

Fatigue anisotropy in single crystal $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$

Koichi Takemura,^{a)} Metin Oztgul, Veronique Bornand, Susan Trolier-McKinstry, and Clive A. Randall^{b)}

Center for Dielectric Studies, Materials Research Laboratory, The Pennsylvania State University, University Park, Pennsylvania 16802-4800

(Received 22 February 2000; accepted for publication 3 August 2000)

Fatigue rates in the $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ perovskite solid solution were investigated for different compositions in the rhombohedral and tetragonal phases in a variety of directions, at various field levels. It was found that the fatigue rates depend on both the ferroelectric phase and crystallographic orientation. In the rhombohedral phase when the field is applied along the $[001]_C$ direction (where the direction is given in terms of the cubic prototype), excellent fatigue resistance was obtained. © 2000 American Institute of Physics. [S0021-8979(00)06321-0]

I. INTRODUCTION

Ferroelectric fatigue is the gradual decrease of switchable charge with polarization reversal under bipolar drive. Early studies of fatigue were mostly confined to single crystals, and fatigue was observed to be a general phenomenon in ferroelectrics. In general, freezing of the switchable polarization is believed to occur through the pinning of domain walls with point defects and space charge.¹⁻⁸

In ferroelectric thin film studies, fatigue as well as imprint and retention are widely recognized as major problems to overcome with ferroelectric nonvolatile random access memories (FeRAMs). IN FeRAM devices, polarization reversal is utilized for read/write operations and the two remanent polarization states correspond to "0" or "1" in the binary memory. Ferroelectric fatigue makes it difficult to distinguish between the two states, and consequently limits the lifetime of the memories.⁹⁻¹¹

There have been innovative advances to overcome the problem of fatigue in perovskite films, such as the utilization of top and bottom oxide electrodes, RuO_2 ,^{12,13} IrO_2 ,¹⁴ SrRuO_3 ,¹⁵ and $(\text{La,Sr})\text{CoO}_3$,^{16,17} which have all been successfully tested. The mechanism responsible for the improved fatigue resistance with oxide electrodes is not fully elucidated; one possibility is that such electrodes can act as oxygen sources, and so help limit pinning of the domain walls associated with point defects. Alternative ferroelectrics have also been explored, such as $\text{SrBi}_2\text{Ta}_2\text{O}_9$ (SBT) and $\text{SrBi}_2\text{Nb}_2\text{O}_9$ (SBN).¹⁸⁻²⁰ These materials have the spontaneous polarization lying in the a - b plane of the orthorhombic unit cell. There are only four possible polarization states with SBT or SBN.²¹ In the polycrystalline case, the remanent polarization is small, unless care is taken to control the crystallization orientation. The SBN family can be co-processed with Pt electrodes and retains good fatigue even in this case. There are, however, technological issues associated with the

lower polarizations levels, the high crystallization temperatures, and Bi-Pt reactions.²²

The objective of this study was to revisit fatigue in perovskite single crystals based on $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$, (PZN-PT) system. These material systems have recently become important owing to the excellent electromechanical performance obtained with engineered domain structures.^{23,24}

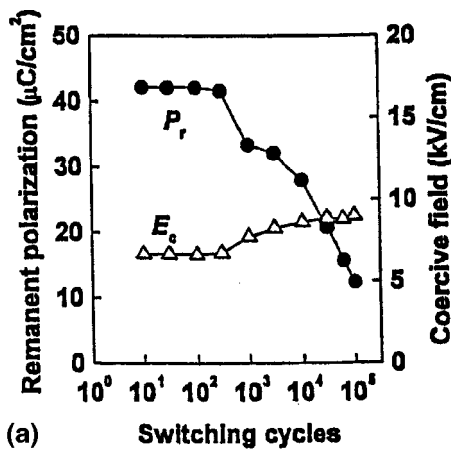
II. EXPERIMENTAL PROCEDURE

PZN-PT crystals were grown by a high temperature flux technique.^{25,26} The ferroelectric crystal compositions studied include 100% PZN(PZN), 95.5% PZN-4.5% PT(PZN-4.5 PT), 92% PZN-8% PT(PZN-8 PT), and 88% PZN-12% PT(PZN-12 PT). At room temperature, PZN and PZN-4.5 PT crystals are rhombohedral (pseudocubic), PZN-8 PT is near the morphotropic phase boundary (MPB) (still rhombohedral), and PZN-12 PT is tetragonal. For the sake of consistency, all of the orientations given throughout the remainder of the article will be given in terms of the prototype cubic perovskite axes. This will be denoted by the subscript C when orientations are given. All the crystals were oriented within $\pm 2^\circ$ along the $[111]_C$ or $[001]_C$ axes by the back-reflection Laue method. Plate-shaped samples were obtained by cutting off the oriented crystals, which were then polished with 3 μm alumina powder to obtain flat and parallel surfaces. Pt 100 nm thick was sputtered as an electrode. The thickness of the samples ranged from 200 to 600 μm , and the electrode area ranged from 0.7 to 7 mm^2 . The samples were annealed at 250 $^\circ\text{C}$ in air for 16 h in order to remove residual strain and defects that were introduced during crystal growth and polishing.

