

## Observation and Analysis of Domain Configurations in Domain Engineered PZN-PT Single Crystals

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The effective macroscopic symmetry of the PZN-PT single crystal systems is a key issue for the characterization of domain engineered single crystals. We report an optical microscopy study on the domain structures of  $0.955\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.045\text{PbTiO}_3$  (PZN-PT) 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. The observed domains are between 10–100  $\mu\text{m}$  in size, which are too big for statistical treatment. Most of the poled samples have only two of the four possible degenerate domain states, making the macroscopic symmetry to be either orthorhombic  $mm2$  or monoclinic  $m$ , or even triclinic  $1$  rather than tetragonal  $4mm$  previously assumed. Physical property measurements also support the conclusion of lower symmetry.

*Keywords:* PZN-PT; ferroelectric material; domain; domain wall; domain engineering

### INTRODUCTION

Rhombohedral relaxor based ferroelectric  $(1-x)\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\text{PbTiO}_3$  (PZN-PT) single crystal system can have very high coupling constant ( $k_{33} > 90\%$ ) and piezoelectric constant ( $d_{33} > 2000\text{pC/N}$ ) if it

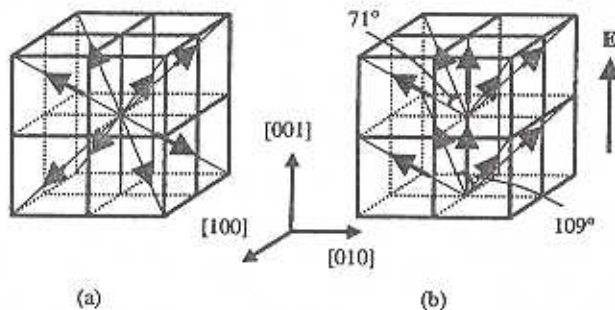
is poled along the [001] of the parent cubic coordinates.[1-3] It has triggered a new wave of material research recently to improve material properties using domain engineering, i.e., using different poling scheme to manipulate domain structures. It also raised many interesting scientific questions, such as the origin of these superior properties and the role of domains in general. The extremely high electromechanical coupling coefficient and piezoelectric coefficient of this system produced by domain engineering method makes the PZN-PT another promising candidate for transducer materials other than the  $\text{PbZrO}_3\text{-PbTiO}_3$  (PZT) solid solution system, which was 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 even more than 90% in some samples.[5,6] However, the composition studied before was at the morphotropic boundary composition between the rhombohedral and the tetragonal phases, therefore, properties were not reproducible. The more recent effort using domain-engineering concept makes it possible to stabilize the polarization of the rhombohedral phase by poling the crystals in [001] rather than the polarization direction of [111] (all refer to the cubic coordinates). [1-3]

Naturally, the key issue is the domain structures produced in the system since the off-polarization direction poling will create multi-domains. This paper reports an experimental study on the domain structures as well as the property measurement in a  $0.955\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-}0.045\text{PbTiO}_3$  (PZN-4.5%PT) system. Based on the experimental results, a macroscopic mm2 symmetry is more plausible than the 4mm symmetry as all previous studies had assumed.

## POSSIBLE DOMAINS

Because the dipoles of the PZN-4.5%PT form along the body diagonal of the parent cubic perovskite structure at the ferroelectric phase transition, the crystal has microscopic 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 with positive projections in [001] could remain, i.e. [111],  $[\bar{1}\bar{1}1]$ ,  $[1\bar{1}\bar{1}]$  and  $[\bar{1}\bar{1}\bar{1}]$  as shown in Figure 1.

Statistically, such a system would have a macroscopic pseudo-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]



**FIGURE 1** Illustration of the assumed domain structure with cross intersecting charged domain walls for the PZN-4.5%PT. (a) Eight possible orientations before poling. (b) Four orientations remain after poling.

The macroscopic symmetry referred here 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; (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 Figure 1.

