Effective macroscopic symmetries and materials properties of multidomain $0.955Pb(Zn_{1/3}Nb_{2/3})O_3$-$0.045PbTiO_3$ single crystals

Jianhua Yin and Wenwu Cao[a)]
Materials Research Institute, The Pennsylvania State University, University Park, Pennsylvania 16802

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The crystal symmetry of a $0.955Pb(Zn_{1/3}Nb_{2/3})O_3$-$0.045PbTiO_3$ (PZN-4.5%PT) single crystal is rhombohedral $3m$. It is in multidomain state after being poled along [001] of its original cubic coordinates. Although most studies on this system assumed the tetragonal $4mm$ effective symmetry, experimental observations show that many of the crystals actually have effective orthorhombic $mm2$ symmetry. Some crystal domain patterns may even become monoclinic m or even lower in symmetry. In other words, domains form a hierarchical symmetry, which controls the effective materials properties of the multidomain system. We report an analysis of the domain symmetry involved and a full set of materials properties measured in crystals having only two of the four possible domains based on $mm2$ symmetry.
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INTRODUCTION

The $(1-x)Pb(Zn_{1/3}Nb_{2/3})O_3$-$xPbTiO_3$ (PZN-PT) rhombohedral relaxor based ferroelectric single crystals have been found to give a very high electromechanical coupling constant k_{33} (>90%) and a piezoelectric constant d_{33} (>2000 pC/N) after being poled along [001] of the parent cubic coordinates.[1,2] The piezoelectric d_{33} constant is more than three times that of the $Pb(Zr_{1-x}Ti_x)O_3$ (PZT) solid solution system, which has been used for the past 40 years in most piezoelectric devices. The study of the PZN-PT single crystal can be traced back to the 1970s.[3,4] However, the composition studied before consists of both tetragonal and rhombohedral symmetry phases, which makes the materials properties not reproducible. More recent crystal growth effort produced better quality materials with purer phases. By using compositions slightly on the rhombohedral side of the phase diagram and pole the crystals in [001] rather than the polarization direction of [111] produced piezoelectric materials with an extraordinarily large piezoelectric coefficient and electromechanical coupling coefficient.[1,2]

Naturally, multidomains are created in the crystal when the poling is not along the polarization direction. Understanding the macroscopic symmetry of multidomain PZN-PT single crystal is very important for the physical property characterization. All studies on the PZN-PT systems[1,2,5] have been based on the effective $4mm$ symmetry, assuming all four possible domain variants exist in equal proportion after poling. We show here, however, that many engineered domain structures consist of only two of the four possible domains and such two domain systems may have much lower symmetry than $4mm$.[6] In fact, experimentally, we found that the two-domain twinned systems are more likely to occur in PZN-PT single crystals than the four-domain systems required for the effective $4mm$ symmetry. In other words, for certain sample geometries, orthorhombic $mm2$ or monoclinic m, or even triclinic 1 could occur in spite of the underlying rhombohedral $3m$ crystal symmetry.[6–8] We report here some detailed symmetry analyses and a set of material properties for a crystal system containing twinning of two domain variants based on the effective symmetry of $mm2$.

DOMAIN STRUCTURES

Because the dipoles of the PZN-4.5%PT forms along the body diagonal of the parent cubic perovskite structure at the ferroelectric phase transition, the crystal structure has rhombohedral symmetry with the symmetry group $3m$ in the ferroelectric state.[3,4] 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], $[\bar{1}11]$, $[1\bar{1}1]$, and $[\bar{1}\bar{1}1]$ as shown in Fig. 1. Figure 2 is an observed pattern of this four-domain state looking down from [001]. Statistically, such a system would have a macroscopic pseudo-tetragonal symmetry considering the energy degeneracy of these four domain states. All previous studies on this system were based on this $4mm$ symmetry assumption.[1,2,5] Our observations on domain patterns in many samples showed that the two-domain type structure is more likely to occur in the PZN-4.5%PT than patterns that contain all four domain variants, particularly for noncubic sample geometry.[6] Figure 3 shows typical two-domain variant structures in PZN-4.5%PT multidomain crystal observed using optical microscopy. The dipoles are orientated in [111] and $[\bar{1}\bar{1}1]$. They form a domain structure as illustrated in Fig. 4. The pictures in Fig. 3 correspond to the top-view and front-view of the domain pattern shown in Fig. 4.

