Journal of the European Ceramic Society 21 (2001) 677–681
www.elsevier.com/locate/jeurceramsoc

Frequency dependence of ferroelectric fatigue in PLZT ceramics

Ningxin Zhang *, Longtu Li, Zhilun Gui

State Key Laboratory of New Ceramic and Fine Processing, Department of Materials Science and Engineering, Tsinghua University, Beijing 100084, People's Republic of China

Received 24 April 2000; received in revised form 13 July 2000; accepted 19 July 2000

Abstract

Electric induced fatigue in ferroelectric PLZT ceramics was investigated. The fatigue occurred with the increasing of accumulative switching cycles in samples. The polarization decreased with the development of fatigue. At the same time, the piezoelectric properties also degraded during the process of ferroelectric fatigue. The different fatigue behaviors were observed in PLZT ceramics when processed under different frequencies of applied electric field, despite the same magnitude. The samples can be easily fatigued at low frequency while hardly fatigued at high frequency. The phenomenon was explained according to the dynamic behavior of ferroelectric domains during their responce to the applied electric field.

Keywords: Fatigue; Ferroelectric domains; Ferroelectric properties; PLZT

1. Introduction

Fatigue was a key problem that hindered the wide application of ferroelectric materials and related devices in many fields such as non-volatile memory, actuators, transducers, high voltage generators and filters. Ferroelectric fatigue was characterized by the degradation of main ferroelectric parameters such as switchable polarization or remanent polarization with the increase switching cycles of an applied electric field due to the reorientation of polarization. It is believed that many factors influenced the fatigue properties, including applied electric field strength, temperature, composition and electrodes.[1–7] Colla[8] had found a dramatic difference between two types of fatigue behaviors of $Pb(Zr,Ti)O_3$ thin films under fast switching (several kHz) and slow switching (1.7 mHz) alternative electric field. The former showed fatigue phenomenon after about 10^7 cycles, which was attributed to the inhibition of domain seeds at the electrode–ferroelectric interface; and the other showed fatigue at only 10 cycles, which was attributed to the freezing of domain walls in bulk of ferroelectrics. Scott[9] had suggested a model that could describe the fatigue process of experimental data successfully. In that model, the dynamic variation of oxygen vacancy concentration in ferroelectric capacitors, as well as the influence of frequency, electric field strength and temperature, was considered to monitor the process of fatigue. The data used in that model located below micro hertz and high frequencies up to tens of kilo-frequencies. A more broad wide of frequency should be considered in order to investigate the influence of applied electric field frequency on ferroelectric fatigue properties. In this paper, we intend to investigate the frequency influence on ferroelectric fatigue of PLZT ceramics in a wide frequency range and suggest a fatigue model based on our research results.

2. Experimental

PLZT ferroelectric ceramic with the Zr:Ti of 70:30 were prepared via convention method of oxides mixing doped by 2 mol% La. The mixed and ball milled oxides were calcined at 850°C for 1 h to form the perovskite structure. The calcined powders were milled again before pressed into pellets with the dimension of 15 mm in diameter and 1 mm in thickness. Sintering was carried out at 1200°C for 4 h with the $PbZrO_3$ samples as

* Corresponding author.
E-mail address: ningxin@mail.cic.tsinghua.edu.cn (N. Zhang).

0955-2219/01/$ - see front matter
PII: S0955-2219(00)00248-X

protecting atmosphere to prevent the evaporation of PbO at high temperature. The density of as-sintered samples was measured via Archimedes method to reach 95% of the theoretic density. Silver slurry was paste on the surface to introduce electrode for the further electrical measurements followed by 5–10 min heat treatment at 600°C. The crystalline structure was confirmed by X-ray diffraction (mode Rigaku using CuK_α $\lambda = 1.5405$ Å). The surface of sintered sample was sputtered with gold for the observation of microstructure on SEM (JSM 6301F). The dielectric and piezoelectric properties were also measured on an impedance analyzer (mode HP4194A) before and after the fatigue process. Hysteresis loop and ferroelectric fatigue induced by an electric field were carried out on a ferroelectric tester (RT6000HVS by Radiant Technology Inc., USA). An alternative electric field with sine wave was applied in the experiment. The magnitude of applying electric field was 13 kV/cm, higher than the coercive field, and four frequencies were chosen thus: 10, 50, 100 and 500 kHz. Before piezoelectric property measurement, the sample was poled in silicon oil at 120°C for 15–30 min under 3000 V DC voltage.