In a  $\bar{m}3m \rightarrow 3m$  ferroelectric phase transition, such as what 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.[8,9] The angle between polarization vectors on the two sides of a domain wall can be either  $109^\circ$  or  $71^\circ$ . All the permissible domain walls between different pairing schemes among the four remaining domains after poling are listed in Table I. Both charged and uncharged walls are possible.

TABLE I Permissible orientations of domain walls in [001] poled PZN-4.5%PT crystals of rhombohedral phase. The polarization directions of  $P_s$  and  $P_s'$  in a twin structure are given in the first row.

$P_s/P_s'$	[111]/[111]	[111]/[111]	[111]/[111]	[111]/[111]	[111]/[111]	[111]/[111]
charged	[100]	[010]	[110]	[110]	[010]	[100]
uncharged	[011]	[101]	[001]	[001]	[101]	[011]

## DOMAIN OBSERVATIONS AND CONFIGURATIONS

For the domain observations, we prepared the samples with three pairs of mutually perpendicular surfaces. These samples have two types of orientations referring to the cubic coordinates: [001]/[010]/[100] and [001]/[110]/[110]. The sample shapes are cubes, plates, or bars with the typical dimension of 1-5 mm. Observations were performed on the surfaces of the following three

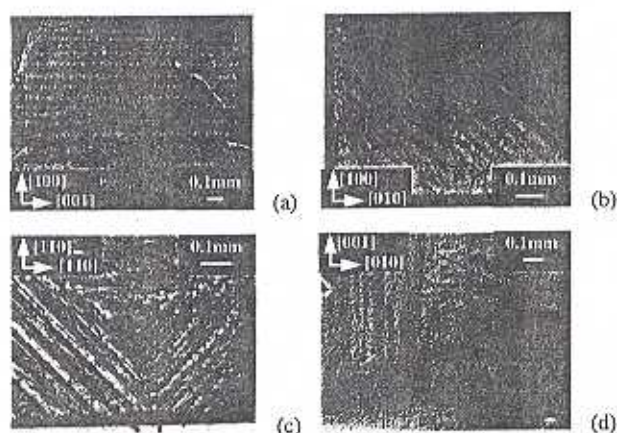


FIGURE 2 Domain patterns observed on different sample surfaces. A set of twins with fairly large domain size are shown in (a) and (b). A charged and an uncharged domain walls join together to form "L" or "T" shaped domain walls shown in (c) and (d).



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. Figure 2 shows a few of the domain patterns obtained in the domain engineered PZN-4.5%PT single crystal system. Figure 3 shows the domain structures correspond to the patterns in Figure 2. One can see that the intersection lines of domain

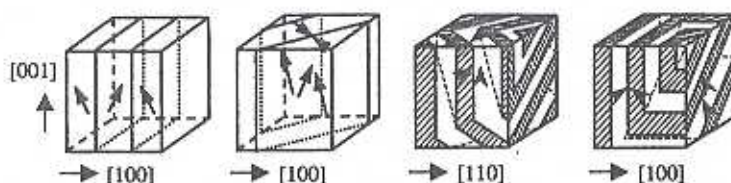


FIGURE 3 Illustration of possible domain structures that form the patterns in Figure 2. (a) front view. (b) top view. (c) top view. (d) front view.

walls with sample surfaces are either parallel or form a  $45^\circ$  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 in Figure 3(a) contain charged walls with the polarizations form either head to head or tail to tail configurations between the two domain states  $P_s \parallel [111]$  and  $P_s \parallel [1\bar{1}1]$ . The polarization vectors of the two domains in the twins form a  $71^\circ$  angle in this case. In Figure 3(b), the domain walls between the two domain states  $P_s \parallel [111]$  and  $P_s \parallel [1\bar{1}1]$  are also charged with the polarization vectors form a  $109^\circ$  angle. The most interesting phenomena observed was the co-existence of charged and uncharged domain walls, which has never been reported in the literature. Figure 2(c) and 2(d) show two complex domain patterns of such co-existence of charged and uncharged domain walls, which join each other to form "L" and "T" shaped patterns. One can see that the macroscopic symmetry of such systems is very low.

