Interweaving domain configurations in [001]-poled rhombohedral phase $0.68Pb(Mg_{1/3}Nb_{2/3})O_3-0.32PbTiO_3$ single crystals

Jiaping Han and Wenwu Cao[a)]
Department of Physics and Materials Science, City University of Hong Kong, Kowloon, Hong Kong, China

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Domain structures in [001]-poled rhombohedral phase $0.68Pb(Mg_{1/3}Nb_{2/3})O_3-0.32PbTiO_3$ single crystals have been investigated using polarized light microcopy. It was found that the observed domain structures are quite different from those previously assumed four domain states with cross intersecting 71° charged domain walls. The pattern can be interpreted as interweaving of two types of twins in three dimensions. Each local twin pattern contains only two domains with a 109° charged domain wall in either [110] or $[1\bar{1}0]$. The stacking of two 90° rotated twins produces a cross-hatching pattern for transmission optical microscope and an effective $4mm$ macroscopic symmetry. The pattern becomes simple twins when the imaging is focused at different depth. The domain size is 1–2 μm in all the samples observed and the twin layer thickness is about 50–100 μm. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1605796]

Recently, the $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3-xPbTiO_3$ (PMN–PT) single crystal system has attracted a lot of attention because these crystals with compositions near the morphotropic phase boundary (MPB) have been found to exhibit extremely high piezoelectric constant d_{33} (>2000 pC/N) and electromechanical coupling coefficient k_{33} (>90%), when they are poled along [001] of cubic coordinates into a multidomain structure.[1–4] Since [001] poling will leave four possible orientations for the dipoles in the rhombohedral phase crystal, it was assumed that the effective macroscopic symmetry of the multidomain structure is $4mm$, in which all domain walls are of 71° type.[1,5] However, the assumed domain pattern has not been reported so far in the literature, although a couple of images showing somewhat look-like cross-hatching patterns.[6] In many samples, the primary domain patterns observed are twins that contain only two of the four possible domain states.[6] In other words, the local structure consists of twins instead of four domain states. Clarifying this question is important for the understanding of the origin of the superior piezoelectric properties in these crystals, and also critical for extending the domain engineering method to other crystal systems.

In this investigation, we have performed optical observations in different depth in [001]-poled $0.68Pb(Mg_{1/3}Nb_{2/3})O_3-0.32PbTiO_3$ (PMN–32%PT) single crystals and discovered that the domain structures are actually cross stacking of 109° twins. This may help to clear the confusion of rhombohedral crystal structure confirmed by x-ray diffraction and the domain patterns observed in these crystals that seem to match the monoclinic crystal symmetry.

The PMN–PT single crystals used in our experiments are provided by the Shanghai Institute of Ceramics, which were grown by a modified Bridgman technique. The crystals were cut and polished into a platelet with three pairs of mutually perpendicular surfaces. The dimensions of the platelets are 2–4 mm in each side and about 0.2–0.4 mm in thickness. The large surfaces of each plate have the orientation of [001], and the other two pairs of surfaces are [010] and [100], respectively. All labeling of orientations in this letter refer to the cubic axes. Transparent conductive indium tin oxide (ITO) films were deposited onto the pair of [001] surfaces to form electrodes. Poling of these samples was done by applying an electrical field along [001] at a temperature above the Curie temperature and then cooling to room temperature under a bias electrical field. The domain structures were observed on the [001] surfaces using a polarized light microscope (Leica DM RX) with charge coupled device camera in transmission mode.

The Curie temperature of the PMN–32%PT single crystal was found to be about 147 °C, which is in good agreement with those reported by other authors[2,7,8] and confirmed the nominal composition of our crystals.