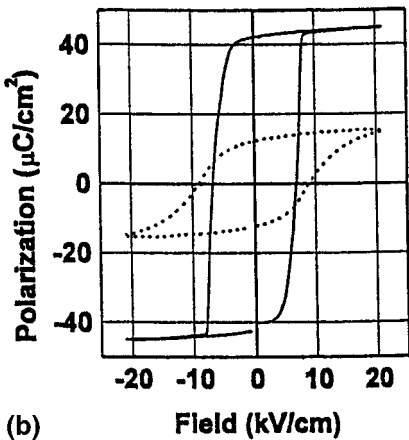
Polarization hysteresis loops were measured at room temperature using a modified Sawyer-Tower circuit. In particular, the electric field (E) was applied as a triangular bipolar wave form using a high voltage dc amplifier (Trek Model 609C-6 or Kepco Model BOM 1000M). The frequency of the alternating field was 10 Hz for polarization measurements as well as the switching in fatigue measurements. During measurement, the samples were immersed in Fluorinert to prevent arcing. The remanent polarization (P_r)

^{a)}Present address: ULSI Device Development Division, NEC Electron Devices, NEC Corporation, 1120 Shimokuzawa, Sagami-hara 229-1198, Japan.

^{b)}Electronic mail: car4@psu.edu



(a)



(b)

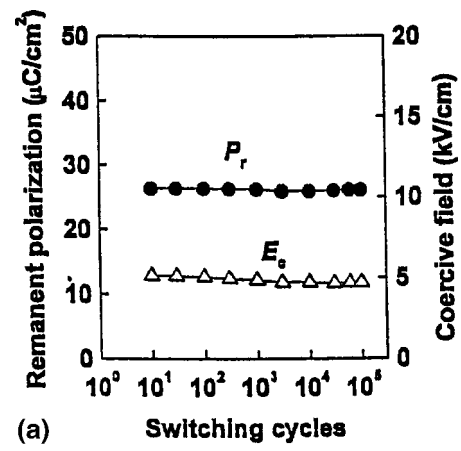
FIG. 1. Switching cycle dependence of (a) remanent polarization, P_r (solid circles), and coercive field, E_c (open triangles), (b) hysteresis loops for $[111]_C$ -oriented PZN-4.5 PT single crystals. In Fig. 1(b), the solid line is the hysteresis loop after ten cycles, and the broken line is that after 1×10^5 cycles.

and the coercive fields (E_c) were computed from the hysteresis loops obtained. On a limited number of samples, the strain-field hysteresis loop was monitored with a linear variable differential transducer to ensure complete switching under the bipolar drive at each driving field frequency and amplitude.

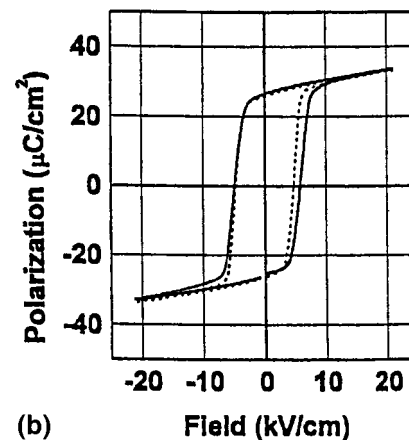
III. RESULTS AND DISCUSSION

A. Composition and orientation dependence

Figures 1 and 2 show P_r , E_c , and hysteresis loops for $[111]_C$ - and $[001]_C$ -oriented PZN-4.5 PT crystals as a function of the number of switching cycles. The amplitude of the alternating triangular electric field (E_{max}) was 20 kV/cm, and the frequency of the field was 10 Hz. The initial P_r value for the $[111]_C$ -oriented crystal ($P_{r,[001]}$) is approximately equal to $1/\sqrt{3}$ of $P_{r,[111]}$. In $[111]_C$ -oriented crystals, the remanent polarization during cycling is along $[111]_C$ for $\mathbf{E} \parallel [111]$, or $[\bar{1}\bar{1}\bar{1}]_C$ for $\mathbf{E} \parallel [\bar{1}\bar{1}\bar{1}]$. Thus, the domains switch between $[111]$ and $[\bar{1}\bar{1}\bar{1}]$ states. In $[001]_C$ -oriented crystals, the spontaneous polarization lies along one of four possible polar directions, for example, $[111]_C$, $[\bar{1}\bar{1}\bar{1}]_C$, $[1\bar{1}\bar{1}]_C$, or $[\bar{1}\bar{1}1]_C$ for $\mathbf{E} \parallel [001]$. With a reverse electric field, then these



