

In Situ X-Ray Diffraction Study of Electric-Field-Induced Domain Switching and Phase Transition in PZT-5H

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In situ X-ray experiments were conducted to examine the electric-field-induced phase changes in PZT-5H materials. The X-ray diffraction profiles at different electric-field levels were analyzed by peak fitting and were used to identify the occurrence of non-180° domain switching and phase transition. We found that in depolarized samples, there exists a threshold electric field for the phase changes, whereas in polarized samples, no such threshold exists. The profound difference in the diffraction profile changes under positive and negative electric fields in polarized samples is responsible for the asymmetry of piezoelectric effects. Peak fitting results show phase transition as well as domain switching at different electric-field levels. These observations further indicate the importance of residual stresses in materials' behavior.

I. Introduction

PEROVSKITE ferroelectric/piezoelectric $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ (PZT), $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\text{PbTiO}_3$ (PMN-PT), and $(1-x)\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\text{PbTiO}_3$ (PZN-PT) have been intensively studied recently. Above the Curie temperature, they all have simple cubic structures, while at lower temperatures, it was believed that they become tetragonal or rhombohedral structures. The composition, x , determines whether a tetragonal or rhombohedral structure is formed at a given temperature. The phase boundary in the phase diagram, which separates the tetragonal from rhombohedral region, is called the morphotropic phase boundary (MPB).¹ Recently, Noheda *et al.*²⁻⁴ reported a new phase in polycrystalline PZT materials, which belongs to one type of monoclinic phases. They suggested that the MPB that was previously believed to separate tetragonal and rhombohedral phases is actually the boundary between tetragonal and monoclinic phases. They also suggested that there exists a "morphotropic phase" region between tetragonal and rhombohedral regions in the phase diagram.³ The new monoclinic phase was also observed by Souza Filho *et al.*⁵

Extraordinarily strong piezoelectric constants are found mostly in materials with compositions close to the MPB. Although the large piezoelectric constants are normally believed to be because of the coexistence of morphotropic phases and the associated phase changes, the underlying mechanisms remain unsettled.⁶⁻¹³ On the other hand, it has been found that piezo-

electric constants exhibit a large nonlinear behavior.¹⁴⁻¹⁸ Above a threshold electric field, the piezoelectric constant increases if the amplitude of the applied electric field increases. The threshold level can be very low or nearly zero,^{15,16} or can be a finite value.¹⁷ It was also observed that the piezoelectric constant depends on the direction of a biased electric field; a positive biased electric field results in decreased piezoelectric constants, while a negative biased field results in increased piezoelectric constants.¹⁸ The nonlinear effect was explained by different mechanisms, such as domain wall motion, 90° domain switching, or residual stresses. However, most of the mechanisms are indirectly deduced from the measurements of material's constants. Only a few direct observations on microstructural changes have been made, especially in the case of polycrystalline materials.

Experiments on single crystalline relaxor-based ferroelectric PMN-PT and PZN-PT showed that enhanced and nonlinear piezoelectric coefficients are likely because of the phase transition between rhombohedral and tetragonal phases induced by electric fields.^{19,20} A first-principle simulation indicated that the phase transition results from an electric-field-induced polarization rotation.²¹ Quantitative experiments on polycrystalline materials are difficult to conduct because of their complex microstructures. However, such experiments can help to identify the mechanisms responsible for the enhanced and nonlinear piezoelectric constants. An X-ray diffraction conducted on polycrystalline PZN-PZT indicated that a large amount of phase transitions between rhombohedral and tetragonal phases and non-180° domain switching (90° domain switching for tetragonal phases and 71° or 109° domain switching for rhombohedral phases) are induced by the poling process.⁸ However, the result does not provide a direct observation of microstructural changes in a poled sample upon an applied electric field.

PZT-5H is one of the most used polycrystalline PZT materials. Its piezoelectric constants have been studied in detail.^{16,22} Some researchers suggested that tetragonal and rhombohedral phases coexist at room temperatures in the PZT materials with compositions close to the MPB.^{16,23,24} Non-180° domain switching and phase transition between those two phases, therefore, were believed to be the source of their strong, nonlinear piezoelectric behavior.¹⁵ Other researchers suggested that residual stresses are the real source.¹⁶ The recently modified MPB suggested the coexistence of tetragonal and monoclinic phases in PZT materials close to the MPB.^{3,4} Some first-principle simulations, however, suggested that the large piezoelectric effects could come from field-induced monoclinic distortions.^{25,26} A direct observation seems to provide some evidence for such distortions.¹¹ But more careful and thorough experiments are needed to confirm the type of these distortions. Therefore, direct observations of electric-field-induced microstructural changes are critical to clarify the mechanisms responsible for the strong and nonlinear behavior in polycrystalline piezoelectric materials.

