J Electroceram (2010) 25:135–139
DOI 10.1007/s10832-010-9602-y

Switching retardation and heterogeneity behavior in fatigued lead zirconate titanate ceramics

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Received: 1 August 2009 / Accepted: 29 March 2010 / Published online: 17 April 2010

Abstract The spatial switching retardation and heterogeneity of fatigue in lead zirconate titanate ceramics were investigated using quasi-static d_{33} measurements. The variation of d_{33} values was measured on the samples with different fatigue states and different reverse switching pulses. Experimental results indicated that the switching retardation exists in the different fatigue stages and increases with increasing cycle number. The d_{33} measurements exhibit a strongly heterogeneous behavior of fatigue. This fatigue heterogeneity weakened in the seriously fatigued samples.

Keywords Fatigue · Switching retardation · Heterogeneity

1 Introduction

As well-known and well-used ferro- and piezoelectric materials, lead zirconate titanate ($Pb(Zr,Ti)O_3$, PZT) ceramics have been of high interest for over 50 years. Researches on PZT have made great progress, whereas many basic issues remain insufficiently understood. For example, the progressive loss of switchable polarization due to electrical and mechanical cycling, i.e., polarization fatigue [1–4], is a serious problem in device application of PZT. In addition, despite the fact that the switching of polarization domains in ferroelectric materials has been intensively studied both theoretically and experimentally [5–8], thorough research of switching mechanism is still needed.

Early investigations attributed ferroelectric fatigue to domain wall pinning, which results from the agglomeration of point defects or isolated charged defects [9]. On the other hand, the domain nucleation suppression at the electrode-ferroelectric interface is also considered as the major cause of fatigue [10, 11]. Recently, in ferroelectric thin films the evolution of the frozen polarization regions during fatigue was studied by means of atomic force microscopy [12]. The experimental results revealed that the polarization loss is due to "region by region" or "grain by grain" freezing of switchable polarization, which considered as heterogeneity in ferroelectric materials. Meanwhile, in ferroelectric ceramics the spatial heterogeneity of fatigue was also found [13]. All parameters measured on fatigued samples are spatially highly heterogeneous including large signal parameters measured from the polarization and strain hysteresis loops, as well as the small signal parameters determined from field dependent converse piezoelectric measurements. Therefore, understanding the underlying heterogeneity may be helpful for establishing the fatigue models for ferroelectric materials.

Since both ferroelectric memory and actuator applications are operated via domain switching and reorientation, studies on switching mechanism are of practical and fundamental importance. PZT experiences a polarization switch at the unit cell level when a sufficiently large electric field is applied. It is generally accepted that the switching mechanism involves two steps: the nucleation of incipient domains, and the growth of these new domains. The polarization switching has been greatly altered due to

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cyclic electrical loading. It is of interest to model the dynamics of domain switching in the context of fatigue.

The switching process is not homogeneous even in single crystals [14]. Studies on the heterogeneity during the fatigue process are truly important to explore the origin of fatigue. However, combination investigations on the details of heterogeneity and the switching mechanism in ferroelectric ceramics are scarce.

In the present work we use a quasi-static method to measure d_{33} values point by point in order to thereby obtain information about the switching retardation and heterogeneity behavior due to fatigue in PZT ceramic samples.

2 Experimental procedure

The $Pb(Zr_{0.525}Ti_{0.475})O_3$ ceramic samples were prepared by the conventional oxide mixing process and donor doped with 1 wt% Nb_2O_5. The raw materials used were reagent grade PbO(Wenzhou Chemical Reagent Factory, Wenzhou, China), ZrO_2(Fuchen Chemical Reagent Co. Ltd, Tianjin, China), TiO_2(Sinopharm Chemical Reagent Co. Ltd, Beijing, China), and Nb_2O_5(Sinopharm Chemical Reagent Co. Ltd, Beijing, China). The purity of the starting raw materials was 99.0%. In addition, 1.5% extra PbO was added to compensate for PbO volatility. The powders were ball milled in ethanol using yttria-stabilized zirconia balls as the milling media. After drying, the mixed powders were sieved and then calcined for 4 h. A calcination temperature of 900°C was required to complete the reaction. The calcined powders were subsequently ball-milled in the same media for 4–6 h, dried and sieved once more. After that, the obtained powders were mixed with a 3 wt% polyvinyl butyral binder and then uniaxially cold pressed at 15 MPa into 22 mm diameter pellets. Following binder burnout at 400°C, the resulting discs were then sintered in closed crucibles at 1200°C for 2 h. Prior to fatigue experiment, the samples were polished to a thickness of 1 mm. After polishing, a silver electrode paste was applied and then fired at 550°C for 30 min.