## MACROSCOPIC SYMMETRY

From Figure 2 and Figure 3, one can see that the two implicit assumptions in treating the multi-domain systems to be macroscopic tetragonal are generally not satisfied. First of all, the domain size is fairly large compared to the sample size, ranging from 10 to 100 $\mu\text{m}$ , 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 multi-domain crystal from  $4mm$  to  $mm2$  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. Theoretical study [9] predicted that the highest macroscopic symmetry of a two-domain system is orthorhombic  $mm2$ . The symmetry could be monoclinic  $m$  if the volume ratios of the two domains in the twin are different.[10]

The physical properties have been measured to corroborate the domain study on the macroscopic symmetry. Both ultrasonic and resonance methods [7] have been used for the measurements. Some of the measured properties of PZN-4.5%PT single crystal are listed in Table II, where  $\rho$  is the density,  $v$  is the ultrasonic velocity and  $d$  is the piezoelectric constant. The subscripts  $l$  and  $s$  represent the longitudinal and shear waves, respectively. For the shear waves, the first superscript direction  $[lmn]$  is for the propagating direction and the second superscript direction  $[lmn]$  is the displacement polarization direction.

TABLE II Measured properties of PZN-4.5%PT single crystal

$\rho(v_l^{[110]})^2$	$\rho(v_l^{[1\bar{1}0]})^2$	$\rho(v_s^{[001][100]})^2$	$\rho(v_s^{[001][010]})^2$	$d_{31}$	$d_{31}^{[110]}$
$10^{10} \text{ N/m}^2$	$10^{10} \text{ N/m}^2$	$10^{10} \text{ N/m}^2$	$10^{10} \text{ N/m}^2$	$10^{-12} \text{ C/N}$	$10^{-12} \text{ C/N}$
17.7	14.9	6.8	6.7	970	1154

The relations between measured values and physical property constants are given by

$$\begin{aligned} \rho(v_i^{(110)})^2 &= \rho(v_i^{(1\bar{1}0)})^2 = \frac{1}{4}(c_{11}^E + c_{22}^E + 2c_{12}^E + 4c_{66}^E) & (1) \\ \rho(v_i^{(001),(100)})^2 &= c_{55}^E & \rho(v_i^{(001),(010)})^2 &= c_{44}^E \\ d_{31}^{(110)} &= \frac{1}{2}(d_{31} + d_{32}) \end{aligned}$$

For the microscopic symmetry of  $4mm$ ,

$$c_{44}^E = c_{55}^E \quad \text{or} \quad \rho(v_i^{(001),(100)})^2 = \rho(v_i^{(001),(010)})^2 \quad (2)$$

$$d_{31} = d_{32} \quad \text{or} \quad d_{31} = d_{31}^{(110)} \quad (3)$$

Obviously, equations (1)-(3) cannot be met by the measured values in Table II. Therefore, the macroscopic symmetry of the domain engineered PZN-4.5%PT single crystal is better represented by the orthorhombic symmetry  $mm2$  or even lower rather than the tetragonal  $4mm$ .

## 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 of the four possible domains after being poled in [001]. The size of the domains is relatively large, ranging from 10-100  $\mu\text{m}$ , therefore, one may conclude that the previously assumed macroscopic  $4mm$  symmetry for the [001] poled rhombohedral phase crystal might not be always appropriate. This conclusion is supported by the ultrasonic measurements. 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 co-existence of charged and uncharged domain walls joining together to form either "L" or "T" shaped domain walls. Based on energy

consideration, in order for the charged walls to exist, charged dopants or charged 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 multi-domain structure to produce high value of dielectric and piezoelectric coefficients.

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