MACROSCOPIC SYMMETRY

From Fig. 3, one can see that treating the PZN-PT multidomain systems to be macroscopic tetragonal $4mm$ is not always appropriate. For the two-domain systems, Erhart and

[a)]Electronic mail: cao@math.psu.edu

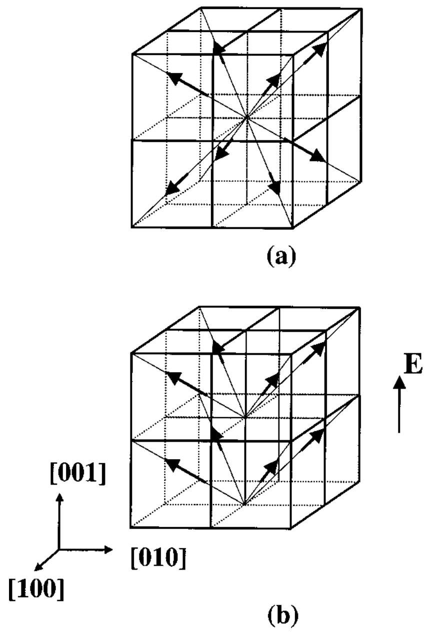

FIG. 1. Illustration of the assumed domain structure with cross intersecting charged domain walls for a PZN-4.5%PT crystal. (a) Eight possible orientations before poling. (b) Four orientations remain after poling.

Cao predicted that the highest macroscopic symmetry is orthorhombic $mm2$.[7] Strictly speaking, the symmetry could be monoclinic m if the volume ratios of the two domains in the twin are different.[8]

In order to verify that the symmetry might be nontetragonal, we conducted ultrasonic measurements on some of the PZN-PT samples. From Christoffel wave equations[9] one can get the relationship between velocities and elastic constants in different orientations:

$$\rho(\nu_l^{[100]})^2=c_{11}^E, \tag{1a}$$

$$\rho(\nu_l^{[010]})^2=c_{22}^E, \tag{1b}$$

$$\rho(\nu_l^{[110]})^2=\rho(\nu_l^{[\bar{1}10]})^2=\tfrac{1}{4}(c_{11}^E+c_{22}^E+2c_{12}^E+4c_{66}^E), \tag{1c}$$

$$\rho(\nu_s^{[001],[100]})^2=c_{55}^E, \tag{1d}$$

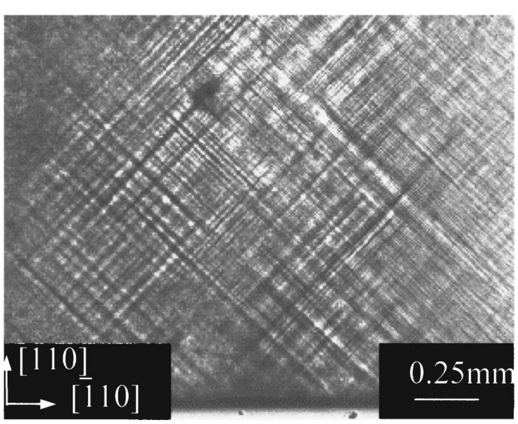

FIG. 2. Domain pattern of a domain engineered crystal having all four energetically equivalent domains. The effective symmetry of this crystal is quasi-tetragonal $4mm$.