(a)



(b)

FIG. 2. Switching cycle dependence of (a) remanent polarization, P_r (solid circles), and coercive field, E_c (open triangles), (b) hysteresis loops for $[001]_C$ -oriented PZN-4.5 PT single crystals. In Fig. 2(b), the solid line is the hysteresis loop after ten cycles, and the broken line is that after 1×10^5 cycles.

domains switch to $[\bar{1}\bar{1}\bar{1}]_C$, $[1\bar{1}\bar{1}]_C$, $[\bar{1}\bar{1}1]_C$, or $[11\bar{1}]_C$, and this can be done via 180° , 71° , or 109° switching processes, assuming rhombohedral symmetry.

As shown in Fig. 1, the P_r values for $[111]_C$ -oriented crystals are almost constant up to 10^3 cycles and then decrease rapidly with further switching cycles. The $[111]_C$ -oriented crystals obviously fatigue. The E_c values increase after the onset of fatigue. In contrast, the P_r and E_c values for $[001]_C$ -oriented crystals are almost constant up to 10^5 switching cycles as shown in Fig. 2(a). The shape of the hysteresis loop does not change even after 10^5 cycles as shown in Fig. 2(b). The E_c value slightly decreases with switching cycles. As will be discussed below, this decrease in E_c as a function of cycling was observed for $[001]_C$ -oriented crystals measured with a wide variation in field amplitudes. We infer that some domain walls are weakly pinned in the initial state, causing some resistance to switching, but during cycling these domain walls are detached from the original pinning sites. Possible origins for the pinning include impurities, oxygen or lead vacancies, or damage produced during crystal growth, polishing, or electroding.

The same orientation dependence of fatigue is also observed in pure PZN single crystals, as shown in Figs. 3 and

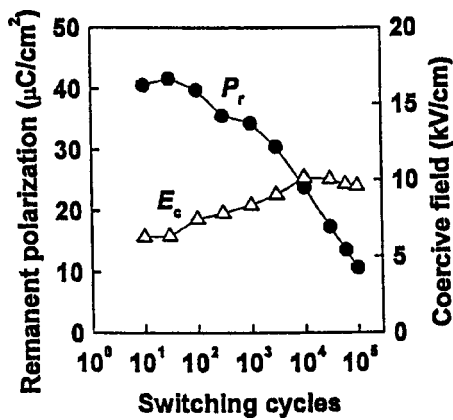


FIG. 3. Switching cycle dependence of P_r (solid circles) and E_c (open triangles) for $[111]_C$ -oriented PZN single crystals.

4. Fatigue in rhombohedral PZN(-PT) single crystals, therefore, is not dominated by the nature of the ferroelectricity, that is to say relaxor or normal behavior.^{27,28}

Unlike the rhombohedral phase, fatigue is observed in $[001]_C$ -oriented PZN-12 PT tetragonal crystals as shown in Fig. 5. In tetragonal PZN-12 PT, the polar direction is along $[001]_C$. Thus, domain switching involves polarization directions normal to the electrode-crystal interface, and presumably is accomplished predominantly through 180° domain wall motion. The origin of fatigue in tetragonal PZN-PT crystals is believed to be similar to that found in tetragonal BaTiO_3 single crystals.

The switching behavior of P_r and E_c in a $[001]_C$ -oriented PZN-8 PT crystal (near the MPB composition) is shown in Fig. 6(a). Whereas the P_r values are almost constant up to 10^5 cycles, the hysteresis loop changes as shown in Fig. 6(b). There is some indication of the development of a pinning phenomenon, as is evidenced by the narrowing of the waist of the hysteresis loop.