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In the present paper, *in situ* X-ray diffraction experiments were performed on a PZT-5H material. Direct observations of non-180° domain switching and phase transition at different electric fields were made for depolarized and polarized samples. Our results provide specific information on the microstructural changes giving rise to the material's piezoelectric properties, and show the effect of residual stresses on the nonlinear piezoelectric behavior.

II. Experimental Procedures

Thin plate specimens of PZT-5H are used in our experiments. The samples have a thickness of 375 μm and in-plane dimensions of 2 cm \times 2 cm. The Curie temperature of the material is 220°C and the coercive field (E_C) is 8 kV/cm. The grain size of the material is about 4 μm . The company that provided the material claimed that the detailed composition of the material is proprietary information, but it is believed to be close to the MPB at room temperature on the rhombohedral side.²² All samples are coated with nickel as electrodes on the top and bottom surfaces and poled in their thickness directions. Some samples were depolarized by submerging them into a silicone-oil bath at 260°C for half an hour, and then cooled down to room temperature gradually. The diffraction patterns of the depolarized samples are close to those of ceramic powder. The measured piezoelectric constant of as-received, polarized samples is $d_{33} = 560 \times 10^{-12}$ C/N, and that of a depolarized sample is $d_{33} = 8 \times 10^{-12}$ C/N, which is within the noise level of the measuring equipment.

Recent research suggested that PZT-5H could have a combination of tetragonal and rhombohedral phases¹⁶ or a combination of tetragonal and monoclinic phases.^{3,4} Figure 1 shows the geometries of a tetragonal, a rhombohedral, and a monoclinic unit cell. The lattice angle α for a rhombohedral unit cell is slightly less than 90°. The monoclinic unit cell is double in volume compared with a tetragonal unit cell. Its a_m and b_m lie along the tetragonal $[\bar{1}10]$ and $[110]$ directions, respectively. Its c_m tilts slightly from the $[001]$ direction with the angle β between a_m and c_m slightly larger than 90°. The polarization directions are along (001) and (111) for tetragonal and rhombohedral unit cells, respectively. The polarization direction can lie anywhere between (001) and (101) in the $a_m c_m$ plane for a monoclinic unit cell.

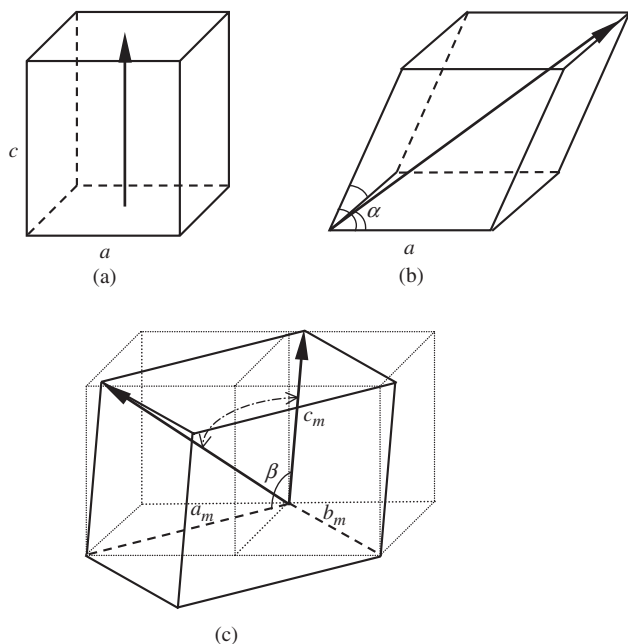


Fig. 1. Unit cells of individual phases in piezoelectric: (a) tetragonal, (b) rhombohedral, (c) monoclinic.