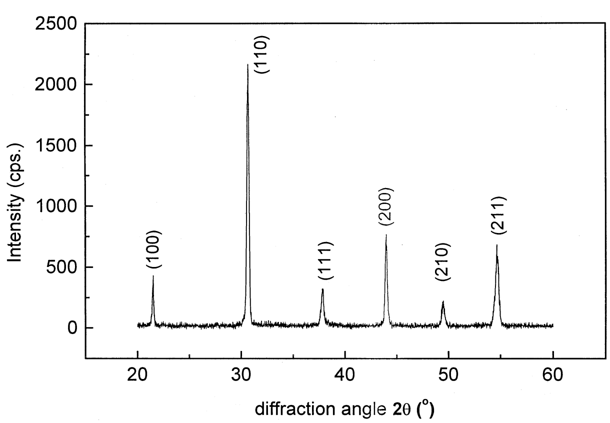

Fig. 1. X-ray diffraction pattern of as-sintered sample.

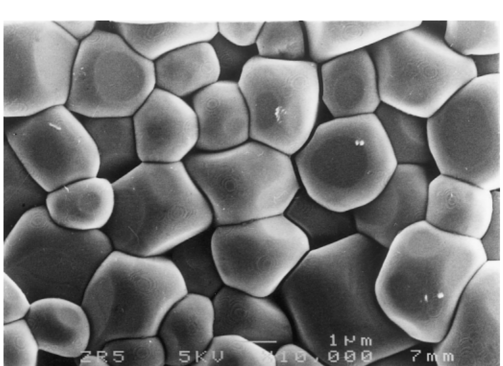

Fig. 2. Microstructure of as-sintered sample.

3. Results and discussion

3.1. Crystalline structure and microscopy observation

Fig. 1 showed the crystalline structure of the sintered sample. As shown, the main diffraction peaks of perovskite structure were clearly observed as indicated in the figure. No other diffraction peaks were found on the diffraction pattern. This implied that a very pure perovskite structure was formed under such sintering condition. According to the Zr:Ti ratio and the doping level of lanthanum, the sample located in the field of rhombhedral structure. Fig. 2 showed the microscopy of as sintered sample surface. The sample was highly densified as shown, and the grain size ranged from 2 to 5 μm.

3.2. Fatigue process and degradation of dielectric and piezoelectric properties

The fatigue process of PLZT ceramic was investigated by switchable polarization with the increase of cyclic electric field. A normal electric fatigue process was researched with the frequency of applying electric field to be 50 Hz to give a whole impression. In Fig. 3(a), both the positive and negative switchable polarization showed an apparent decrease when the accumulative cycles reached at 10^4. The switchable polarization held about 48% (26 μC/cm^2: 54 μC/cm^2) of the original values

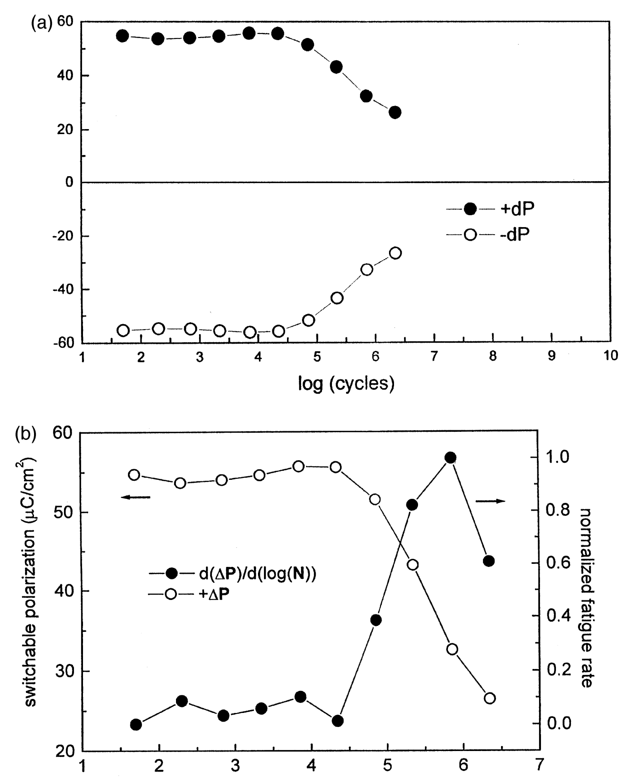

Fig. 3. Electric fatigue of ferroelectric PLZT ceramics (a) decreasing of switchable polarization and (b) fatigue rate.

at about 10^7 cycles. To investigate the fatigue process more carefully, the differential form of the variation of positive switchable polarization was listed simultaneously and defined as the normalized fatigue rate in Fig. 3(b). As shown, fatigue rate reach a local maximum at about 10^6 cycles, followed by a slowing down tendency. This indicated that some mechanism existed which prevented the further decrease of switchable polarization with the applied alternative electric field after a certain accumulation of ferroelectric domain reorientation.