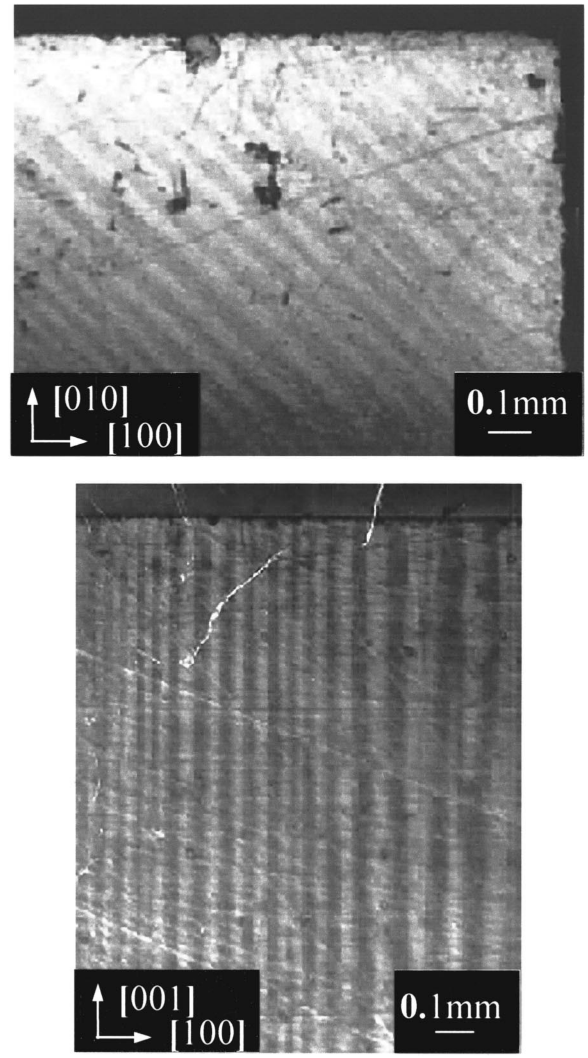

FIG. 3. Top and side view of observed twin domains in a system with quasi-orthorhombic symmetry.

$$\rho(\nu_s^{[001],[010]})^2=c_{44}^E, \tag{1e}$$

$$\rho(\nu_s^{[001],[lm0]})^2=l^2c_{44}^E+m^2c_{55}^E \tag{1f}$$

where ρ is the density and ν is the ultrasonic velocity. The subscripts l and s represent the longitudinal and shear waves, respectively. For shear waves, the first superscript $[lmn]$ indicates the wave propagation direction and the second superscript $[lmn]$ after the comma is the displacement direction. For the microscopic symmetry of $4mm$ we have

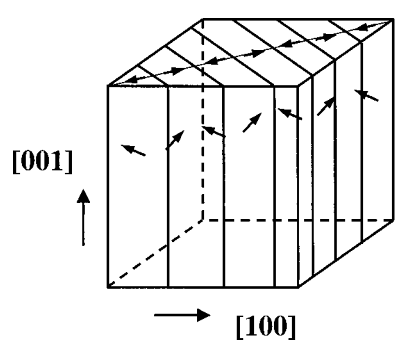

FIG. 4. Illustration of the twin domain structures in Fig. 3.

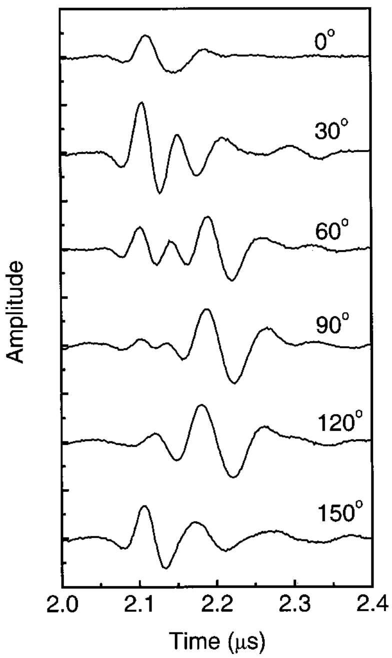

FIG. 5. Echo pulse of a shear wave propagating in [001] with polarization in a different angle with respect to [110] for a poled multidomain system.

TABLE I. Measured longitudinal and shear wave phase velocities in a poled multidomain PZN-4.5%PT single crystal. The superscript [001],[110] represents that the shear wave propagates along [001] with displacement along [110]. Unit in m/s.

$v_l^{[110]}$	$v_l^{[1\bar{1}0]}$	$v_s^{[001],[110]}$	$v_s^{[001],[1\bar{1}0]}$
4615	4235	2860	2840

TABLE II. Piezoelectric constant d_{31} of a PZN-4.5%PT single crystal obtained from k_{31} resonance bars with the long dimension of the bar forming an angle θ with the [001] direction.