The above results indicate again that the rate of fatigue is strongly dependent on both the ferroelectric phase and the crystal orientation in relaxor-PT single crystals. The $[001]_C$ -oriented rhombohedral phase showed no notable fa-

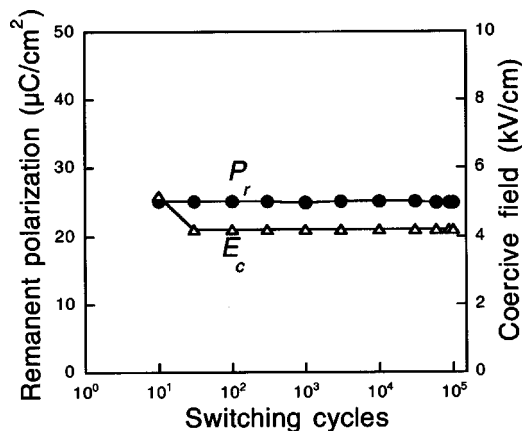


FIG. 4. Switching cycle dependence of P_r (solid circles) and E_c (open triangles) for $[001]_C$ -oriented PZN single crystals.

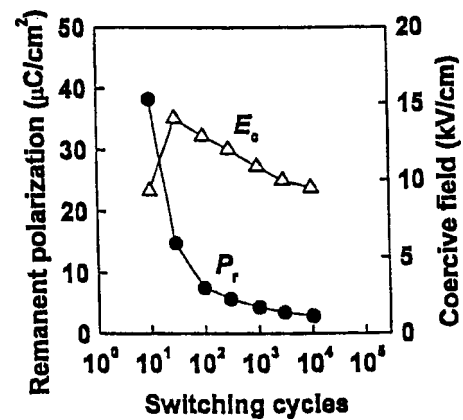
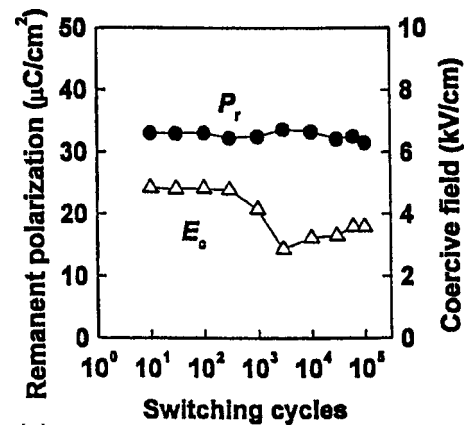


FIG. 5. Switching cycle dependence of P_r (solid circles) and E_c (open triangles) for $[001]_C$ -oriented PZN-12 PT single crystals.

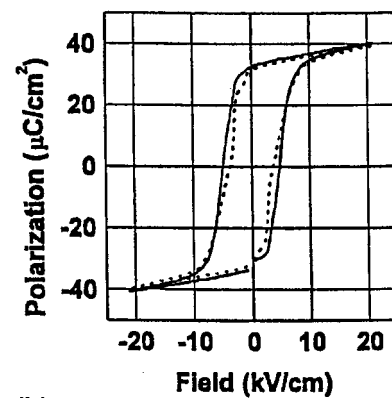
tigue up to 10^5 cycles for the slow alternating field required to switch the polarization in the crystal capacitors.

B. Switching condition dependence of fatigue

In ferroelectric thin films, the magnitude of the applied fields can influence the fatigue rates.^{29,30} Figure 7 shows that the $[111]_C$ -oriented PZN-4.5 PT single crystals fatigue for a



(a)



(b)

FIG. 6. Switching cycle dependence of (a) remanent polarization, P_r (solid circles), and coercive field, E_c (open triangles), (b) hysteresis loops for $[001]_C$ -oriented PZN-8 PT single crystals. In Fig. 6(b), the solid line is the hysteresis loop after ten cycles, and the broken line is that after 1×10^5 cycles.

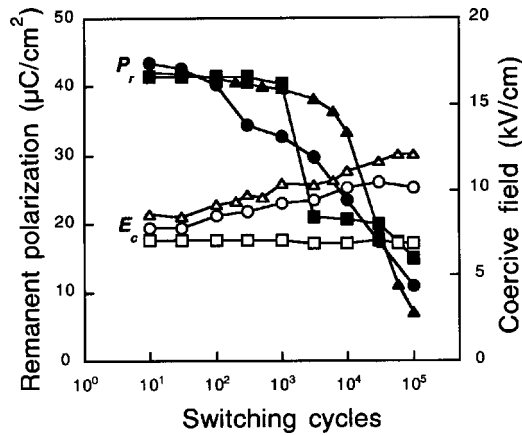


FIG. 7. Switching cycle dependence of P_r (solid symbols) and E_c (open symbols) for $[111]_C$ -oriented PZN-4.5 PT single crystals under various switching field strengths (\blacksquare, \square ; 10 kV/cm, \bullet, \circ ; 20 kV/cm, $\blacktriangle, \triangle$; 30 kV/cm). The switching frequency was 10 Hz.

