Domain configurations in domain engineered $0.955Pb(Zn_{1/3}Nb_{2/3})O_3-0.045PbTiO_3$ single crystals

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We report an optical microscopy study on the domain structures of $0.955Pb(Zn_{1/3}Nb_{2/3})O_3-0.045PbTiO_3$ rhombohedral phase single crystals poled along [001] of the cubic coordinates. Both charged and uncharged domain walls are observed in domain engineered samples and they could join together to form ''L'' and ''T'' shaped domain walls, which are very unique. The observed domains are between 10 and 100 μm in size, which are much bigger than expected. Most of the samples have only two of the four possible degenerate domain states, making the macroscopic symmetry to be *mm2* or lower rather than *4mm* previously assumed. © *2000 American Institute of Physics.* [S0021-8979(00)02710-9]

Single crystal $(1-x)Pb(Zn_{1/3}Nb_{2/3})O_3-xPbTiO_3$ (PZN–PT) system of the rhombohedral ferroelectric phase can have very high coupling constant and piezoelectric constant after being poled along [001].[1–3] It has triggered a new wave of material research recently to improve material properties using domain engineering, i.e., using a different poling scheme to manipulate domain structures. It also raised many interesting scientific questions, such as the origin of these superior properties and the role of domains in general. The very high electromechanical coupling coefficient ($k_{33}>90\%$) and piezoelectric coefficient ($d_{33}>2000$ pC/N) produced by domain engineering method make the PZN–PT a much better candidate for transducer materials than the $PbZrO_3$–$PbTiO_3$(PZT) solid solution system used for the past 40 years. The PZN–PT single crystal solid solution system has been made in the late 1960s[4] and it was found that the electromechanical coupling coefficient k_{33} could be more than 90% in some samples.[5,6] However, the composition studied was at the boundary composition of the tetragonal phase, therefore, properties were not as high and not as consistent. The newly established domain engineering method makes it possible to stabilize the polarization of the rhombohedral phase by poling the crystals in [001] rather than the polarization direction of [111].[1–3]

Understanding the physical mechanism of this property enhancement is very important for extending this domain engineering idea to other materials. Naturally, the key issue is the domain structures since the off-polarization direction poling will create a multidomain single crystal system. This article reports an experimental study on the domain structures in a $0.955Pb(Zn_{1/3}Nb_{2/3})O_3-0.045PbTiO_3$ [PZN–4.5%PT] system, which has a microscopic symmetry of *3m*.

Because the dipoles of the PZN–4.5%PT form along the body diagonals of the parent cubic perovskite structure at the ferroelectric phase transition, the crystal has rhombohedral symmetry with the symmetry group *3m* in the ferroelectric state.[4,5] Poling was done by applying an electric field along [001] of the cubic coordinates so that only four of the eight possible polarization orientations remain, i.e., [111], $[\bar{1}11]$, $[1\bar{1}1]$, and $[11\bar{1}]$. Statistically, such a system would have a pseudomacroscopic tetragonal symmetry considering the degeneracy of these four domain states. All previous studies on this system were based on this *4mm* symmetry assumption.[1–3,7,8]

However, it was found experimentally that the material properties of the domain engineered PZN–4.5%PT could

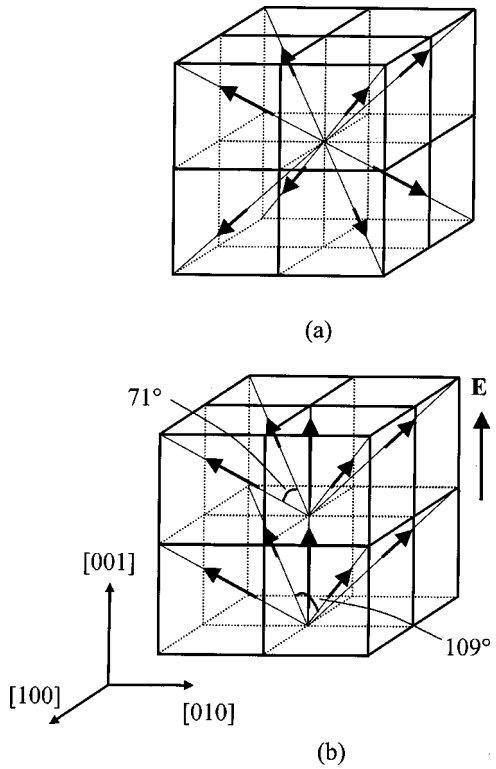

FIG. 1. Illustration of the assumed domain structure with cross intersecting charged domain walls for the PZN–4.5%PT. (a) There are eight possible orientations of dipoles before poling. (b) Four orientations remain after poling for the polarization. The structure is macroscopically tetragonal.