In Fig. 4(a), the hysteresis loops before and after electric fatigue were listed for comparison. The original hysteresis loop showed a conductive behavior at the maximum electric field, which could not be observed at the fatigued ones. This might be due to a slight decrease of dielectric loss from 0.04 to 0.02 after fatigue, as listed in Table 1. The saturated P_{sat} and remnant polarization

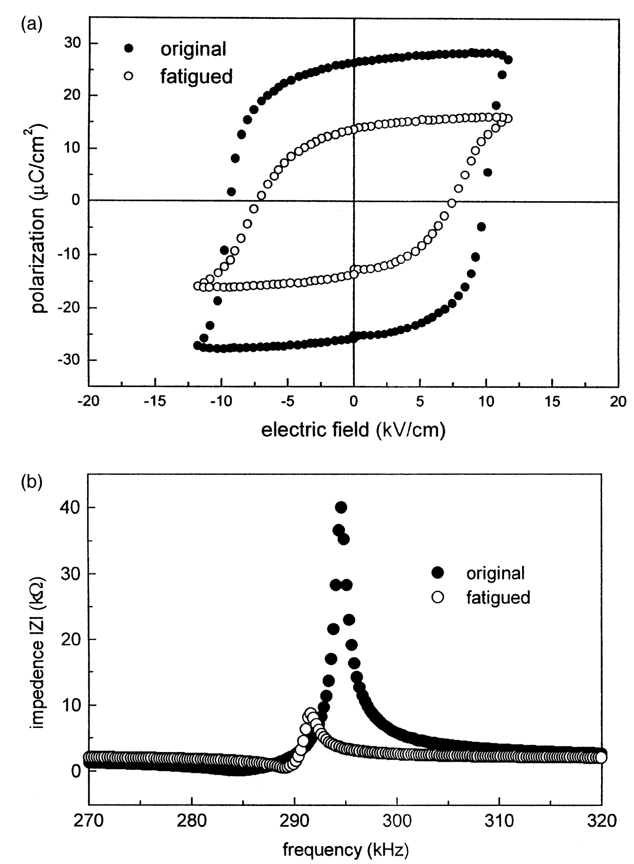

Fig. 4. (a) Hysteresis loop variation and (b) resonant peak variation after fatigue test of ferroelectric PLZT ceramics.

Table 1
Degradation of dielectric and piezoelectric properties due to electric fatigue in PLZT ceramics

	ε	tanδ	k_p	Q_m
Original	552	0.04	0.30	197
Fatigued	417	0.02	0.15	119

P_r both decreased after fatigue process from 28 and 27 $\mu C/cm^2$ to 16 and 14 $\mu C/cm^2$, respectively, implying the degradation of ferroelectric properties. On the contrary, the coercive field E_c decreased from 9.5 to 7.5 kV/cm after fatigue process. The relationship between impedance and measuring frequency at the first resonant state was measured in Fig. 4(b). The magnitude and width of basic resonant peak both decreased heavily, implied the weakening of piezoelectric resonance. Table 1 compared the dielectric and piezoelectric property deterioration after electric fatigue. The planar electromechanical coupling factor k_p and electromechanical quality factor Q_m were calculated according to Fig. 4(b) using resonant and anti-resonant method. In Table 1, the dielectric constant, k_p and Q_m decreased after electric fatigue, while dielectric loss showed a slight increase. Since piezoelectricity phenomenon resulted from the coupling of mechanical effect and electrical effect, the results in Table 1 indicated that electric fatigue might induce some damage to ferroelectric materials.

3.3. Frequency dependence of ferroelectric fatigue

The different behaviors were observed for ferroelectric fatigue when carried out at different frequencies of applied electric field as shown in Fig. 5(a)–(d). In Fig. 5(a) and (b), low frequency of applied electric field were 10 and 50 Hz, respectively. The switchable polarization strength decreased greatly at certain accumulative cycles, however, an interesting phenomenon was observed in Fig. 5(c) and (d): the switchable polarization showed little decrease even after about 10^{10} cycles corresponding to 100 and 500 kHz, respectively.