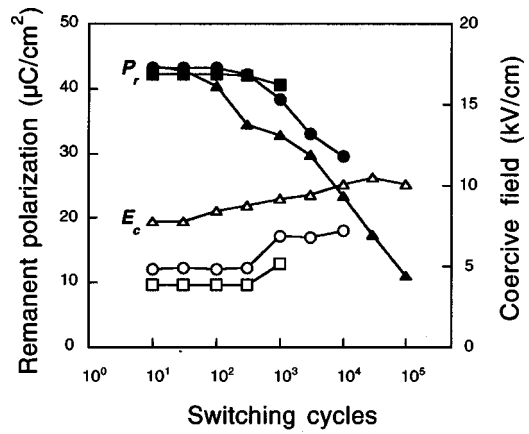


FIG. 9. Switching cycle dependence of P_r (solid symbols) and E_c (open symbols) for $[111]_C$ -oriented PZN-4.5 PT single crystals measured at various switching frequencies (\blacksquare, \square ; 0.1 Hz, \bullet, \circ ; 1 Hz, $\blacktriangle, \triangle$; 10 Hz). E_{max} was 20 kV/cm.

wider range of E_{max} values. $[001]_C$ -oriented PZN-4.5 PT crystals, in contrast, do not fatigue under various E_{max} levels, as shown in Fig. 8. We therefore can infer that the crystal orientation, rather than E_{max} , governs the fatigue resistance for these PZN-PT crystals, provided the E_{max} does not induce ferroelectric phase transitions.³¹ Figures 9 and 10 show the switching cycle dependence of P_r and E_c values for $[111]_C$ - and $[001]_C$ -oriented PZN-4.5 PT single crystals measured at various switching frequencies between 0.1 and 10 Hz. In the present study, fatigue lifetime does not depend on the switching frequency for $[111]_C$ -oriented crystals.

It has been shown previously that large strain changes of 0.1% accompany polarization reversal in $[111]_C$ -oriented crystals.²³ Strain sometimes results in microcracking, and microcracks have often been associated with fatigue in bulk ceramics.³² Figure 11 shows that annealing improves the P_r value of a fatigued $[111]_C$ -oriented PZN-4.5 PT crystal. When a fatigued crystal was annealed at 450 °C for 16 h in air, P_r increased to more than 80% of the initial P_r value. This result proves that the fatigue observed in the present

study is recoverable, and rules out fatigue by microcracking. Therefore, fatigue in the $[111]_C$ -oriented PZN-4.5 PT single crystals is believed to result from domain wall pinning via defects during polarization reversal, as has been reported in earlier single crystal studies.

C. Optimum orientation of crystals

Figure 12(a) shows the fatigue behavior for PZN-4.5 PT single crystals oriented along $[001]_C + \alpha$, where α is the degree of deviation from $[001]_C$ ($\alpha = 0^\circ$) toward $[111]_C$ ($\alpha = 54.7^\circ$), as shown in Fig. 12(b). The initial P_r and E_c values increase with α , and the initial P_r magnitude is consistent with projection of the $P_{r,[111]}$, i.e., $P_{r,[111]} \cos(54.7^\circ - \alpha)$. The fatigue rate is enhanced when crystals are oriented with $\alpha \geq 15^\circ$. The induction period before fatigue onset gradually decreases with increasing α . Fatigue in the rhombohedral PZN-PT single crystals is systematically dependent on crystallographic orientation, with $[001]_C$ -oriented rhombohedral ferroelectric single crystals believed to have the lowest fatigue rate.

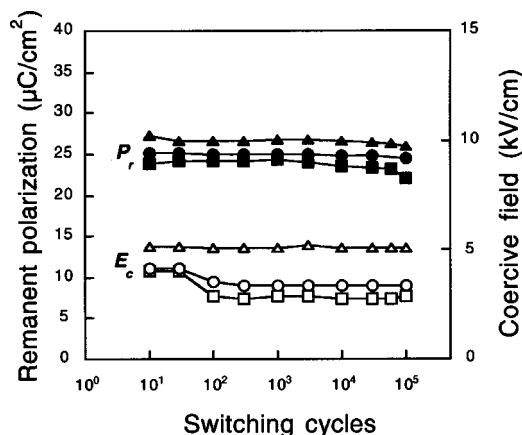


FIG. 8. Switching cycle dependence of P_r (solid symbols) and E_c (open symbols) for $[001]_C$ -oriented PZN-4.5 PT single crystals under various switching field strengths (\blacksquare, \square ; 5 kV/cm, \bullet, \circ ; 10 kV/cm, $\blacktriangle, \triangle$; 20 kV/cm). The switching frequency was 10 Hz.