Figure 1 shows the domain structures observed in the poling direction of [001] with different level of poling electrical fields and different sample thickness (an image for unpoled sample is also shown for comparison). The domain structure in the undoped sample cannot be clearly observed by an optical microscope, since the domains are too small and random. However, after poling, clear domain patterns are revealed. It can be seen that, in spite of different poling electrical fields and sample thickness, all domain patterns exhibit similar configuration, i.e., layered twins interweaving in three dimensions, although the sizes of the domains may be different for different poling conditions. As expected, Fig. 1 shows the size increase of domains with increasing poling field. In general, the domain sizes are in the order of 1–2 μm for all samples tested. For the poled crystals with domain structures shown in Figs. 1(b), 1(c), and 1(d), the piezoelectric constant, d_{33}, was determined to be about 2000, 2800, and 2400 pC/N, respectively, by measuring strain versus electric field curves or by a Berlincourt d_{33} meter. The electromechanical coupling constant, k_t was measured to be 58.5%, 61.7%, and 63.2%, respectively, using a resonance

[a)]Author to whom correspondence should be addressed; on leave from: the Department of Mathematics and Materials Research Institute, The Pennsylvania State University, University Park, PA 16802; electronic mail: cao@math.psu.edu

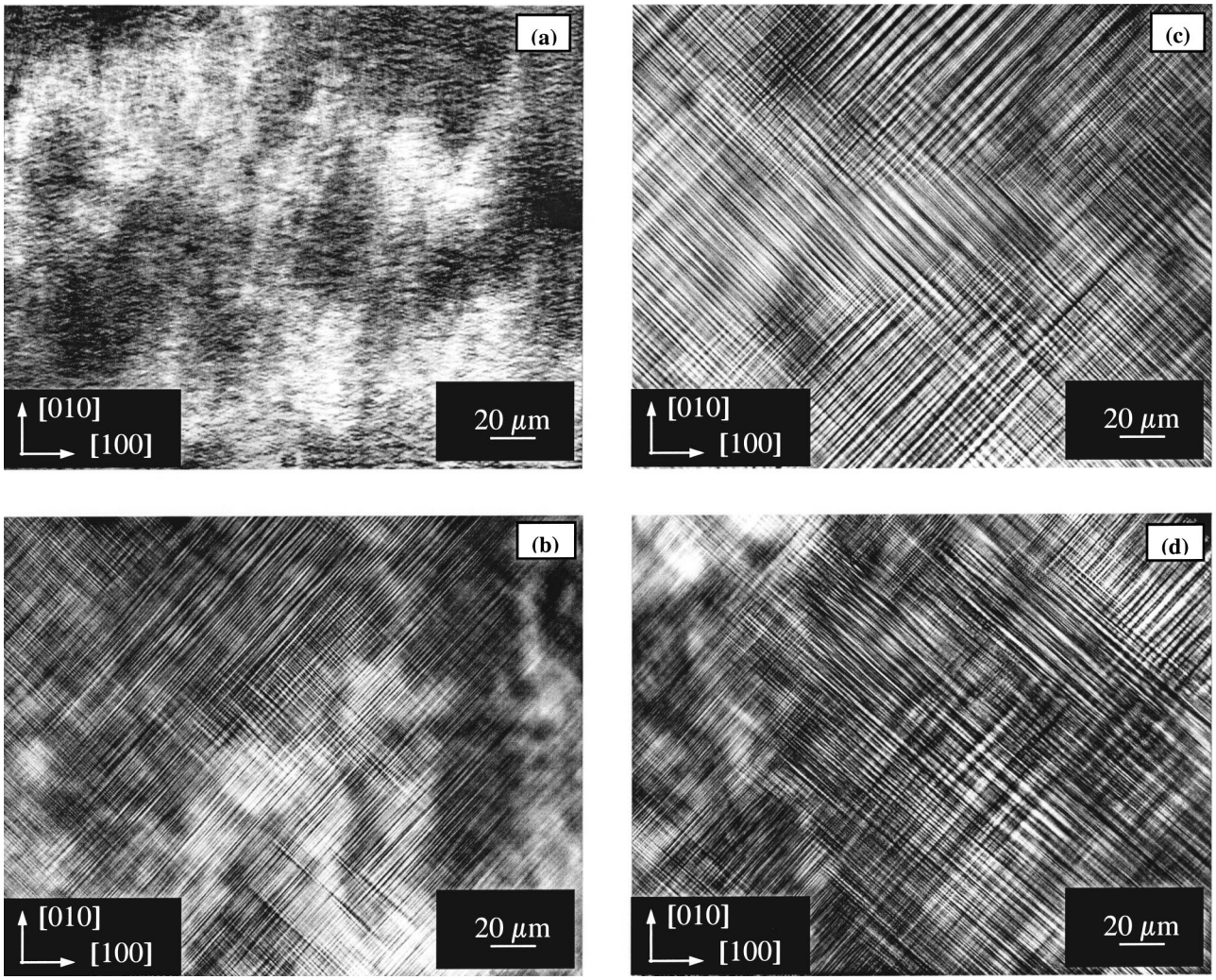

FIG. 1. Domain structures observed from [001]-oriented PMN–32%PT single crystals with different poling electrical fields or sample thickness. (a) Unpoled sample, (b) 0.67-mm-thick poled at an electrical field of 0.5 kV/cm, (c) 0.36-mm-thick sample poled at an electrical field of 1 kV/cm, and (d) 0.19-mm-thick sample poled at an electrical field of 1 kV/cm.