Fatigue was induced by subjecting the samples to bipolar voltage cycling with amplitude of 1.4 kV/mm and a frequency of 50 Hz. The samples were mounted in between two spherical metal clamps and immersed in silicone oil to avoid arcing. During fatigue experiment the samples can oscillate freely.

The samples were fully poled initially before the switching experiments. Then nearly square pulses of 1, 2, 5, and 10 s duration and 1.4 kV in amplitude with a rise time of about 1 μs in reverse polarity were applied to the samples. All square pulses were supplied by a high voltage power supply (Trek 609-B, NY, USA) driven by a frequency generator (HP33220A, CA, USA). After every measurement across the whole electrode area another reverse square pulse with longer duration was applied to revert the sample to initial status.

The d_{33} values after switching as a function of position were measured using a quasi-static d_{33} Berlincourt-meter (Institute of acoustic science, Chinese Academy of Science, Beijing, China) with a top spherical probe of 1 mm radius. The applied force is kept at 0.23 N (frequency: 110 Hz). Values were measured on an 11×11 point grid. The Berlincourt-meter displays the measured data of d_{33} as a positive value or a negative one, which depends on the direction of polarization.

3 Results and discussions

The switching process in non-fatigued and fatigued PZT ceramics has already been investigated by direct measurement of time dependence of polarization [15]. The switching time of the reversal in non-fatigued PZT ceramics is assumed to be below microseconds when an electric field of sufficient strength (higher than the coercive field) is applied. In the following we will demonstrate that the switching retardation and heterogeneity caused by fatigue in ferroelectric ceramics could be evaluated by a simple d_{33} measurement. Firstly, the switching retardation in PZT ceramic samples at different fatigue stages is reported and discussed, then a similar approach to describe the heterogeneity behavior is adopted.

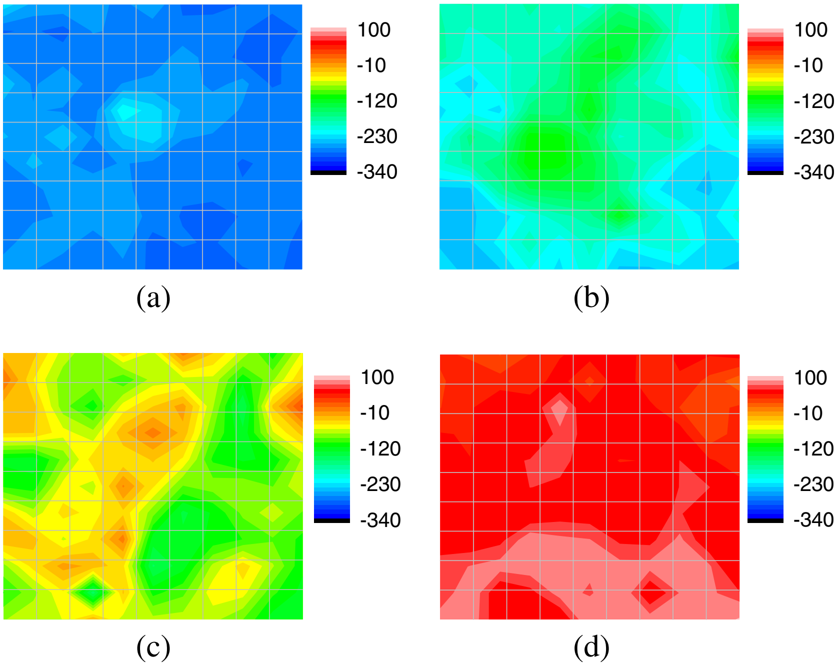
3.1 Switching retardation

The piezoelectric d_{33} coefficient has been measured from the direct piezoelectric effect as a function of position across disc shaped samples 20 mm in diameter. The current sample shape is a good approximation to measure the d_{33} distribution. The same parameter was measured on the samples with different fatigue states and different reverse switching pulses. With such measurements both the switching retardation and the heterogeneity behavior can be detected, because a nonzero d_{33} corresponds to a nonzero polarization. The relationship between the piezoelectric d_{33} coefficient and polarization P can be expressed as

$$d_{33} = 2Q_{eff}P\varepsilon_{33} \qquad (1)$$

Where Q_{eff} is the electrostriction coefficient and ε_{33} is the dielectric constant.