θ	0°	30°	45°
d_{31}^{θ} (10^{-12} C/N)	907	927	1134

$$c_{11}^E = c_{22}^E \quad \text{so that} \quad v_l^{[100]} = v_l^{[010]}, \tag{2a}$$

$$c_{44}^E = c_{55}^E \quad \text{so that} \quad v_s^{[001],[100]} = v_s^{[001],[010]} = v_s^{[001],[lm0]}. \tag{2b}$$

Figure 5 shows the echo pulses of the shear wave propagating in the [001] direction with the displacement direction in different angle θ from [110]. One can see that the wave velocity, which is related to the time of flight of echoes, has been changed whenever the displacement polarization direction is changed. For $4mm$ symmetry, there should be no change in velocity as indicated in Eq. (2). Table I lists the measured velocities of the longitudinal wave and shear wave propagating in different directions. The results show again that the measured PZN-4.5%PT multidomain crystal has symmetry lower than $4mm$.

Resonant measurements were also carried out for s_{11} bars, which further corroborate the lower symmetry conclusion. The samples were cut into thin bars with thickness t in [001] and length l in directions for a θ angle with [100], where θ has been chosen as 0°, 30°, and 45°, respectively. The piezoelectric constants d_{31} calculated from measured resonant and antiresonant frequencies[10] are listed in Table II. The piezoelectric constant in the direction θ is given by $d_{31}^{\theta} = (d_{31} \cdot \cos^2\theta + d_{32} \cdot \sin^2\theta)$. For $4mm$ symmetry, $d_{31} = d_{32}$, then we should have $d_{31}^{\theta} = d_{31}$. This means that the piezoelectric constant d_{31} should not change for the longitudinal resonance bar made for any direction perpendicular to [001]. Obviously, this does not hold true for the measured values in Table II.

MATERIAL PROPERTIES FOR DOMAIN ENGINEERED CRYSTALS WITH *mm*2 SYMMETRY

In the case shown in Fig. 3, the domain walls are oriented in the [110] of the cubic coordinates. They are formed by dipoles oriented in [111] and $[\overline{111}]$. Macroscopically, the system has an effective $mm2$ orthorhombic symmetry on average and the two mirror planes are in the [110] and $[1\bar{1}0]$ directions of the original cubic coordinates. Based on the ultrasonic and resonance measurements and the constitutive relationships for the $mm2$ symmetry,[10] we have derived a full set of material constants as listed in Table III. The data in Table III was obtained by using both the resonance and the ultrasonic methods with the assistance of low frequency ca-

TABLE III. Measured full set material properties of a poled PZN-4.5%PT multidomain single crystal based on $mm2$ symmetry.

Density: ρ (kg/m^3)								
8310								
Elastic constants: c_{ij} (10^{10} N/m^2)								
c_{11}^E	c_{12}^E	c_{13}^E	c_{22}^E	c_{23}^E	c_{33}^E	c_{44}^E	c_{55}^E	c_{66}^E
17.7	3.6	10.1	14.9	9.7	10.7	6.8	6.7	0.36
Piezoelectric constants: d (10^{-12} C/N)					Dielectric constants: ε (ε_0)			
d_{15}	d_{24}	d_{31}	d_{32}	d_{33}	ε_{11}^T	ε_{22}^T	ε_{33}^T	
140	140	−1154	−786	2000	3100	3100	5200	

TABLE IV. Comparison between the rotated properties in the $mm2$ symmetry assumption with that of the $4mm$ symmetry reported in Ref. 5. The units for different quantities are the same as in Table III.