method. The electromechanical coupling constant k_{33} cannot be directly measured using the present samples with platelet shape. To avoid cutting the samples into k_{33} bars, which will damage the domain structures, the values of k_{33} were calculated, using the equation $k_{33}^2 = d_{33}^2/(\epsilon_{33}^T * s_{33}^E)$, where ϵ_{33}^τ and s_{33}^E are dielectric constant and elastic compliance constant, respectively. Note that d_{33} and ϵ_{33}^T were measured directly using the platelet samples, and s_{33}^E were obtained from other PMN–32%PT samples, considering s_{33}^E is nearly constant among different samples with the same composition.

The observed multidomain structures in Fig. 1 are different from the assumed domain structure in two aspects. First, the domain wall orientation is in $\langle 110 \rangle$ family instead of $\langle 100 \rangle$ family. The former is for 109° domain walls while the latter is for 71° domain walls. Second, the seemingly crosshatching pattern is actually twin stacking in different layers instead of four domain coexisting on the same layer. On any given plane along [001], the domains look like tweed structures with each small local twin vanishing gradually and another perpendicular twin appears if one walks along the plane.

As illustrated in Fig. 2(a), one type of domain pattern (domain pattern A) contains two types of domains forming 109° charged domain walls along [110], and the other domain pattern (domain pattern B) with two other domains forming a different set of 109° charged domain walls along $[1\bar{1}0]$, as illustrated in Fig. 2(b). These two domain patterns interweave to form the tweed domain structures as observed in Fig. 1. Statistically, such tweed domain configuration would have a $4mm$ macroscopic symmetry when the sample contains a large amount of domains. On the other hand, at a

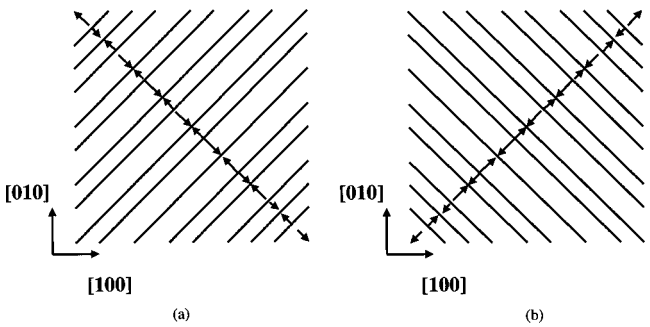

FIG. 2. Illustration of the observed domain structure. (a) Domain pattern A, which is a twin with 109° charged domain walls along [110]. The arrows represent the projections of the polarization orientations on the [001] surface. (b) Domain pattern B which is a twin with domain walls along $[1\bar{1}0]$.

