The Polarization Fatigue Behavior in Pb(Mg_{1/3}Nb_{2/3})O_3-0.32PbTiO_3 Single Crystals

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Abstract. Polarization hysteresis (P-E) change was investigated as a function of the strength, frequency and cycles of electric field alternating for [001]c, [110]c, [111]c oriented Pb(Mg_{1/3}Nb_{2/3})O_3-0.32PbTiO_3 (PMN-0.32PT) single crystals. Under 1.5kV/cm (< E_c), the fatigue rates after 10^5 cycles were 13%, 16% and 34% for [001]c, [110]c and [111]c orientations, respectively. Under 7.5kV/cm (>E_c), obvious polarization fatigue was presented for [001]c, [110]c, [111]c orientations and the biggest fatigue rate was around ∼70% in [110]c orientations after 10^5 cycles. The fatigue rate decreased with the increasing of electric field frequency. The influences of crystallographic orientation and electric field strength and frequency on polarization fatigue behavior in PMN-0.32PT single crystals was discussed based on space charge, domain reverse and phase transition process.

1. Introduction

Relaxor-based ferroelectric single crystals Pb(Mg_{1/3}Nb_{2/3})O_3-PbTiO_3 (PMN-PT) and Pb(Zn_{1/3}Nb_{2/3})O_3-PbTiO_3 (PZN-PT) with morphotropic phase boundary (MPB) composition along [001]_c orientation exhibit extraordinary large electromechanical coupling coefficient k_{33}>90% and piezoelectric coefficient d_{33}>2000pC/N. The intermediate phase monoclinic (M) and orthorhombic (O) phases between rhombohedral (R) and tetragonal (T) phases were observed in PMN-PT single crystals with MPB composition based on the results of high-resolution synchrotron X-ray diffraction, polarized light microscopy, and dielectric properties. It is reasonable that intermediate phases induced by electric field play an important role for enhanced piezoelectric properties. Ferroelectric materials exhibit polarization fatigue under applied cyclic electric field, meanwhile, electric field could induce phase transition in PMN-PT single crystals. Much attention has been focused on the physical origin of great piezoelectric properties in relaxor-based single crystal. However less study was concerned with the effects of complex phase transition under electric field on ferroelectric fatigue.

In earlier studies, fatigue in ferroelectrics is thought from internal stress, switching mechanisms, domain configuration and space charge etc. The formation of space charges is usually from oxygen vacancies or electrons-hole pairs. It is expected to display the intrinsic origin of ferroelectric fatigue based on ferroelectric single crystals. The fatigue behavior of PZN-0.045PT single crystals concerned with the crystallographic orientation. The rhombohedral PZN-0.045PT single crystal have no fatigue along [001]_c orientation after 10^5 cycles under 30kV/cm and fatigue in [111]_c, direction of [001]_c oriented PZN-0.10PT crystal around MPB was serious fatigue after 10^3 cycles at low temperatures. The fatigue rate is severe along [001]_c orientation for tetragonal PZN-0.12PT single
crystal. Metin Ozgul et al. reported the polarization fatigue of PZN-PT with respect to composition, orientation, temperature and electric field strength. The ferroelectric fatigue behavior of PMN-PT single crystal has been less reported until now. In this paper, the effects of orientation, electric field strength (E<Ec and E>Ec) and frequency on the polarization fatigue behavior of PMN-0.32PT single crystal was studied. The ferroelectric fatigue mechanism in PMN-0.32PT single crystals was discussed.

2. Experimental Procedure
PMN-0.32PT single crystals were grown by a modified Bridgman method in our laboratory. The pseudo-cubic [001], [110], and [111] directions of samples were determined by X-ray diffraction (XRD). The final dimensions of samples for ferroelectric fatigue measurement were nominally 4 x 4 x 0.6 mm³. Silver electrodes were painted onto both surfaces. Hysteresis loops were measured using a modified Sawyer-Tower circuit (TF ANALYZER 2000 and MTI 2000 FOTONIC SENSOR). The remnant polarizations (Pr) and the coercive fields (Ec) were computed from the recorded hysteresis loops. The electric field was applied with a triangular bipolar wave form for fatigue experiments. The applied ac electric field strength were 1.5kV/cm (<Ec), 7.5kV/cm (>Ec) and frequencies were 1Hz, 10Hz, 100Hz, respectively. The hysteresis loops after 10⁴, 10⁵, 10⁶, 10⁷ switching cycles at different electric fields were measured during fatigue experiments. For hysteresis loop measurement of before and after fatigue in PMN0.32PT single crystal, the applied electric field was generally 7.0kV/cm at 1Hz with a sine wave form.