The X-ray diffraction is performed with a Rigaku D-Max powder X-ray diffractometer (XRD: Rigaku Corp., Tokyo, Japan) at the Frederick Seitz Materials Research Laboratory at the University of Illinois. The instrument uses copper radiation with lines K_{α_1} and K_{α_2} (wavelength $\lambda_{\alpha_1} = 1.5406$ Å and $\lambda_{\alpha_2} = 1.5444$ Å). The top and bottom electrodes of the samples are connected to a DC power supply. The X-ray diffraction is measured *in situ* under applied electric fields. Because of their morphotropic and polycrystalline microstructures, diffraction patterns are rather complicated. A moderate-speed scan (3°/min) is first conducted for a large 2θ range to locate the peak positions approximately. Slow scans (0.3°/min) are then conducted for individual peaks in a 3°–4° 2θ range. The effect of the electric field on diffraction peaks is studied first. Domain and phase changes are further studied by peak fitting. Those peaks are carefully fitted by a peak fitting program Xfit-Koalariat developed by Cheary and Coelho.²⁷ The peaks are fitted by a pseudo-Voigt (PV) shape function and the two-wavelength effect is taken into account. Furthermore, the anisotropic peak width and coexisting phases are also considered.^{3,4}

III. Results and Discussions

(1) Effect of Electric Fields on Diffraction Peaks

Figure 2 shows the diffraction profile of a PZT-5H sample over a wide 2θ range, indicating the pseudo-cubic peak locations. Figure 3 shows the slow-scan diffraction profiles at pseudo-cubic (111), (200), and (220) regions in a depolarized sample at several applied electric-field levels. It clearly shows that there exists a threshold electric field between $0.33E_C$ and $0.5E_C$ for all peaks. Below the threshold field, the diffraction profiles do not change. Experimental results show that the peaks at other pseudo-cubic regions behave in a similar way.

Figure 4 shows the change of the pseudo-cubic (200) peak in a polarized sample, where a positive electric field is along the poling direction. Unlike the case of a depolarized sample, there is no clear threshold electric field for peak profile change. Under a positive electric field, the change in diffraction profiles is very small and gradual, indicating, as expected, very small amount of non-180° domain switching or phase transition. Under a negative electric field, the peak profile changes slightly at low fields and profoundly when $|E| > 0.5E_C$. These observations are consistent with the value ($0.5E_C$) observed by Wang *et al.*,²² in which they applied an electric field perpendicular to the poling direction and measured strains in both the poling direction and that normal to the poling direction.

The fact that there exists a threshold value of electric field for depolarized samples indicates that the residual stresses in PZT-5H play an important role in non-180° domain switching and

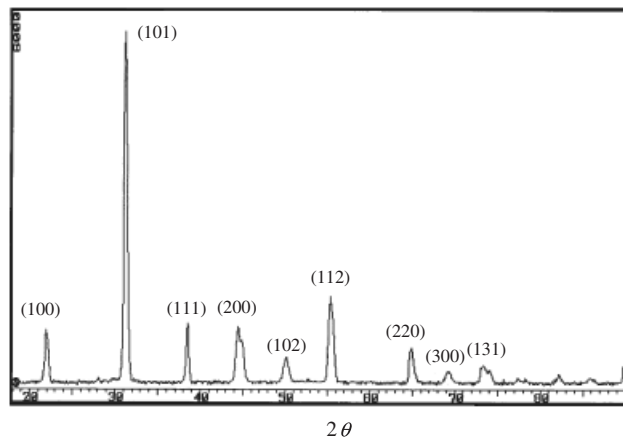


Fig. 2. Diffraction profile of a polarized sample.