Rotated properties of $mm2$ symmetry around [001] by 45°	Properties for $4mm$ symmetry taken from Ref. 5
$c^{E\prime}=\begin{bmatrix} 10.31 & 9.59 & 9.9 & 0 & 0 & -0.7 \\ 9.6 & 10.31 & 9.9 & 0 & 0 & -0.7 \\ 9.9 & 9.9 & 10.7 & 0 & 0 & -0.2 \\ 0 & 0 & 0 & 6.75 & 0.05 & 0 \\ 0 & 0 & 0 & 0.05 & 6.75 & 0 \\ -0.7 & -0.7 & -0.2 & 0 & 0 & 6.35 \end{bmatrix}$	$c^{E}=\begin{bmatrix} 11.1 & 10.2 & 10.1 & 0 & 0 & 0 \\ 10.2 & 11.1 & 10.1 & 0 & 0 & 0 \\ 10.1 & 10.1 & 10.5 & 0 & 0 & 0 \\ 0 & 0 & 0 & 6.4 & 0 & 0 \\ 0 & 0 & 0 & 0 & 6.4 & 0 \\ 0 & 0 & 0 & 0 & 0 & 6.3 \end{bmatrix}$
$d'=\begin{bmatrix} 0 & 0 & 0 & 0 & 140 & 0 \\ 0 & 0 & 0 & 140 & 0 & 0 \\ -970 & -970 & 2000 & 0 & 0 & 184 \end{bmatrix}$	$d=\begin{bmatrix} 0 & 0 & 0 & 0 & 140 & 0 \\ 0 & 0 & 0 & 140 & 0 & 0 \\ -970 & -970 & 2000 & 0 & 0 & 0 \end{bmatrix}$
$\varepsilon^{T\prime}=\begin{bmatrix} 3100 & 0 & 0 \\ 0 & 3100 & 0 \\ 0 & 0 & 5200 \end{bmatrix}$	$\varepsilon^{T}=\begin{bmatrix} 3100 & 0 & 0 \\ 0 & 3100 & 0 \\ 0 & 0 & 5200 \end{bmatrix}$

pacitance measurements. Details of the method used can be found in Ref. 5, in which the same procedure has been used to measure a $4mm$ symmetry system. The ultrasonic and resonance measurements have been carried out in both [110] and $[1\bar{1}0]$ directions instead of measured in [100]/[010] directions for the $4mm$ symmetry system. Therefore, subscripts 1 and 2 in Table III are used to distinguish the measurement in the [110] and $[1\bar{1}0]$ directions, respectively. Because of the rotation of the crystal coordinates with respect to the original cubic coordinates, the data look very different from the data calculated based on $4mm$ symmetry.[5] For example, there is a large difference between c_{11} and c_{12} here, while for the $4mm$ symmetry, the values of c_{11} and c_{12} are almost the same. One must note that such a comparison is not appropriate since the two sets of data were calculated in their own coordinate systems and the two crystal coordinates differ by a 45° rotation around [001]. In order to compare with the previously published data based on the $4mm$ symmetry, we make a coordinate rotation by 45° around [001] based on the transformation matrix given in Ref. 9. The elastic, piezoelectric, and dielectric permittivity matrices after a 45° rotation are given in the left column of Table IV, while properties in the right column of Table IV are taken from Ref. 5.

One can see that the main elements, such as the diagonal elements, in the matrices above are either the same or very similar in both columns except that there are nonzero elements c_{16}, c_{26}, c_{36}, c_{45}, and d_{36} in the left column. In practice, if the crystal is operating in [001] vibration modes, the difference is not so obvious, which might be the reason why people did not find out the symmetry changes before. This also shows that one could not observe the symmetry change through conventional dielectric and piezoelectric measurements since the only difference is the appearance of d_{36}, which is not being measured conventionally. Our ultrasonic measurements, on the other hand, can see the symmetry changes through the shear wave velocity variation with orientation, as shown in Fig. 5.

SUMMARY AND CONCLUSIONS

In conclusion, the [001] poled PZN-4.5%PT single crystals have four possible domain states. These domain states could form a quasi-tetragonal $4mm$ symmetry configuration, but they may also form other lower symmetry configurations, such as orthorhombic $mm2$, monoclinic m, and even triclinic 1.[7,8] Some experimental results indicated that many of the domain engineered crystals actually have a quasi-orthorhombic symmetry $mm2$. We show, by using both ultrasonic and resonant measurements, that the crystal systems under study indeed have $mm2$ symmetry. This conclusion agrees with earlier reported optical domain microstructure observations, which found only two types of domains instead of four. It has been shown theoretically that the highest macroscopic symmetry of a two-domain system is orthorhombic $mm2$.[7,8] Based on the $mm2$ symmetry we have determined that the full set of elastic, piezoelectric, and dielectric constants for a system consists of 109° twins. For such a system, the principle coordinates are rotated 45° from that used for the $4mm$ symmetry. By rotating the matrix properties we found that the lowering of symmetry mainly created some more off-diagonal elements, while the main elements, such as the diagonal elements, do not have much difference.

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