3. Results and Discussion
Figure 1(a), (b) and (c) show unfatigue (1cycle) P-E loops and loops after 10⁵ cycles under E=1.5kV/cm (<Ec) ac electric field in PMN-0.32PT single crystals along with [001], [110], and [111] orientations at room temperature, respectively. The remnant polarization (Pr) obviously decreased and coercive field strength increased along [111] orientation after 10⁵ cycles, comparing with [001] and [110] orientations. The fatigue rate is defined as the remnant polarization change, ΔPr/Pr, where the remnant polarization at 1 cycle is denoted as Pr and the difference of remnant polarization before and after fatigue is denoted as ΔPr. ΔPr/Pr as a function of crystallographic orientation and switching cycles is shown in Figure 2. The remnant polarization decreases obviously after 10² cycles for both [001] and [110] orientations and decreases quickly after 10 cycles for [111] orientation. After 10⁵ cycles, the fatigue rates are 13%, 16% and 34% for [001], [110] and [111] orientations, respectively. The ferroelectric fatigue rate along [111] direction is the biggest among three orientations in PMN-0.32PT single crystals.

The domain reversion is not easy during switching cycles if the applied electric field is below Ec. So ferroelectric fatigue in PMN0.32PT single crystal isn’t directly related to the domain reversion when E=1.5kV/cm (<Ec). For [001], and [110], orientations, it is maybe assumed that domain wall pinning induced by the accumulating of space charge which restricts the polarization. PMN-0.32PT single crystal is considered to be R phase at room temperature, in which the spontaneous polarization is along [111] direction. The polarization vector is paralleled to the electric field and the switching is presumably dominated by 180° domain walls. Ferroelectric fatigue is mostly induced by 180° domain reversion for [111] orientation. Furthermore the accumulating of space charge intensifies the local electric field and accelerates the deflection of spontaneous polarization. As a result, the strong fatigue is presented for [111] orientation PMN0.32PT single crystal.

Figure 3(a), (b) and (c) show unfatigue (1cycle) P-E loops and loops after 10⁵ cycles under E=7.5kV/cm (>Ec) ac electric field in PMN-0.32PT single crystals along with [001], [110], and [111] orientations at room temperature, respectively. As shown in Figure3, ferroelectric fatigue is obvious for all samples after 10⁵ cycles. Meanwhile, the coercive field Ec increases in [110], and [111] orientation and Ec is almost unchanged in [001] orientation. The fatigue rate as a function of crystallographic orientation and switching cycles is shown in Figure 4. The polarization decreases quickly after 10 cycles for all samples. After 10⁵ cycles, the fatigue rates are about 38%, 71% and 55%
for [001], [110], and [111], orientations, respectively. Comparing Figure 2 and Figure 4, the fatigue under 7.5 kV/cm (>Ec) is stronger than that under 1.5 kV/cm (<Ec).

Figure 1. Hysteresis loop change after $10^5$ cycles under 1.5 kV/cm in PMN-0.32PT single crystal along with (a) [001], (b) [110], and (c) [111], orientation.

Figure 2. Polarization fatigue behavior of PMN-0.32PT single crystals under 1.5 kV/cm ac field at 10 Hz.
Figure 3. Hysteresis loop change after $10^5$ cycles under 7.5kV/cm in PMN-0.32PT single crystal along with (a) [001]$_c$, (b) [110]$_c$ and (c) [111]$_c$ orientation

Figure 4. Polarization fatigue behavior of PMN-0.32PT single crystals under 7.5kV/cm ac field at 10Hz.