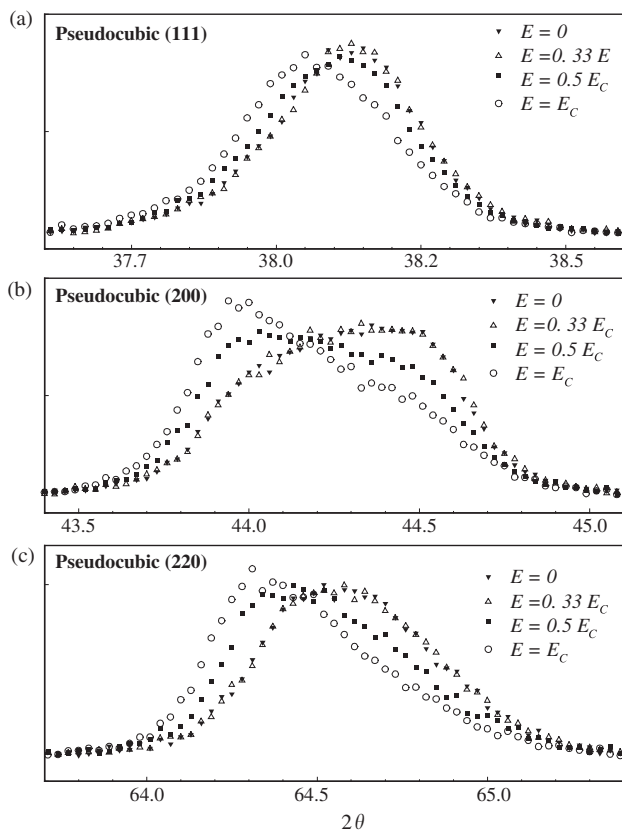


Fig. 3. Pseudo-cubic peaks of a depolarized sample under several positive electric-field levels: (a) (111) peak, (b) (200) peak, (c) (220) peak.

phase change. In depolarized samples, residual stresses are low and relatively uniformly distributed throughout the material. Therefore, the intrinsic threshold energy for domain switching and phase change is similar in all grains. Once such a threshold

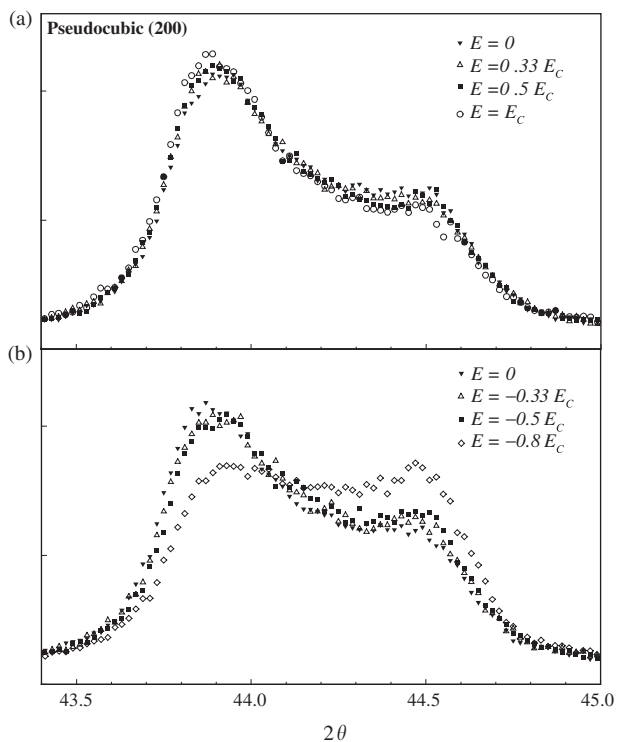


Fig. 4. Pseudo-cubic (200) peak of a polarized sample: (a) under different positive electric field levels, (b) under different negative electric field levels.

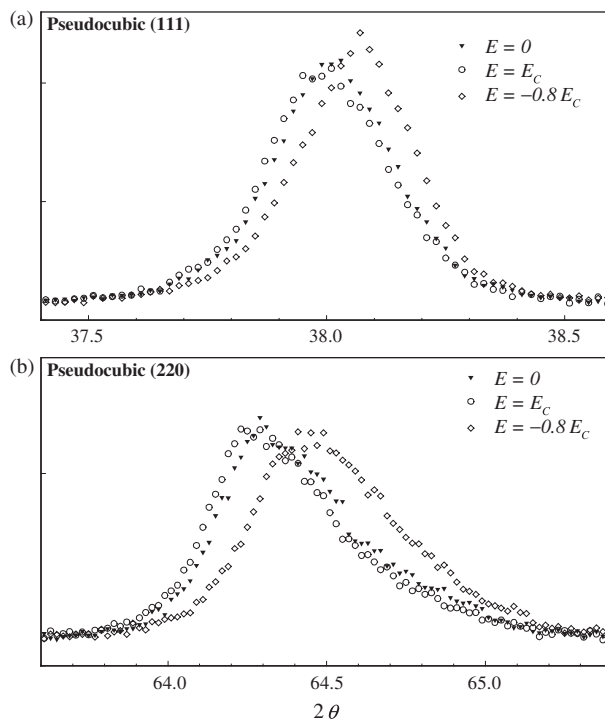


Fig. 5. Pseudo-cubic (111) and (220) peaks of a polarized sample under zero, a positive, and a negative electric field: (a) (111) peak, (b) (220) peak.

energy level is reached upon an applied electric field, non-180° domain switching and phase transition occur. In a polarized sample, however, the residual stress level differs profoundly from grain to grain and so does the threshold energy for switching. Therefore, non-180° domain switching and phase transition in different grains/domains may be induced at different applied electric-field levels, resulting in a continuous change in nonlinear piezoelectric constants.^{15,16} However, the present X-ray technique is not appropriate to provide quantitative information on the level of residual stresses in the material.