Figure 1 displays contour plots of the d_{33} values on the sample surface after different fatigue cycles with a switching pulse width of 2 s. Four cycling steps (4.5×10^4, 1.8×10^5, 9×10^5, 3.8×10^6) were chosen. After poling (5 h at 1.4 kV/mm) the measured d_{33} values across the disc sample



(a) (b)

(c) (d)

Fig. 1 Contour plots of the d_{33} [pC/N] values from the direct piezoelectric effect determined for a sample after **(a)** 4.5×10^4, **(b)** $1.8\times10_{,}^{5}$ **(c)** 9×10^5, **(d)** 3.8×10^6 cycles. After poling (5 h at 1.4 kV/mm) reverse switching pulses were applied with the duration of 2 s

are almost same. Then the reversal pulse with width of 2 s was applied. The d_{33} values across the disc sample change from positive to negative after this pulse reversal.

As shown in Fig. 1, the cycle number dependence of the d_{33} value reflects the switching retardation. For 4.5×10^4 fatigue cycles the switching process is almost finished within the 2 s pulse. The d_{33} values across the sample clearly exhibit this tendency. In case of sample after 9×10^5 cycles, the negative d_{33} values increase, showing a relatively small retardation. With the cycle number increasing, only partial switching occurs and serious retardation appears. For the sample after 3.8×10^6 cycles the d_{33} values still keep positive and there is even no switching.

The switching time dependence of d_{33} values are determined on an identical position. Figure 2 shows the measured d_{33} values for the samples of different fatigue states as a function of the reversal time. Upon application of longer reversal time, the negative d_{33} value decreases, showing that more switching occurs and that the retardation improves. The same tendency is obtained for the four samples of different fatigue states.

The d_{33} value changed rapidly from the positive to the negative direction during the 1 s reversal for the samples after 4.5×10^4 and 1.8×10^5 cycles. However, for the samples after 9×10^5 and 3.8×10^6 cycles the big change of d_{33} values did not happen. This switching behavior as a function of fatigue cycles shows that the switching retardation exists in the different fatigue stages and increases with increasing cycle number. As for the slopes of the four curves between 0 and 1 s reversal time, it can be clearly seen that the slope of the sample of 4.5×10^4 cycles is larger than the one of 3.8×10^6 cycles. Lower slope values were achieved with cycle number increasing, confirming again switching retardation is caused by fatigue.

The ferroelectric domain switching process needs waiting time to finish switching. The expression for switching identical to the prediction of KAI (Kolmogorov-Avrami-Ishibashi) model for the case of one-dimensional domain growth is below, where p(t) is the volume fraction of the domains switched by time t [5]:

$$p(t) = 1 - e^{-(t/\tau)^{\beta}} \qquad (2)$$

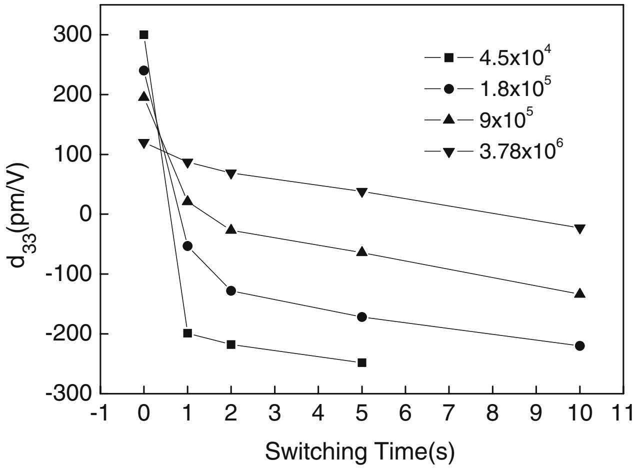
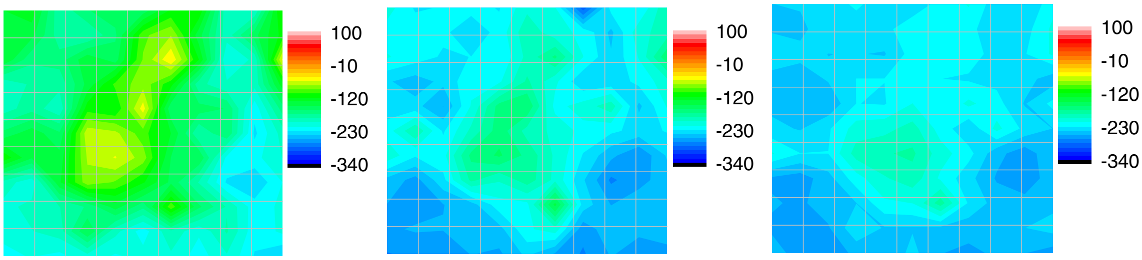