This result reflected that some mechanism influenced the dynamic responding behavior of ferroelectric domains under the electric field. When an electric or mechanical field was applied to ferroelectric materials, the ferroelectric domains would shift their polarization directions to the most favorable direction of applied field to alleviate the induced the strain or stress, which led to the reorientation of ferroelectric domains or ferroelectric polarization. This process would cause the redistribution of crystalline lattice stress, which was named as the ferroelastic switching. Ferroelectric domain's reorientation consisted of three steps:[10] inhomogeneous nucleation of anti-phase ferroelectric domains at the electrode surfaces; needle-like growth of domains parallel or antiparallel to the applied field and the sideways spreading out of the new domains within the bulk ceramics. Typically, the last step is the rate-limiting step.

Eng[11] had researched the in-situ switching properties of nano-scale ferroelectric domain evolution in barium titanate ceramic via atomic force microscopy (AFM). He found that the ferroelectric domain only switched under certain electric field, the relationship between switching time and applied electric field was:

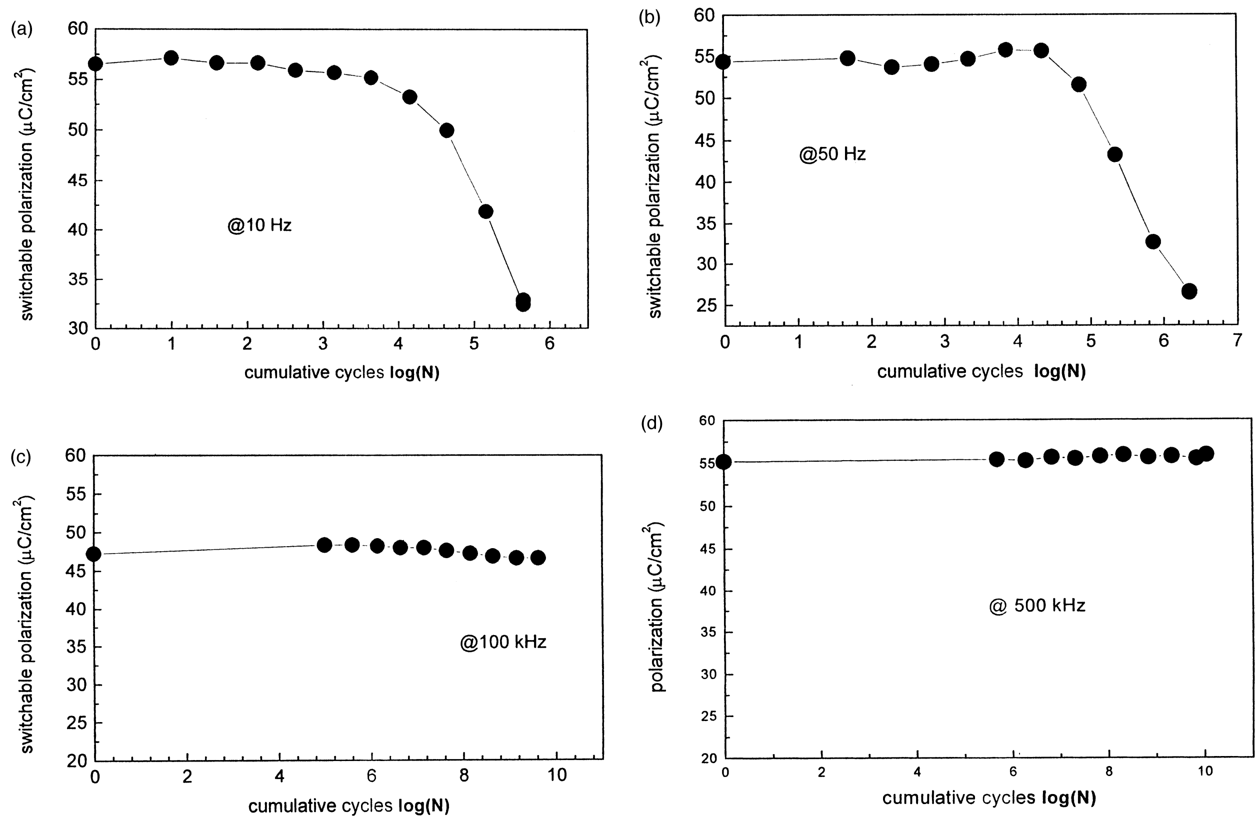

Fig. 5. Frequency dependence of feroelectric fatigue: (a) 10 Hz; (b) 50 Hz; (c) 100 kHz; (d) 500 kHz.

$$E_c \geqslant m^*(\tau_s)^n$$

where, τ_s was the switching time of ferroelectric sample, m and n were both empirical constant derived in experiment; m is positive and n is negative.