Figure 5 shows pseudo-cubic (111) and (220) peaks in polarized samples. Under positive electric fields, the magnitudes of the peak change are very small. However, the changes under negative electric fields are rather large. The pseudo-cubic peaks clearly shift to higher values of 2θ . Perrin *et al.*¹⁸ found that the nonlinear behavior of piezoelectric effects depends on the direction of the applied electric field. The strong direction-dependent peak profile changes shown in Figs. 4 and 5 are responsible for this nonlinear behavior. Moreover, it is noted that upon application of a negative electric slightly below E_C ($-0.8E_C$ in the present study), a large profile change is induced. The change corresponds to a large piezoelectric contraction and can explain the deep minima found in the strain-electric-field hysteresis loops.^{16,28} It is commonly believed that a negative coercive electric field induces 180° domain switching. Our results in Fig. 5 show that a negative electric field slightly below E_C also induces a large amount of non-180° domain switching.

(2) Fitting of Peaks

Because of the coexistence of morphotropic phases, each of the above pseudo-cubic diffraction peaks is composed of multiple peaks corresponding to different phases. Table I lists all the possible peaks at pseudo-cubic (111), (200), and (220) regions for tetragonal, rhombohedral, and monoclinic phases in PZT-5H. In principle, all these phases, therefore the corresponding peaks, may be present in the material and thus within a particular pseudo-cubic peak. To study possible domain switching and phase transition, we conducted peak fitting to determine the individual peaks for different phases. We focused on the pseudo-cubic (111), (200), and (220) regions since other peaks

Table I. Peaks at Pseudo-Cubic (111), (200), and (220) Regions

Pseudo-cubic	(111)	(200)	(220)
Tetragonal	(111)	(002), (200)	(202), (220)
Rhombohedral	(111), ($\bar{1}11$)	(200)	(220), ($\bar{2}20$)
Monoclinic	(201), (021), (201)	(002), (220)	(222), ($\bar{2}22$), (400), (040)

would either contain too many individual peaks for different phases or have too low a 2θ angle to be very accurate.

We consider a mixture of two phases, either a mixture of tetragonal and rhombohedral phases or that of tetragonal and monoclinic phases. Practically, the number of individual peaks would be too large if we tried to fit the peaks to a mixture of three phases. Two methods are used in the fitting: One is to fit the individual peaks of the two phases to each of the three experimentally measured pseudo-cubic peaks; the other is to fit the individual peaks of the two phases to the pseudo-cubic (220) peak to determine the lattice parameters of the two phases, and then use the lattice parameters to calculate the 2θ values of other peaks in the two-phase mixture at pseudo-cubic (111) and (200) regions.

As seen in Table I, for the pseudo-cubic (111), (200), and (220) peaks, we need to fit 3, 3, and 4 individual peaks for a mixture of tetragonal and rhombohedral phases, or 4, 4, and 6 peaks for a mixture of tetragonal and monoclinic phases, respectively. The fitted 2θ values of individual peaks are listed in the third column in Table II, where T, R, and M stand for tetragonal, rhombohedral, and monoclinic phases.

With the second method mentioned above, by using the pseudo-cubic (220) peak, we minimized the low angle distortion effect. Moreover, there are enough peaks to determine all lattice parameters. The lattice parameters for a mixture of tetragonal and rhombohedral phases are determined as, tetragonal: $a = 4.0596 \text{ \AA}$, $c = 4.1158 \text{ \AA}$, rhombohedral: $a = 4.0857 \text{ \AA}$, $\alpha = 89.668^\circ$, and those for a mixture of tetragonal and monoclinic phases, tetragonal: $a = 4.0595 \text{ \AA}$, $c = 4.1140 \text{ \AA}$, monoclinic: $a_m = 5.7920 \text{ \AA}$, $b_m = 5.7541 \text{ \AA}$, $c_m = 4.0989 \text{ \AA}$, $\beta = 90.443^\circ$. The calculated peak positions at pseudo-cubic (111) and (200) directions using these lattice parameters are given in the second column in Table II. It is clearly seen in Table II that the peak positions obtained by these two methods agree with each other extremely well, rendering confidence in the current peak fitting methods and in the accuracy of the determined lattice parameters.

