internal modulation of the domain states perpendicular to the poling direction. Spatial modulation of twins is a form of tiling. The symmetry of the modulation (i.e., the number of splits in the  $\psi$ - $\phi$  scan) can vary, without affecting the domain-averaged monoclinic limiting symmetry. We can conclude that the monoclinic macrodomains are constituted from a tiling of microtwins along the  $[010]_c$  and  $[100]_c$ .

A  $\omega$ - $\phi$  scan utilizes a series of  $\omega$  curves taken at different  $\phi$  positions, at constant  $2\theta$ . The integration volume of reciprocal space appears as thin rods perpendicular to the diffraction plane, as the instrument broadening is quite large in this direction.<sup>5</sup> The resolution of our instrument in the  $\phi$  direction is significantly higher than that in the  $\psi$  direction. Thus,

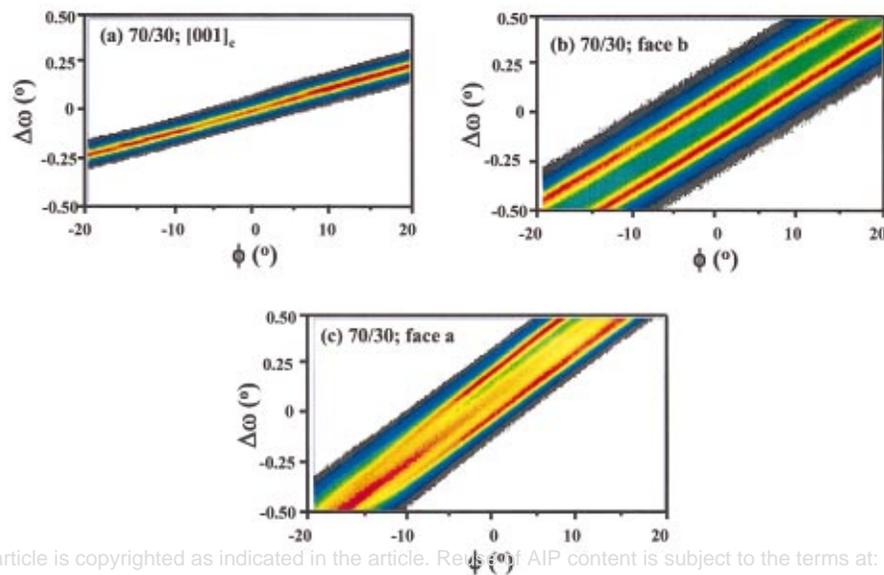


FIG. 3. (Color) The  $\omega$ - $\phi$  scans for 70/30 taken from various faces that were either parallel or perpendicular to the poling direction. (a)  $(001)_c$ , which was parallel, (b)  $(100)_c$  which was perpendicular, and (c)  $(010)_c$  which was also perpendicular.

the  $\omega$ - $\phi$  scan will offer better resolution in mapping of the spatial distribution of domains. In our investigations, rotations in  $\phi$  were limited to  $\pm 20^\circ$ , thus mapping the distribution of modulations (or splittings) within one domain state.

Figures 3(a)–3(c) show  $\omega$ - $\phi$  scans taken along the  $(001)_c$  for 70/30. Along the poling direction [Fig. 3(a)], a single thin rod can be seen that has nearly uniform diffraction intensity. This demonstrates that the domain state is spatially uniform in this direction. These results are consistent with the observation of a long lateral correlation length along the  $[001]_c$ . Figures 3(b) and 3(c) show  $\omega$ - $\phi$  scans taken perpendicular to the poling direction. Multiple rods were found. Two along one face [Fig. 3(b)] and three along the other [Fig. 3(c)]. These rods were significantly wider than those along the  $[001]_c$ . The rods in Fig. 3(b) were uniformly split along  $\omega$  by  $0.25^\circ$ . The rods in Fig. 3(c) can be seen to have strong nonuniform diffraction contrast. The relative intensity of the outer two rods to that of the center rod can be seen to vary as a function of  $\phi$ . At some  $\phi$  positions, the intensity of the outer two peaks was much stronger than that of the center, whereas at other  $\phi$  positions the intensity of the center peak was much stronger. These results are consistent with a spatial modulation (or stacking arrangement) of microtwins of different symmetry within the limiting monoclinic symmetry of the domain.

The results of the XRD investigations for  $[001]_c$  poled PMN–PT crystals can be summarized as: (i) the limiting macrosymmetry of the crystal cubes is monoclinic, thus by

Neumann's law the property matrices must have monoclinic symmetry; and (ii) there is a hierarchy of domains, monoclinic macrodomains are mosaic constituted from tiling of microtwins.

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