The equation above implied that when we fixed the applied electric field, then a critical switching time τ_c should be satisfied to induce the reorientation of ferroelectric domains. Any applied electric field with the frequency higher than $1/\tau_c$ would cause no or little reorientation of ferroelectric domains. The further application of such electric field would cause no or little degradation of materials as we could observe in Fig. 5(c) and (d). Just at this meaning, the importance of frequency of applied electric field should not be avoided or looked down. Therefore, we believe that the fatigue properties of ferroelectric materials mainly originate from the full reorientation of ferroelectric domains other than other factors, such as the immigration of electrode element into the bulk materials. The immigration of electrode element, for example silver ion into ceramics was initiated and accelerated by the enough switching of ferroelectric domains during fatigue process. Defect pinned ferroelectric domain walls during the ferroelectric fatigue process which was commonly accepted ideal is the accumulative result of the enough reorientation of ferroelectric domains resulted from the low frequency of applied electric field.

4. Conclusion

PLZT ferroelectric ceramics were fatigued with different applying frequencies. During common fatigue process, the switchable polarization decreased with the increase of accumulative cycles, accompanied by the degradation of dielectric and piezoelectric properties. Despite the same magnitude of applying the electric field, different fatigue behaviors were observed: the samples only showed fatigue phenomenon at low frequencies of applying the electric field and showed little variation at high frequencies. This phenomenon was explained according to the switching dynamics of ferroelectric domains.

Acknowledgements

This work was supported by the National Foundation of Nature and Science of China, Grant No. 59995523.

References

1. Weitzing, H., Schneider, G. A., Steffens, J., Hammer, M. and Hoffmann, M. J., Cyclic fatigue due to electric loading in ferroelectric ceramics. *Journal of the European Ceramic Society*, 1999, **19**, 1333–1337.
2. de Araujo, C.A-Paz, Cuchiaro, J.D., Mcmillan, L.D., Scott, M.C. and Scott, J.F., Fatigue-free ferroelectric capacitors with platium electrodes. *Nature*, 1995, **374**, 627–629.
3. Stolichnov, I., Tagantsev, A., Setter, N., Cross, J. S. and Tsukada, M., Top-interface-controlled switching and fatigue endurance of $(Pb,La)(Zr,Ti)O_3$ ferroelectric capacitors. *Applied Physics Letters*, 1999, **74**, 3552–3554.
4. Yin, J., Zhu, T., Liu, Z. G. and Yu, T., Enhanced fatigue and retention properties of $Pb(Ta_{0.05}Zr_{0.48}Ti_{0.47})O_3$ films using $La_{0.25}Sr_{0.75}CoO_3$ top and bottom electrodes. *Applied Physics Letters*, 1999, **75**, 3670–3698.
5. Chae, B. G., Park, C. H., Yang, Y. S. and Jang, M. S., asymmetry in fatigue and recovery in ferroelectric $Pb(Zr,Ti)O_3$ thin-films capacitors. *Applied Physics Letters*, 1999, **75**, 2135–2137.
6. Brazier, M., Mansour, S. and Mcelfresh, M., Ferroelectric fatigue of $Pb(Zr,Ti)O_3$ thin films measured in atmosphere of varing oxygen concertration. *Applied Physics Letters*, 1999, **74**, 4032–4034.
7. Bobnar, Vid, Kutnjak, Zdravko, Levstik, Adrijan, Holc, Janez and Kosec, Marija, Correlation between fatigue and piezoelectric properties in $(Pb,La)(Zr,Ti)O_3$ thick films. *Journal of Applied Physics*, 1999, **85**, 622–624.
8. Colla, E. L., Taylor, D. V., Tagantsev, A. K. and Setter, N., Discrimination between bulk and interface scenarios for the suppression of the switchable polarization (fatigue) in $Pb(Zr,Ti)O_3$ thin films capacitors with Pt electrodes. *Applied Physics Letters*, 1998, **72**, 2478–2480.
9. Dawber, Matthew and Scott, J. F., A model for fatigue in ferroelectric perovskite thin films. *Applied Physics Letters*, 2000, **76**, 1060–1062.
10. Scott, J. F. and De Araujo, C. A., Paz, Ferroelectric Memories. *Science*, 1989, **246**, 1400–1405.
11. Lukas, M., Eng, Nanoscale domain engineering and characterization of ferroelectric domains. *Nanotechnology*, 1999, **10**, 405–411.