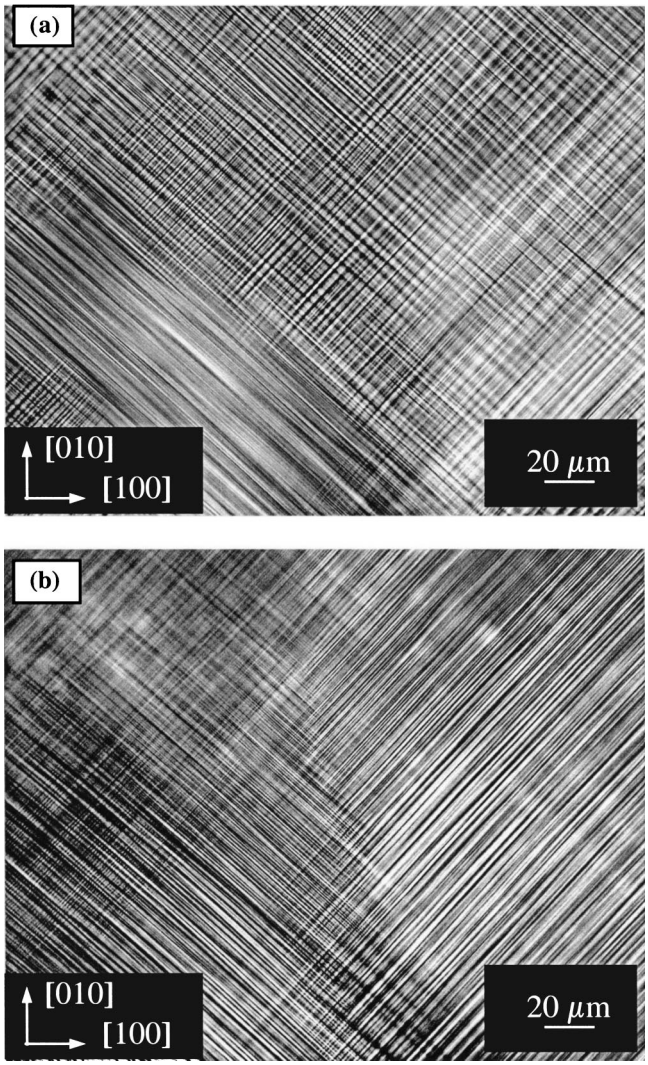

FIG. 3. Domain structures of a PMN–32%PT single crystal observed at the same area on the [001] surface but focusing at different depths.

small local region, only domain pattern A or B can be observed. When the size of the domains is not so small compared to that of the sample, domain pattern A or B could occupy the entire sample to give $mm2$ effective symmetry, as previously reported in the [001]-poled $0.955Pb(Mg_{1/3}Nb_{2/3})O_3-0.045PbTiO_3$ single crystals with rhombohedral phase.[6]

By focusing at a different depth along [001] of the same area using a polarized light microscopy, multilayered structures can be observed. The obtained images are shown in Fig. 3. Clearly, from Figs. 3(a) to 3(b), with the increase of the focal depth along [001], a local area experiences a gradual change from domain pattern A to B or vice versa. This is a typical characteristic of the multilayered interweaving structure in many of the PMN–PT or PZN–PT samples. By measuring the focal depth, we estimated that the thickness of one twin layer is 50–100 μm.

In summary, multidomain structures with a tweed configuration were observed in [001]-poled rhombohedral phase PMN–32%PT single crystals, which are significantly different from the previously assumed domain patterns containing intersecting 71° domain walls. The tweed domain structures consist of interweaving of twin layers of 50–100 μm in thickness. Each local domain pattern contains two domain states and 109° charged domain walls along either [110] or $[1\bar{1}0]$. The domain sizes, ranging from 1 to 2 μm, are much smaller than the sample dimensions in our experiments. Therefore, a large amount of domains/domain walls exist, which makes the effective symmetry of the whole structure to be $4mm$. A major difference from previous assumed domain patterns is that the domain walls are 45° rotated from $\langle 100\rangle$ to $\langle 110\rangle$ family and the local symmetry of $mm2$.

From experience, charged domain walls are not allowed in a regular ferroelectric material. The reasons for the presence of charged walls in these crystal systems are the existence of large amount of charged defects, including aliovalent dopants and vacancies. These charged defects would stabilize charged walls. In addition, the charge neutrality may also be accomplished through the injection of free charges to the walls during poling process. Therefore, in considering the domain pattern stability, we could ignore the electric energy by assuming all the charged are neutralized. This leaves the dominant factor to be the elastic energy. Since the crossintersecting of 71° domain walls causes larger elastic deformation, the 109° twinning is more preferred. The most interesting phenomena found in our investigation is the interweaving of two twin sets, which is a type of domain pattern never observed in other known ferroelectric crystals.

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