Locking of electric-field-induced non-180° domain switching and phase transition in ferroelectric materials upon cyclic electric fatigue

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In situ x-ray diffraction measurements are conducted on a polycrystalline ferroelectric material lead-zironate-titanate-5H at different levels of static electric field. The locking of electric-field-induced non-180° domain switching and phase transition after experiencing cyclic electric field is investigated by examining the changes in pseudocubic diffraction profiles. The results show that cyclic electric field with an amplitude lower than the coercive field has little effect on ferroelectric fatigue of the material, whereas cyclic field with an amplitude above the coercive field results in nearly complete locking of non-180° domain switching and phase transition. The results also demonstrate that the locking occurs rather suddenly after 10^3-10^4 cycles. This locking phenomenon can explain the dramatic change in piezoelectric coefficients in these materials upon cyclic electric field. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1626262]

Perovskite ferroelectric ceramics are promising materials for applications in microactuators and nonvolatile memories.[1–4] However, under cyclic bipolar electric fields, ferroelectric materials often undergo electric fatigue, resulting in significant decrease in the number of switchable domains. The locking of switchable domains causes the loss of memory function, reduces the piezoelectric effect, and causes the actuators to function improperly. Such behavior has therefore been the topic of extensive study in the past few years.[5–18] There are two main approaches to the analysis of ferroelectric fatigue. One approach is through investigation of the change of the material properties, such as the reduction of remanent polarization and piezoelectric constants.[5–13] Another approach is by observing the locking of switchable domains directly.[14,15] To date, the observation has only been conducted to detect the locking of 180° domain switching, although some efforts have been made to distinguish the 180° domain switching from the non-180° domain switching.[19,20]

A literature survey often shows conflicting conclusions with respect to the cause of ferroelectric fatigue. The change in materials constants usually indicates that the repeated 180° domain switching causes locking of switchable domains.[9,12] Recent research, by applying an electric field inclined to the material's spontaneous polarization direction, seems to indicate that domain locking was likely caused by field-induced phase transitions.[8] On the other hand, the extraordinarily strong and nonlinear piezoelectric constants found in the ferroelectric materials with compositions near the morphotropic phase boundary (MPB)[21,22] are believed to result from the combined electric-field-induced non-180° domain switching and phase transition, as well as from the residual stresses generated by the poling process.[23–25] A thorough understanding of the ferroelectric fatigue behavior, therefore, depends critically on direct, *in situ* observations of non-180° domain switching and phase transition under an applied electric field.

In this work, we conduct an *in situ* x-ray diffraction (XRD) study on freshly poled and electrically fatigued samples under different levels of static electric field. Lead zirconate titanate (PZT)-5H, a material with compositions near the MPB, is considered. Thin plates with dimensions of 2 cm$\times$2 cm$\times$375 μm, coated with nickel electrodes on top and bottom surfaces, and poled in the thickness direction, are used. The material has a coercive field of $E_C=8$ kV/cm. The main objective of the measurements is to provide definitive information on the non-180° domain switching and phase transition induced by static electric fields in freshly poled and electrically fatigued specimens.

The experiment is conducted in two steps. The first step involves subjecting three groups of specimens with different cyclic electric fields: the first group is electrically fatigued with cyclic electric field of $\pm 1.1\ E_C$ in amplitude at 50 Hz; the second group is electrically fatigued with cyclic electric field of $\pm 0.8\ E_C$ in amplitude at 50 Hz; and the third group, as a comparison group, is left in the freshly poled state. The numbers of cycles applied to the fatigued specimens are 10^3, 10^4, and 10^5, respectively. Since the terminating field level cannot be controlled during cyclic loading, to ensure consistency of the results, a static electric field of the same magnitude as the amplitude of cyclic electric field is applied in the initial poling direction for 1 min. The second step involves recording *in situ* XRD profiles of each specimen at static electric field levels of 0.8 E_C, 0, $-0.8\ E_C$, and $-1.0\ E_C$, respectively. The positive static field is in the poling direction.