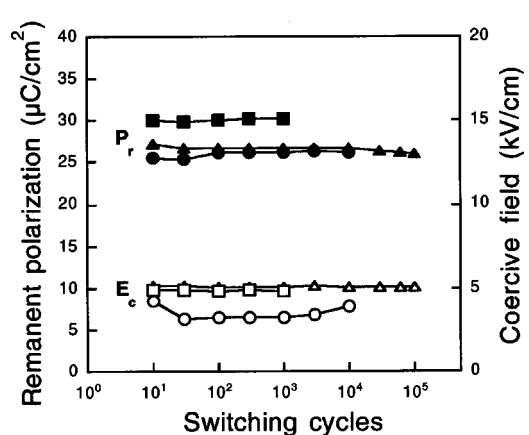
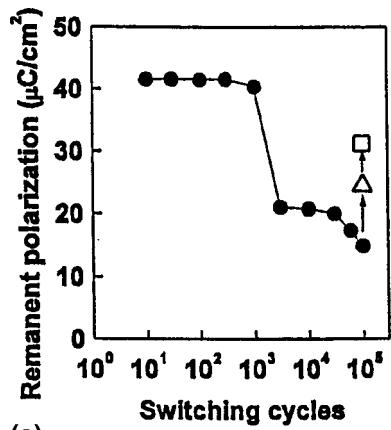
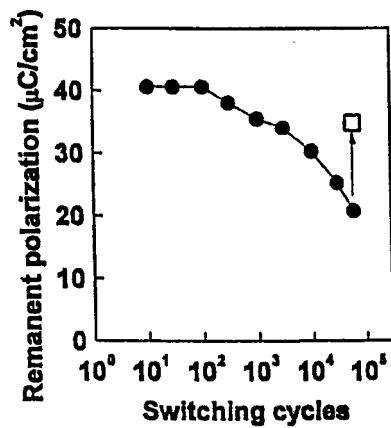


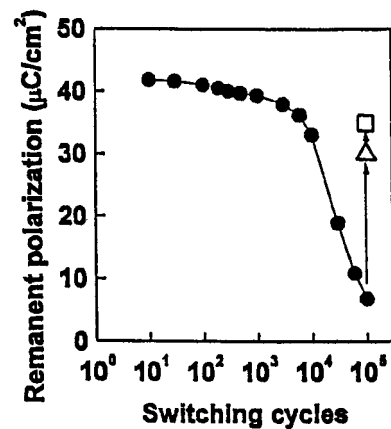
FIG. 10. Switching cycle dependence of P_r (solid symbols) and E_c (open symbols) for $[001]_C$ -oriented PZN-4.5 PT single crystals measured at various switching frequencies (\blacksquare, \square ; 0.1 Hz, \bullet, \circ ; 1 Hz, $\blacktriangle, \triangle$; 10 Hz). E_{max} was 20 kV/cm.



(a)



(b)

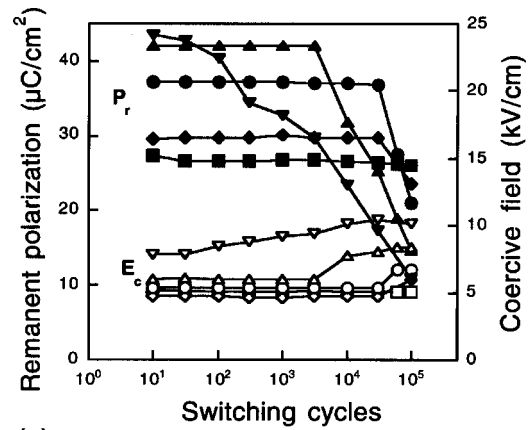


(c)

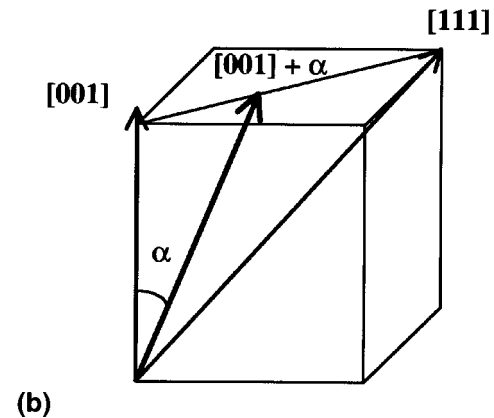
FIG. 11. Recovery of remanent polarization, P_r , for $[111]_C$ -oriented PZN-4.5 PT single crystals fatigued under different E_{\max} conditions; (a) 10 kV/cm, (b) 20 kV/cm, and (c) 30 kV/cm. After fatigue, the crystal was annealed at 250 °C (open triangle), and then 450 °C (open square) for 16 h in air.