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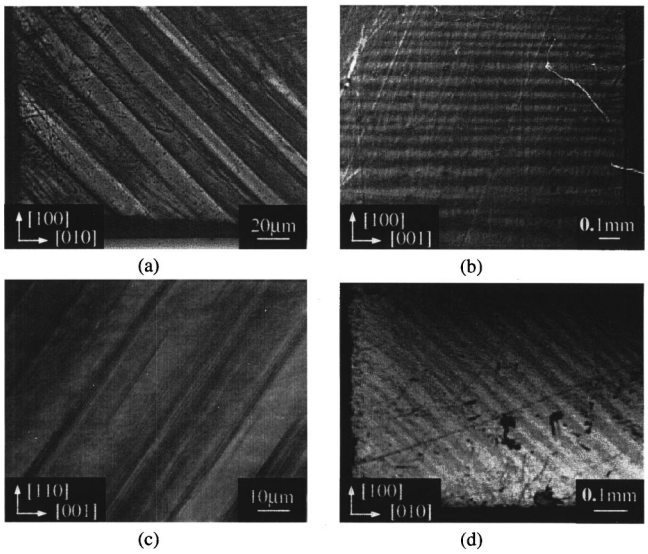


FIG. 2. Domain patterns observed on different sample surfaces. In each sample, there is only one set of twins with fairly large domain size. (a) On (001) surface; (b) on (010) surface; (c) on $(\bar{1}10)$ surface; and (d) same as (a) but in different sample and different scale.

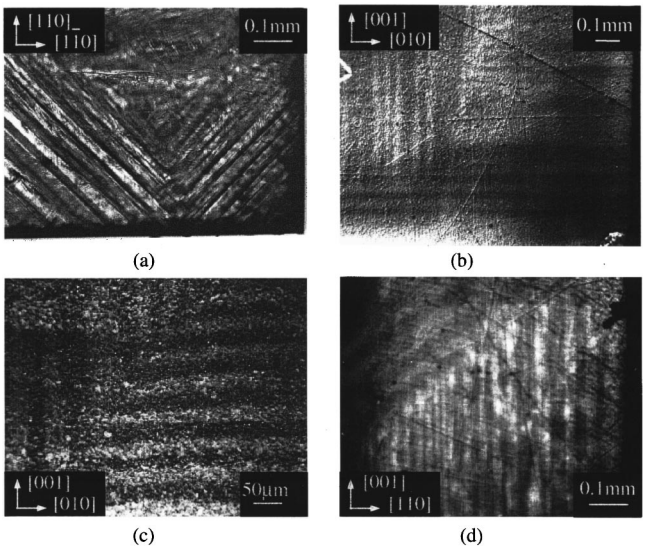


FIG. 3. A charged and an uncharged domain walls join together to form L or T shaped domain walls. (a) on (001) surface; (b) and (c) on (001) surface; and (d) on $(1\bar{1}0)$ surface.

change substantially from sample to sample, particularly sensitive to the sample geometry.[7,8] There are also indications from our ultrasonic measurements that the elastic properties deviate from the *4mm* symmetry in many of the samples. In order to understand this issue, we used optical microscopy to exam the domain patterns in the [001] poled PZN–4.5%PT multidomain single crystals and performed some simple analyses to interpret these observed domain structures. The most interesting phenomena observed was the coexistence of charged and uncharged domain walls, which has never been reported in the literature.

The macroscopic symmetry defined in this article is what reflected in the macroscopic material properties, which do not change with the overall shape of the sample but only with the domain configurations. The *4mm* macroscopic tetragonal symmetry assumption implicitly assumed the following two conditions: (1) the domain size is very small compared to sample dimensions so that large amount of domains exist to allow the use of statistical principle; and (2) the domain walls are all charged and are parallel to the effective polarization direction (i.e., the wall normal is perpendicular to the applied poling field) as shown in Fig. 1.

For the domain observations, we prepared many samples with three pairs of mutually perpendicular surfaces. These samples have two types of orientations: [001]/[010]/[100] and [001]/[110]/[1$\bar{1}$0]. The sample shapes are cubes, plates, or bars with the typical dimension of *1–5mm*. Observations were performed on the surfaces of the following three orientations: [001], [110], and [100], with the samples being poled along [001] in all cases. Because the crystal is translucent, domains could be observed by polarizing optical microscopy in either reflection mode or transmission mode.