2θ–θ scans were performed using a Rigaku D-Max powder x-ray diffractometer. The instrument uses copper radiation with two lines K_{α_1} and K_{α_2} (wavelength $\lambda_{\alpha_1}=1.5406$ Å and $\lambda_{\alpha_2}=1.5444$ Å). Reflections at pseudocubic (200), (111), and (220) regions were recorded over a 3°–4° 2θ range at a speed of 0.3°/min. Due to the material's morphotropic and polycrystalline microstructures, the diffraction profiles are

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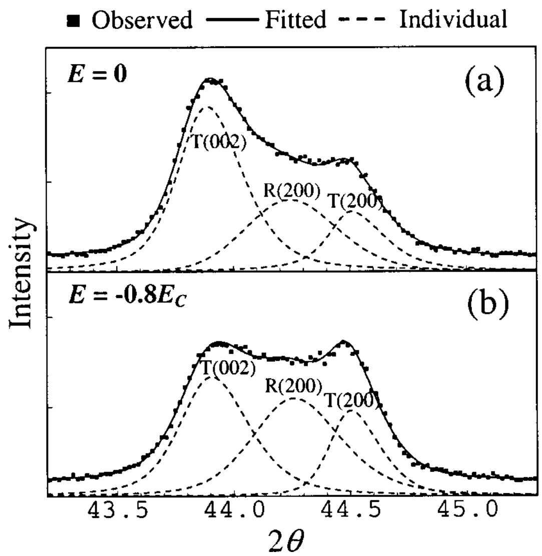

FIG. 1. Change of pseudocubic (200) peak and the fitted peaks of individual domain/phase for a freshly poled sample upon static electric fields at (a) $E=0$ and (b) $E=-0.8E_C$.

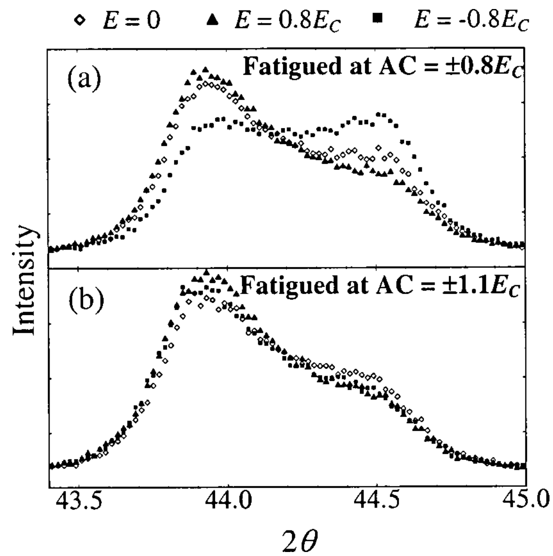

FIG. 3. The pseudocubic (200) profiles at different static electric fields for specimens after cyclic electric fields (AC, 50 Hz, 10^5 cycles): (a) at AC $\pm 0.8E_C$, (b) at AC $\pm 1.1E_C$.

rather complicated. Each pseudocubic peak consists of multiple peaks from different phases.

A peak-fitting algorithm was used to identify the peaks of individual phases coexisting in the material. Figure 1 shows the reflections at pseudocubic (200) region and the fitted peaks of individual phases in a fresh sample at static electric field 0.0 and $-0.8\ E_C$, in which "T" and "R" stand for tetragonal and rhombohedral phases, respectively. Comparing the fitted peaks at static field levels of 0.0 E_C and $-0.8\ E_C$ in Fig. 1, we can see that there exist 90° domain switching from T(002) to T(200) and phase transition from T(002) to R(200). Such non-180° domain switching and phase transition dramatically change the profile of the pseudocubic (200) peak. The details of the peak fitting method is given elsewhere.[26]

Figure 2 shows the reflections at pseudocubic (200) region in a freshly poled sample at static field levels of 0.8 E_C, 0, $-0.8\ E_C$, and $-1.0\ E_C$. It is seen that, at 0.8 E_C, the left peak at pseudocubic (200) region increases slightly while the right peak decreases slightly, indicating some amount of non-180° domain switching and phase transition that realign some domains to the poling direction.[26] Upon a negative electric field close to the negative coercive field ($-0.8\ E_C$), profound non-180° phase and domain changes occur, which rotate the domain polarization to directions perpendicular or inclined to the poling direction. The changes can induce a large contraction (i.e., negative strain) in the poling direction, which enhances the piezoelectric effect and is responsible for the large minima in the strain–electric-field hysteresis loops.[27] However, at $-1.0\ E_C$, the polarization of domains switches to the negative poling direction, as demonstrated by the similar pseudocubic (200) reflections at 0.8 E_C and $-1.0\ E_C$.