D. Domain structure in field cycled PZN-PT crystals

Optical microscopy has shown in the $[111]_C$ -oriented PZN-4.5 PT crystal the domain density increases with cycling and fatigue, whereas in the $[001]_C$ -oriented PZN-4.5 PT crystal, the density of domain walls decreases. In the case of $[111]_C$ -oriented crystals, it is anticipated that as domain walls are pinned by the fatigue process, new domains are activated from preexisting nuclei, initially enabling the maximum polarization to be reversed for each cycle. As cycling



(a)



(b)

FIG. 12. (a) Effect of deviation from $[001]_C$ direction on fatigue for PZN-4.5 PT single crystals. (b) The deviation angle from $[001]_C$ toward $[111]_C$ (α) is defined. Solid markers show P_r , and open markers show E_c (\blacksquare, \square ; $\alpha=0^\circ$ $[001]$, \blacklozenge, \lozenge ; $\alpha=15^\circ$, \bullet, \circ ; $\alpha=30^\circ$, $\blacktriangle, \triangle$; $\alpha=45^\circ$, $\blacktriangledown, \triangledown$; $\alpha=54.7^\circ$ $[111]$). The switching frequency was 10 Hz and $E_{\max}=20$ kV/cm.

continues the process of pinning, activation of new domains, and then ultimately freezing, the result is a high density of frozen-in domain walls in fatigued crystals. Recently, in our group, switching analysis of $[111]_C$ - and $[001]_C$ -oriented PZN-PT crystals has shown that the mobility of domain walls in $[001]_C$ cuts is much higher.³³ This results in the ferroelectric being able to lower its total energy by systematically having the fastest domain walls control the switching and the domains can grow to define the largest volumes in the crystal and reduce the total domain wall density. This is consistent with observations made with optical microscopy, where only a few domains are observed in $[001]_C$ -oriented crystals driven under bipolar fields to 10^3 – 10^5 cycles. Clearly more work needs to be conducted to establish the orientation and nature (i.e., charged or uncharged) of the residual domain walls in both fatigued and unfatigued crystals of both orientations. Higher resolution techniques that can verify the local domain structures will also be necessary, together with a determination of the switching mechanism.

IV. CONCLUSIONS

Fatigue in PZN-PT single crystals was studied at room temperature for a variety of crystallographic orientations, electric field strengths, frequencies, and compositions. It is

observed that the rhombohedral PZN-PT crystals oriented with the field along $[001]_C$ have no fatigue. At room temperature, $[111]_C$ -oriented rhombohedral PZN-PT fatigues as does tetragonal PZN-PT in $[001]_C$ and $[111]_C$ directions. Close to the morphotropic phase boundary the presence of tetragonal phase will dominate and complicate the fatigue process; this will be addressed in a future paper.

The fatigue free nature of the rhombohedral phase in the $[001]_C$ orientation is suggested to be related to the engineered domain configuration, and to the observation that the $[001]_C$ direction has a high domain mobility. Following these studies, epitaxial ferroelectric thin films of $\text{Pb}(\text{Yb}_{1/2}\text{Nb}_{1/2})\text{O}_3\text{-PtTiO}_3$ have been fabricated and tested to verify fatigue at higher switching frequencies and thinner crystals. The results are consistent with the fundamental observations made here.³⁴

ACKNOWLEDGMENTS

The authors would like to thank Professor T. R. Shrout and Dr. S.-E. Park for their helpful suggestions, and by S.-F. Liu and H. Lei for supplying single crystals. This work was partially supported by DARPA, Grant No. N00014-98-1-0527 and a grant-in-aid from NEC Corporation.

- ¹E. Fatuzzo and W. J. Merz, *Ferroelectricity* (Wiley, New York, 1967).
- ²F. Jona and G. Shirane, *Ferroelectric Crystals* (Pergamon, Oxford, 1962) and (MacMillan, New York, 1962).
- ³D. S. Campbell, *Philos. Mag.* **79**, 1157 (1962).
- ⁴W. J. Merz and J. R. Anderson, *Bell Lab. Rec.* **33**, 335 (1955).
- ⁵R. Williams, *J. Phys. Chem. Solids* **26**, 399 (1965).
- ⁶J. R. Anderson, G. W. Brady, W. J. Merz, and J. P. Remeika, *J. Appl. Phys.* **26**, 1387 (1955).
- ⁷H. L. Stadler, *J. Appl. Phys.* **29**, 743 (1958).
- ⁸J. F. Scott and C. A. Pas de Araujo, *Science* **246**, 140 (1989).
- ⁹S. B. Desu, *Phys. Status Solidi A* **151**, 467 (1995).
- ¹⁰P. K. Larsen, G. J. M. Dormans, D. J. Taylor, and P. J. van Veldhoven, *J. Appl. Phys.* **76**, 2405 (1994).