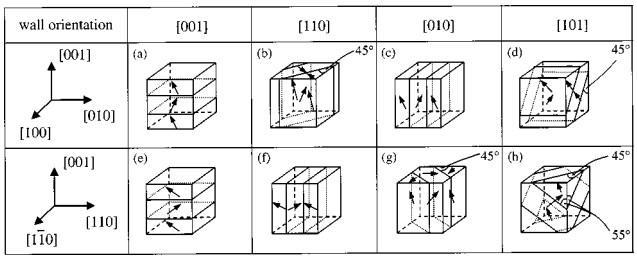
Figures 2 and 3 show a few of the domain patterns obtained in the domain engineered PZN–4.5%PT system. One can see that the two implicit assumptions in treating the system to be macroscopic tetragonal are not satisfied. First of all, the domain size is fairly large compared to the sample size, ranging from 10 to 100 μm, so that there will be only 20–100 domains across the sample. Second, the domains are coupled strongly to each other in the form of elastic twins. These two facts invalidate the use of statistical description, which requires a large ensemble of independent elements. In fact, we found that only two of the four possible domains exist in most of the samples. This effectively reduced the macroscopic symmetry of this multidomain crystal from *4mm* to *mm 2* or even lower. In addition, both charged and neutral domain walls are present in the system, while the *4mm* macroscopic symmetry requires all the walls to be charged.

In a $m\bar{3}m \rightarrow 3m$ ferroelectric phase transition, such as occurred in the PZN–4.5%PT system, the permissible domain walls formed in the ferroelectric phase are orientated in $\langle 100 \rangle$ and $\langle 110 \rangle$ family. The angle between polarization vectors on the two sides of a domain wall can be either 109° or 71°. We listed in Table I, all the permissible domain walls

TABLE I. Permissible orientations of domain walls in [001] poled PZN–4.5%PT crystals of rhombohedral phase. The polarization directions of $\mathbf{P}_s$ and $\mathbf{P}_s'$ in a twin structure are given in the first row.

$\mathbf{P}_s/\mathbf{P}_s'$	$[111]/[\bar{1}11]$	$[111]/[1\bar{1}1]$	$[111]/[11\bar{1}]$	$[\bar{1}11]/[1\bar{1}1]$	$[\bar{1}11]/[\bar{1}\bar{1}1]$	$[1\bar{1}1]/([\bar{1}\bar{1}1]$
Charged	[100]	[010]	[110]	$[1\bar{1}0]$	[010]	[100]
Uncharged	[011]	[101]	[001]	[001]	$[\bar{1}01]$	$[0\bar{1}1]$

TABLE II. Illustration of possible twin patterns in [001]/[010]/[100] and [001]/[110]/[1$\bar{1}$0] oriented rhombohedral PZN–4.5%PT single crystals poled along [001].



between different pairing schemes among the four remaining domains after poling. It can be shown that the intersection lines of the domain walls on the sample surface may form 0°, 45°, and 55° angles with respect to the edges of the samples as shown in Table II.

Figure 2 shows the domain patterns of types (b), (c), (f), and (g), respectively, listed in Table II. One can see that the intersection lines of domain walls with sample surfaces are either parallel or form a 45° angle with one of the edges of the sample. More importantly, contrary to the conventional reported ferroelectric twins of head to tail charge neutral configurations, the twin patterns type (b) and type (f) in Table II contain charged walls with the polarizations form either head to head or tail to tail configurations between the two domain states $\mathbf{P}_s \| [111]$ and $\mathbf{P}_s \| [\bar{1}\bar{1}\bar{1}]$. The polarization vectors of the two domains in the twins form a 109° angle in this case. Types (c) and (g) in Table II are the twin patterns between $\mathbf{P}_s \| [111]$ and $\mathbf{P}_s \| [\bar{1}1\bar{1}]$. The domain walls are also charged with the polarization vectors form a 71° angle. Uncharged walls, such as type (h) in Table II between $\mathbf{P}_s \| [111]$ and $\mathbf{P}_s \| [\bar{1}\bar{1}1]$, were also observed in some of the samples. The intersection lines between the charge neutral walls and the sample surfaces form either a 45° or 55° angle with respect to the sample edges as indicated in Table II.

Figure 3 shows several observed complex domain patterns. They are both charged and uncharged domain walls and it is very interesting to see that the charged and uncharged walls could join each other to form ''L'' and ''T'' shaped patterns. In part of one sample with the orientations of [100]/[010]/[001] and the corresponding dimensions of *2.4mm/2.27mm/0.43mm*, respectively, all four possible domains were found to coexist after poling in [001] as shown in Fig. 4.

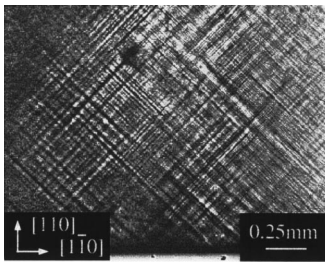


FIG. 4. Two sets of twins intersecting each other to form a network of four different domain states. This is the top view from [001].

In order to better understand these observed patterns, we have made simple analysis based on the crystal structure and illustrated in Fig. 5 some possible complex patterns made of two and four domain states. The observed patterns in Figs. 3 and 4 could be matched to those patterns of Fig. 5 as the following:

Fig. 3(a)→the top view of Fig. 5(e);

Fig. 3(b)→front view of the configuration Figs. 5(b) or 5(c);

Fig. 3(c)→front view of Fig. 5 (a);

Fig. 3(d)→front view of Fig. 5 (d) (upside down), and

Fig. 4→front view of Fig. 5(f).