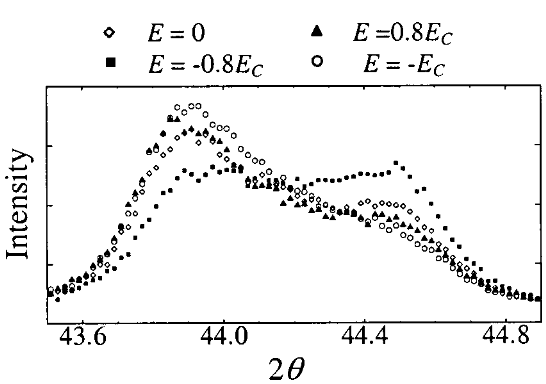

FIG. 2. The pseudocubic (200) profiles for a freshly poled specimen at different static electric field levels.

Figure 3 shows the effects of cyclic electric field (10^5 cycles) on the material's ability to undergo non-180° domain switching and phase transition upon static field. Figures 3(a) and 3(b) show the pseudocubic (200) reflections under different static field levels for samples fatigued at $\pm 0.8\ E_C$ and fatigued at $\pm 1.1\ E_C$, respectively. It clearly shows that cyclic electric field at $\pm 0.8\ E_C$ has little effect on further domain and phase changes. However, when the amplitude of the cyclic field is beyond the coercive field ($\pm 1.1\ E_C$), the result in Fig. 3(b) shows that the non-180° domain switching and phase transition are not present upon a static field of $-0.8\ E_C$. The measured ferroelectric hysteresis loops for specimens before and after electric fatigue (measurement result not shown here) show that there exists a shift: the hysteresis loop shifts toward the positive field direction after electric fatigue. However, the shift does not seem be sufficient to explain the observation in Fig. 3(b). The result in Fig. 3(b) indicates that, upon electric fatigue at $\pm 1.1\ E_C$, the material's ability to undergo further non-180° domain switching and phase transition upon static electric field is suppressed.

Figure 4 shows the change of the pseudocubic (200) peak upon a static electric field of $-0.8\ E_C$ after experiencing different number of cycles of electric field of $\pm 1.1\ E_C$. It shows that the locking of the non-180° domain switching and phase change takes place between 10^3 and 10^4 cycles, which is a very short lifetime. Furthermore, such locking appears to occur relatively suddenly.

The present work employs *in situ* XRD to investigate the phenomenon of the locking of non-180° domain switching

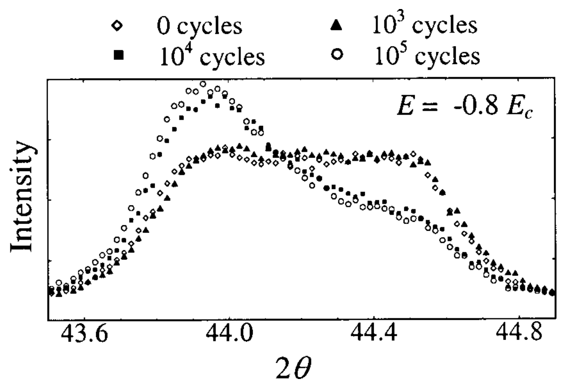

FIG. 4. Effect of the number of cycles of electric fields (AC, 50 Hz, $\pm 1.1E_C$) on the pseudocubic (200) profiles at a static electric field $E = -0.8E_C$.

and phase transition in ferroelectric materials upon cyclic electric field. Major findings of this study are: (1) in a freshly poled PZT-5H, a static negative electric field of magnitude below the coercive field induces significant non-180° domain switching and phase transition, while a negative coercive field induces predominantly 180° domain switching; (2) the material's ability to undergo non-180° domain switching and phase transition is not affected when the material is electrically fatigued at amplitudes lower than the coercive field, but such ability is suppressed if the cyclic field amplitude is above the coercive field; and (3) the locking of non-180° domain switching and phase transition occurs rather suddenly upon cyclic electric field between 10^3 and 10^4 cycles. Similar observations were found for other pseudocubic peaks such as (111) and (220). The mechanisms for such locking are not definitively known. However, we observed that a fatigued specimen, when left untouched for a prolonged period of time (e.g., a month), seemed to be able to recover its ability to undergo non-180° domain switching. This observation, together with the fact that the ferroelectric hysteresis loop shifts upon electric fatigue, seems to indicate that preferential accumulation of electric charges, rather than permanent damage such as microcracking, may be the cause for the locking of non-180° domain switching upon electric fatigue. One effect of such locking phenomenon is to decrease the piezoelectric coefficients greatly, which may explain why there is only a small minima in the strain–electric-field hysteresis loop measured in similar PZT materials.[28]

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