The results in Table II seem to suggest that both morphotropic phase compositions, i.e., mixture of tetragonal and rhombohedral phases or mixture of tetragonal and monoclinic phases, are possible compositions at room temperature. The

current method is not able to determine which of these is the more likely microstructure of PZT-5H.

(3) Effects of Electric Fields on Domain Switching and Phase Change

With the information on individual peak positions and intensities of different phases, we are now able to study the domain switching and phase change induced by the applied electric field. In Figs. 6 and 7, the solid squares are data from measurements of X-ray profiles; the solid lines with different symbols represent the fitted individual peaks of tetragonal (T), rhombohedral (R), or monoclinic (M) phase; and the dashed line represents the combined profiles from the fitted individual peaks. Figure 6 illustrates the fitted peaks at the pseudo-cubic (200) region in a depolarized sample at $E = 0$ and E_C . Figure 6(a) shows the fitted individual peaks for a mixture of tetragonal and rhombohedral phases. It clearly shows that, as an electric field of E_C is applied, the intensity of T(002) increases while that of T(200) decreases, indicating 90° domain switching of tetragonal phase from the (200) to the (002) orientation. Moreover, the intensity of R(200) is decreased upon applied electric field, indicating a phase transition from rhombohedral to tetragonal, R(200) to T(002). A similar phenomenon is observed in Fig. 6(b) for a mixture of tetragonal and monoclinic phases. Upon applied electric field of E_C , there is a clear indication of 90° domain switching of the tetragonal phase from (200) to (002) orientation, and a phase change from M(220) to T(002). However, the intensity of the peak M(002) remains nearly the same upon applied electric field, indicating that this orientation is still the preferred one for the monoclinic phase upon applied electric field.

Results for the pseudo-cubic (200) peak of a polarized sample are given in Fig. 7. Figure 7(a) shows fitted peaks for a mixture of tetragonal and rhombohedral phases at $0.0E_C$, $1.0E_C$, and $-0.8E_C$. The changes of the peak intensities indicate that, upon an applied electric field of E_C , 90° domain switching from T(200) to T(002) and phase transition from R(200) to T(002) are induced, but only in a very small amount. On the other hand, upon an electric field of $-0.8E_C$, 90° domain switching from

Table II. Fitted and Computed Peaks at Pseudo-Cubic (111), (200), and (220) Regions (wavelength $K_{\alpha 1}$: 1.5406 \AA)

Tetragonal and rhombohedral			Tetragonal and monoclinic		
Peak	Computed 2θ ($^\circ$)	Fitted 2θ ($^\circ$)	Peak	Computed 2θ ($^\circ$)	Fitted 2θ ($^\circ$)
R(111)	37.892	37.936	M($\bar{2}01$)	37.871	37.936
T(111)	38.194	38.114	M(201)	38.158	38.114
R($\bar{1}\bar{1}\bar{1}$)	38.197	38.114	M(021)	38.187	38.114
T(002)	43.964	43.967	T(111)	38.200	38.114
R(020)	44.306	44.271	T(002)	43.984	43.920
T(200)	44.605	44.516	M(002)	44.156	44.129
R(220) [†]	64.246	64.246	M(220)	44.347	44.362
T(202) [†]	64.422	64.422	T(200)	44.606	44.539
R(220) [†]	64.662	64.662	M(222) [†]	64.172	64.172
T(220) [†]	64.917	64.917	M(400) [†]	64.280	64.280
			T(202) [†]	64.438	64.438
			M(222) [†]	64.565	64.565
			M(040) [†]	64.753	64.753
			T(220) [†]	64.919	64.919
Lattice parameters: tetragonal: $a = 4.0596 \text{ \AA}$, $c = 4.1158 \text{ \AA}$; rhombohedral: $a = 4.0857 \text{ \AA}$, $\alpha = 89.668^\circ$			Lattice parameters: tetragonal: $a = 4.0595 \text{ \AA}$, $c = 4.1140 \text{ \AA}$; monoclinic: $a_m = 5.7920 \text{ \AA}$, $b_m = 5.7541 \text{ \AA}$, $c_m = 4.0989 \text{ \AA}$, $\beta = 90.443^\circ$		

[†]Peaks used to calculate lattice parameters.