Figure 4 is a pattern showing the coexistence of all four possible domains, $\mathbf{P}_s \| [111]$, $\mathbf{P}_s \| [\bar{1}\bar{1}1]$, $\mathbf{P}_s \| [\bar{1}11]$, and $\mathbf{P}_s \| [1\bar{1}\bar{1}]$. Statistically speaking, this configuration should be the most probable structure after poling in [001], since the four ferroelectric variants are energetic degenerate. However, because the wall intersection causes energy, we only have seen such domain patterns in a small potion of one of the samples.

In summary, our optical microscopy studies showed that the domain patterns in the domain engineered PZN–4.5%PT single crystals are predominantly twins containing only two

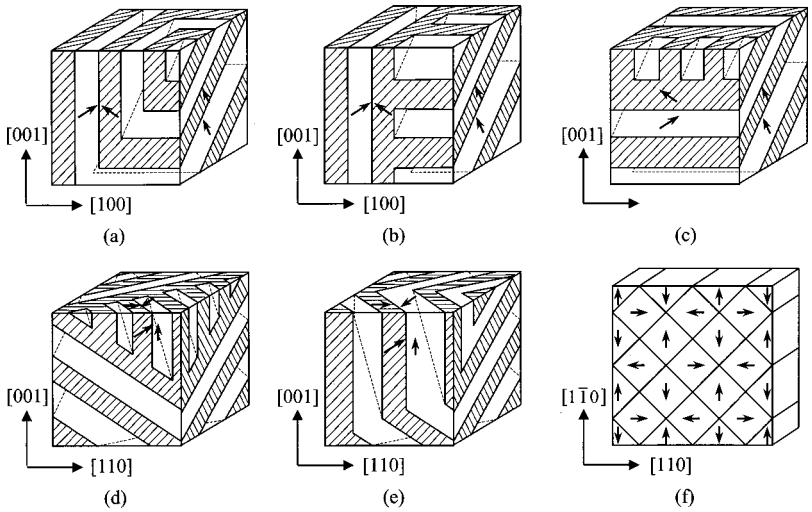


FIG. 5. Illustration of domain patterns that can be formed by the combination of charged and uncharged domain walls. (a)–(e) are patterns of twinning by two domains. One can see that L and T shaped domain walls are formed by joining a charged and an uncharged wall. (f) is the domain pattern for the coexistence of all four possible domains.

of the four possible domains after being poled in [001]. The size of the domains is relatively large, ranging from 10 to 100 μm, therefore, one may conclude that the previously assumed macroscopic *4mm* symmetry for the [001] poled rhombohedral phase crystal might not be always appropriate. As theoretically predicted[9] the highest macroscopic symmetry of a two-domain system is orthorhombic *mm2*. The symmetry could be even lower if the volume ratios of the two domains in the twin are different.[10] The most intriguing phenomenon observed was the coexistence of charged and uncharged domain walls joining together in a poled PZN–4.5%PT system, and these joined walls could form either L or T shaped domain walls. Based on energy consideration, in order for the charged walls to exist, charged dopants or defects must be distributed near the wall region to reduce the electrostatic energy. On the other hand, the existence of these intersected domain walls could introduce high elastic strain energy, making the domain structures less stable, which could be one of the main reasons for the multidomain structure to be more responsive to external drive, producing high value of dielectric and piezoelectric coefficients.

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[1] S. E. Park and T. R. Shrout, IEEE Trans. Ultrason. Ferroelectr. Freq. Control **44**, 1140 (1997).
[2] S. E. Park and T. R. Shrout, J. Appl. Phys. **82**, 1804 (1997).
[3] S. F. Liu, S. E. Park, T. R. Shrout, and L. E. Cross, J. Appl. Phys. **85**, 2810 (1999).
[4] S. Nomura, T. Takahashi, and Y. Yokomizo, J. Phys. Soc. Jpn. **27**, 262 (1969).
[5] J. Kuwata, K. Uchino, and S. Noemura, Ferroelectrics **37**, 579 (1981).
[6] J. Kuwata, K. Uchino, and S. Noemura, Jpn. J. Appl. Phys., Part 1 **21**, 1298 (1982).
[7] J. Yin, B. Jiang, and W. Cao, Proc. SPIE, Medical Imaging, San Diego, CA (1999).
[8] J. Yin, B. Jiang and W. Cao, IEEE Trans. Ultranson. Ferroelectr. Freq. Control **43**, 285 (2000).
[9] J. Erhart and W. Cao, J. Appl. Phys. **86**, 1073 (1999).
[10] J. Erhart and W. Cao (unpublished).