Vanderbilt and Cohen$^{22}$ conceived a thermodynamic model to describe three possible monoclinic phases (M$_A$, M$_B$ and M$_C$) from Devonshire theory. The intermediate phases (monoclinic and orthorhombic phases) between rhombohedra and tetragonal phase have been found in PMN-PT single crystal around MPB$^{23}$. The phase transformation sequence in MPB PMN-PT crystals is strongly dependent on the amplitude and the direction of applied electric field. For example, the phase transition sequence of [001]$_c$, [110]$_c$ and [111]$_c$ oriented are R$\rightarrow$M$_A$$\rightarrow$M$_C$$\rightarrow$T$^{24}$, R$\rightarrow$M$_B$$\rightarrow$O$^{25}$ and
R→M_A→T→M_A→R_{111}, respectively. According to our dielectric measurement results, the different phase transition process induced by electric field for different orientations in PMN-0.32PT single crystals were exhibited. When the applied electric field was 7.5kV/cm, it was presented that M_c phase induced from R phase through M_A phase for [001]_c orientation, mixed phase between R and O phase including M_B phase for [110]_c and only R phase for [111]_c orientation in PMN-0.32PT single crystals, respectively. It is supposed that the fatigue is controlled by the polarization reverse in M_c phase, the mixed phases and R phase for [001]_c, [110]_c and [111]_c orientation under 7.5kV/cm, respectively. From Figure 3 and Figure 4, the biggest remnant polarization change is shown in [110]_c orientation after 10^5 cycles. The spontaneous polarization in O-phase is along with [110]_c direction. So the direction of polarization is paralleled to applied electric field for [110]_c orientation. As a result, the switching is presumably dominated by 180° domain walls. At the same time, besides O phase, R and M phases coexist. The phase transition among O, R and M phases induced by ac electric field would contribute to the ferroelectric fatigue. And R phase only exists for [111]_c orientation sample under electric field 7.5kV/cm. The phase transition process in [110]_c orientation is more complex than that in [001]_c and [111]_c orientations. This may be the main reason that the fatigue rate in [110]_c orientation is the biggest among [100]_c, [110]_c and [111]_c orientations.

In PMN-0.32PT single crystal, the polarization vectors in ferroelectrics phase is paralleled to the electric field direction induced by high alternating electric fields. This implies that switching mechanisms become more dominant when the polarization direction paralleled to the electric field. The complex domain switching mechanism induced by the existence of mixed ferroelectric phases may lead to fatigue isotropy. Domain switching anisotropy may be one of the origins of the fatigue anisotropy. It presumably shows that the ferroelectric fatigue is concerned with the phase transition process. Therefore, the existence of mixed phase under high electric field and the phase transition among the mixed phase under cycling electric field will enhance the ferroelectric fatigue.

The frequency dependence of the fatigue rate for [110]_c orientation sample under 1.5kV/cm and 7.5kV/cm are shown in Figure 5(a) and 5(b), respectively. In Figure 5(a), \( \Delta P_r/P_r \) at low frequency is bigger than that at high frequency. The long interval of electric field at low frequency is favored for accumulating space charge at domain boundaries. The domain wall motion is restricted during polarization switching due to space charges. It implies that the space charges play a dominant role under 1.5kV/cm. Comparing Figure 5(a) with 5(b), the effect of frequencies on the fatigue rate under 7.5kV/cm obviously decreases. That is to say, effect of space charges on ferroelectric fatigue is reduced under high electric field. It is assumed that the fatigues are dominated by the space charges under below \( E_c \) and the complex domain switching mechanism under above \( E_c \) in PMN-0.32PT single crystals. Actually, PMN-PT single crystals have complex phase relation under electric field. The fatigue mechanism will be studied further.

![Figure 5](image-url)

**Figure 5.** Comparison of the fatigue rate in [110]_c oriented PMN-0.32PT single crystal at different frequency under (a) 1.5kV/cm, and (b) 7.5kV/cm
4. Conclusions
The ferroelectric fatigue was investigated as a function of the strength, frequency and cycles of electric field alternating for [001]c, [110]c, [111]c orientations in PMN-0.32PT single crystals. Under 1.5kV/cm (< Ec), the fatigue rate after 10^5 cycles for [111]c orientation was the biggest among three orientations. The ferroelectric fatigue is mostly induced by 180° domain reversion for [111] orientation. Under 7.5kV/cm (>Ec), obvious fatigue was presented for [001]c, [110]c, [111]c orientations and the biggest fatigue rate is around ∼70% in [110]c orientations after 10^5 cycles. It was related the mixed phases between R and O phase including M_B phase for [110]c orientation. The fatigue rate decreased with electric field frequency increasing. The domain switching mechanism can be expected to control the fatigue rate of single crystal with single phase structure. The fatigue was concerned with the relation between the polarization direction and electric field direction in single crystal with mixed ferroelectric phases.