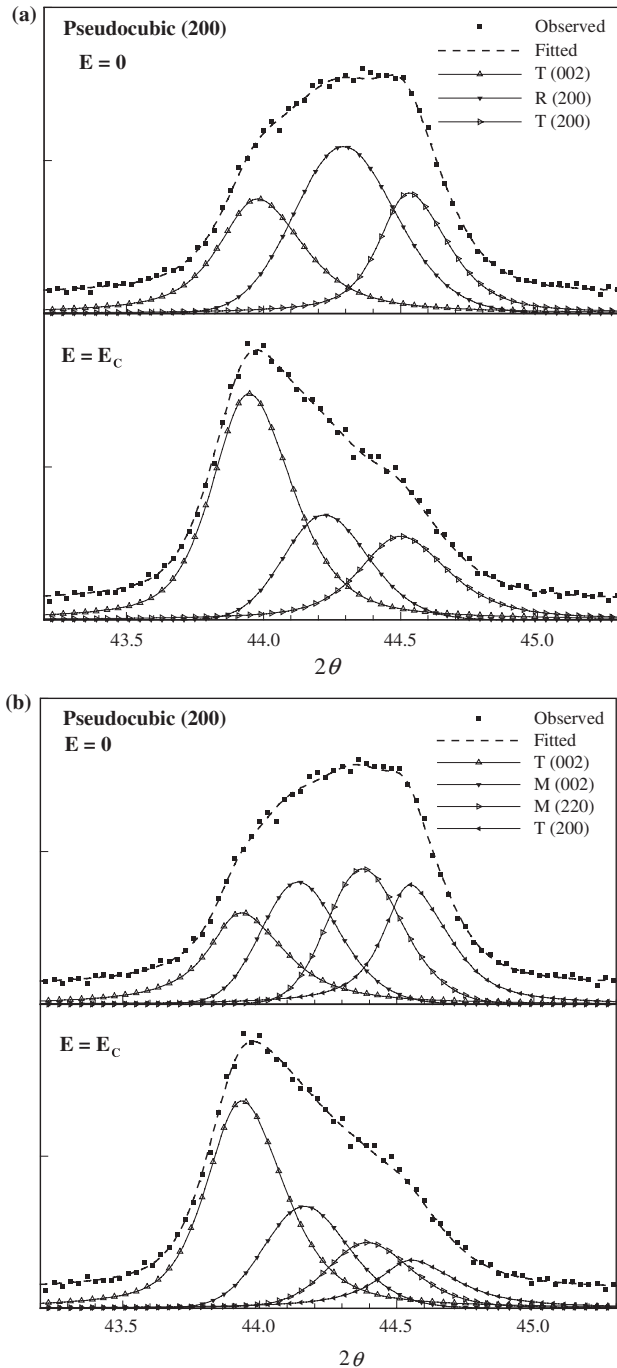


Fig. 6. Fitted peaks at the pseudo-cubic (200) region of a depolarized sample: (a) mixture of tetragonal and rhombohedral phases, (b) mixture of tetragonal and monoclinic phases.

T(002) to T(200) and phase transition from T(002) to R(200) are clearly induced in a large amount. Figure 7(b) shows fitted peaks for a mixture of tetragonal and monoclinic phases at $0.0E_C$, $1.0E_C$, and $-0.8E_C$. Upon an electric field of E_C , similar domain switching and phase transition behaviors as those observed in Fig. 6(b) are also induced in a polarized sample, but in a very small amount, whereas upon an electric field of $-0.8E_C$, domain switching and phase transition in the opposite direction to those in Fig. 6(b) are induced in a large amount.