- ¹¹D. P. Vijay and S. B. Desu, *J. Electrochem. Soc.* **140**, 2640 (1993).
- ¹²T. Nakamura, Y. Nakao, A. Kamisawa, and H. Takasu, *Jpn. J. Appl. Phys., Part 1* **33**, 5207 (1994).
- ¹³H. N. Al-Shareef, K. R. Bellur, A. I. Kingon, and O. Auciello, *Appl. Phys. Lett.* **66**, 239 (1995).
- ¹⁴T. Nakamura, Y. Nakano, A. Konisawa, and H. Takasu, *Appl. Phys. Lett.* **65**, 1552 (1994).
- ¹⁵J. T. Cheung, P. E. D. Morgan, and R. Neurgaonkar, *Proceedings of the 4th International Symposium on Integrated Ferroelectrics*, Colorado Springs, CO, 1992, p. 518.
- ¹⁶R. Ramesh, H. Gilchrist, T. Sands, V. G. Keranidas, R. Haakenaasen, and D. K. Fork, *Appl. Phys. Lett.* **63**, 3592 (1993).
- ¹⁷C. B. Eom, R. B. Van Dover, J. M. Phillips, D. J. Werder, J. H. Marshall, C. H. Chen, R. J. Cava, R. M. Fleming, and D. K. Fork, *Appl. Phys. Lett.* **63**, 2570 (1993).
- ¹⁸S. Aggarwal, I. G. Jenkins, B. Nagaraj, C. J. Kerr, C. Canedy, R. Ramesh, G. Valasquez, L. Boyer, and J. T. Evans, Jr., *Appl. Phys. Lett.* **75**, 1787 (1999).
- ¹⁹R. Dat, J. K. Lee, O. Auciello, and A. I. Kingon, *Appl. Phys. Lett.* **67**, 572 (1995).
- ²⁰C. A. Paz de Araujo, J. K. Cuchiaro, L. D. McMillan, M. C. Scott, and J. F. Scott, *Nature (London)* **374**, 627 (1995).
- ²¹R. E. Newnham, R. W. Wolfe, R. S. Horsey, F. A. Diaz-Colon, and M. I. Kay, *Mater. Res. Bull.* **8**, 1183 (1973).
- ²²J. F. Scott, *Ferroelectrics* **206-207**, 365 (1990).
- ²³S.-E. Park and T. R. Shrout, *J. Appl. Phys.* **82**, 1804 (1997).
- ²⁴T. Kobayashi, S. Saitoh, K. Harada, S. Shimanuki, and Y. Yamashita, *Proceedings of the 1998 11th IEEE International Symposium on Applications of Ferroelectrics (ISAF-XI)*, August 24–27, 1998.
- ²⁵M. L. Mulvihill, S.-E. Park, G. Rish, Z. Li, K. Uchino, and T. R. Shrout, *Jpn. J. Appl. Phys., Part 1* **35**, 51 (1996).
- ²⁶S.-E. Park, M. L. Mulvihill, G. Risch, and T. R. Shrout, *Jpn. J. Appl. Phys., Part 1* **36**, 1154 (1997).
- ²⁷L. E. Cross, *Ferroelectrics* **76**, 241 (1987).
- ²⁸C. A. Randall and A. S. Bhalla, *Jpn. J. Appl. Phys., Part 1* **29**, 327 (1990).
- ²⁹X. Du and I. W. Chen, *J. Appl. Phys.* **83**, 7789 (1998).
- ³⁰I. K. Yoo and B. Desu, *Phys. Status Solidi* **133**, 565 (1992).
- ³¹S.-F. Liu, S.-E. Park, T. R. Shrout, and L. E. Cross, *J. Appl. Phys.* **85**, 2810 (1999).
- ³²D. Wang, Y. Fotinich, and G. P. Carman, *J. Appl. Phys.* **83**, 5342 (1998).
- ³³H. Yu, V. Gopalan, and C. A. Randall, *J. Appl. Phys.* (submitted).
- ³⁴V. Bornand, S. Trolier McKinstry, K. Takemura, and C. A. Randall, *J. Appl. Phys.* **87**, 3965 (2000).