Acknowledgements
This work was supported by National Natural Science Foundation of China No.90205030 and New Century Excellent Talent (2007) of the Ministry of Education

Reference
[1] Shrout T R, Chang Z P and Klm N 1990 Markgraf S: Ferroelectric. Lett. 12 63
[2] Lu Y, Jeong D.-Y, Cheng Z.-Y, Zhang Q M, Luo H S, Yin Z W and Viehland D 2001 Appl. Phys. Lett. 78 3109
[3] Ye Z.-G, Noheda B, Dong M, Cox D and Shirane G 2001 Phys. Rev. B 64 184114
[4] Xu G, Luo H, Xu H and Yin Z W 2001 Phys. Rev. B 64 020101
[5] Noheda B, Cox D E, Shirane G, Gao J and Ye Z.-G 2002 Phys. Rev. B 66 054104
[6] Tu C S, Hung L.-W, Chien R R and Schmidt V H 2004 J. Appl. Phys. 96 4411
[7] Viehland D, Amin A and Li J F 2001 Appl. Phys. Lett. 79 1006
[8] Arlt G and Pertsev N A 1991 J. Appl. Phys. 70 2283
[9] Duiker H M, Beale P D, Scott J F, Paz de Araujo C A, Melnick B M, Cuchiario J D and McMillan L D 1990 J. Appl. Phys. 68 5783
[10] Lohkomper R, Neumann H and Arlt G 1990 J. Appl. Phys. 68 4220
[11] Scott F, Araujo C, Melnick B M, McMillan L D and Zuleeg R 1991 J. Appl. Phys. 70 382
[12] Chen, Harmer M P and Smyth D M 1994 J. Appl. Phys. 76 5394
[13] Duiker H M and Beale P D 1990 Phys. Rev. B 41 490
[14] Warren W L, Dimos D, Tuttle B A, Nasby R D and Pike G E 1994 Appl. Phys. Lett. 65 1018
[15] Nakamura T, Nakao Y, Kanisawa A and Takasu H 1994 Appl. Phys. Lett. 65 152
[16] Ramesh R, Girchlist H, Sands T, Keramidas V G, Haakenaasen R and Fork D K 1993 Appl. Phys. Lett. 63 3592
[17] Dat R, Lee J K, Auciello O and Kingon A I 1995 Appl. Phys. Lett. 67 572
[18] Ozgul M, Takemura K, Susan Trolier McKinstry and Clive A. Randall 2001 J. Appl. Phys. 89 5100
[19] Metin Ozgul, Susan Trolier-McKinstry and Clive A. Randall 2004 J. Appl. Phys. V95 4296-4302.
[20] Koichi Takemura, Metin Ozgul, Veronique Bornand, Susan Trolier-McKinstry and Clive A. Randall 2000 J. Appl. Phys. 88 7272
[21] Li Z R, Xi Z Z, Xu Z and Yao X 2002 J. Mater. Sci. Lett. 21 1325
[22] Vanderbilt David and Cohen Morrel H 2001 Phys. Rev. B 63 214112
[23] Noheda B 2002 Curr. Opin. Solid State Mater. Sci. 6 27
[24] Feiming Bai, Naigang Wang, Jiefang Li and Viehland D 2004 J. Appl. Phys. 96 1620
[25] Viehland V and Li J F 2002 J. Appl. Phys. 92 7690
[26] Chi-shun Tu, Hugo Schmidt V, Shih I C and Chien R 2003 Phys. Rev. B. 67 020102
[27] Li Z R, Xu Z, Yao X and Cheng Z.-Y 2008 J. Appl. Phys. 104 024112