IV. Conclusions

Electric-field-induced domain switching and phase transition were studied using *in situ* X-ray diffraction. Through the

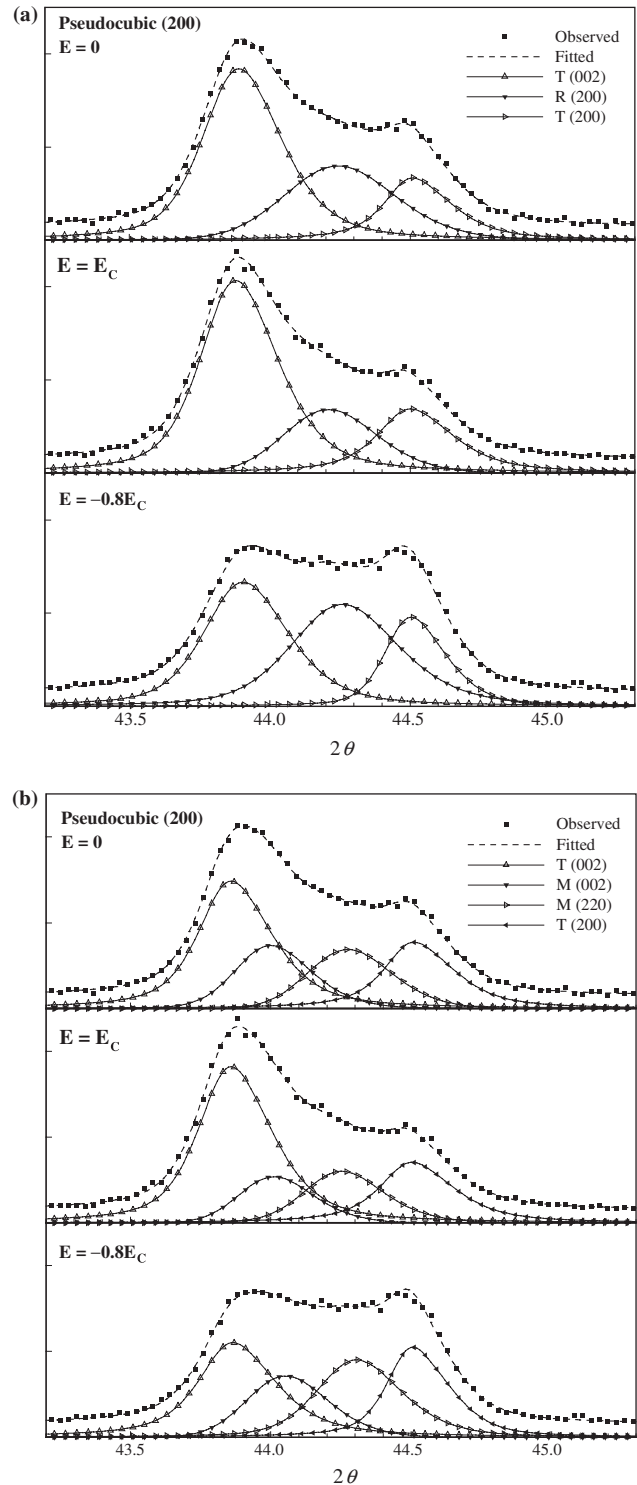


Fig. 7. Fitted peaks at the pseudo-cubic (200) region of a polarized sample: (a) mixture of tetragonal and rhombohedral phases, (b) mixture of tetragonal and monoclinic phases.

changes of X-ray diffraction profiles of pseudo-cubic peaks upon applied electric field, we identified when the switching and transition occur. Our results indicate that, for a depolarized PZT-5H sample, there exists a threshold field level below which little non- 180° domain switching or phase transition occurs. This threshold value is significantly lower than the material's coercive field. In a polarized sample, on the other hand, no obvious threshold exists. When the applied electric field is in the same direction as the poling direction, the non- 180° domain switching and phase change occur from a low electric field, although the switching and transition occur rather slowly as the applied

electric-field level increases. When the applied electric field is in the opposite direction from the poling direction, however, the changes are much more profound. These observations indicate that residual stresses in the material play an important role in inducing domain switching and phase change. The dependence of the non-180° domain switching and phase transition on the applied electric field in polarized materials is believed to be responsible for the electric-field direction-dependent nonlinear piezoelectric behavior of PZT-5H.

Furthermore, by fitting the individual peaks of tetragonal, rhombohedral, and/or monoclinic phases to the measured pseudo-cubic (111), (200), and (220) peaks, we established that the material may be composed of a mixture of tetragonal and rhombohedral phases or a mixture of tetragonal and monoclinic phases. The peak fitting method also allows us to identify the electric-field-induced 90° domain switching in the tetragonal phase as well as the phase transitions between the tetragonal and rhombohedral phases or between the tetragonal and monoclinic phases. This method has been used by us to study the locking of non-180° domain switching and phase transition under cyclic electric fatigue.²⁹

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