Fig. 2 d_{33} values as a function of reversal time for different fatigue states in PZT ceramic samples



(a) (b) (c)

Fig. 3 Contour plots of the d_{33} [pC/N] values from the direct piezoelectric effect determined for a sample after 1.8×10^5 cycles. After poling (5 h at 1.4 kV/mm) reverse switching pulses were applied with different durations: (**a**) 1 s; (**b**) 5 s; (**c**) 10 s

Where τ and β are the typical waiting time of the certain local elementary region and the so-called stretching exponent [15] respectively. The parameter τ depends on the density of nuclei of reverse domains, mobility of the domain walls, and the electric field acting on the moving domain walls. When the sample is fatigued, the typical waiting time (τ) increases. The switching needs more waiting time and thus is retarded seriously. Given long enough time, the switching will be nearly complete. Consequently, the d_{33} value can be reversed to negative direction as the same absolute value as initially. However, the switching occurs region by region. Fatigue yields switching inhomogeneity, that is, some parts of domain switched and others did not. And the switching in one region does not necessarily lead to the subsequent switching of the neighboring ones as is expected. The resulting d_{33} values thus yield retarding behavior during the switching process. Switching as determined from d_{33} measurements becomes highly retarded by fatigue.

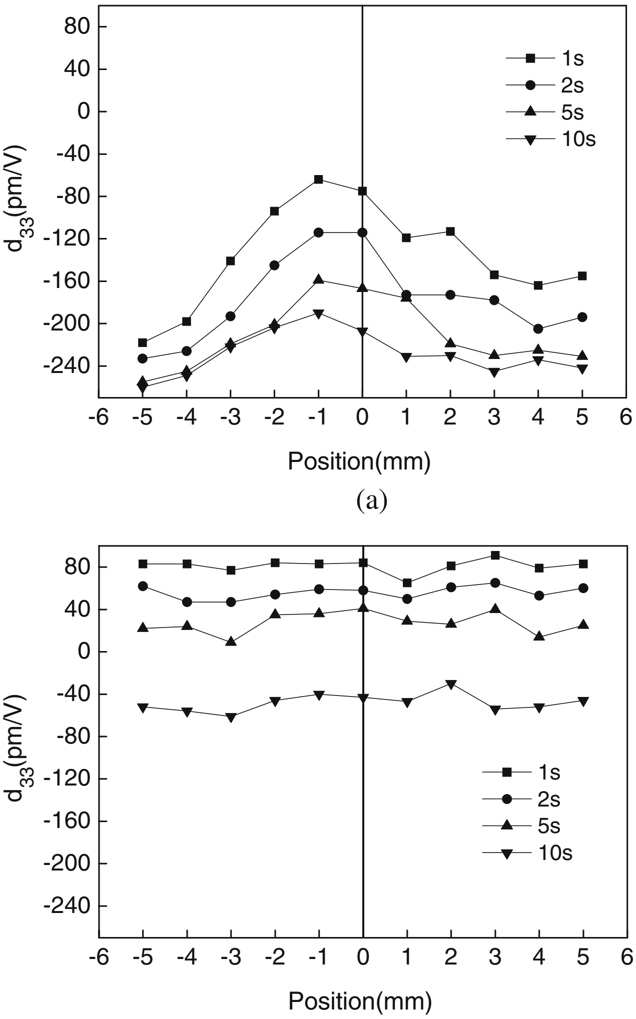
3.2 Heterogeneity behavior

Figure 3 displays the heterogeneous distribution of d_{33} across the sample surface for switching experiments of different durations. Like the other parameters of the sample, the d_{33} values are highly heterogeneous. The d_{33} switched from positive value to negative one after pulse reversal. The longer time the sample was loaded, the larger the d_{33} values reduced, that is, the absolute values increased in the negative direction.

For the duration of 1 s, it was shown from the d_{33} values that some part of the sample has switched quickly and some part just starts to switch. With the duration time increasing, the d_{33} value decreases and the heterogeneity is maintained. In case of the duration of 10 s, a large part of the sample has finished switching and only a small part has not finished, showing the fatigue states inside the sample differ significantly.

The variation of d_{33} values along one diameter direction have been extracted from the distribution contour plots of d_{33} across the samples. The d_{33} values along one diameter direction are shown in Fig. 4 as a function of position at different reversal time for two fatigue states.

In the case of the sample after 1.8×10^5 cycles, there is a maximum d_{33} value at the sample center for all reversal times while the d_{33} values drop down sharply from the



(b)

Fig. 4 d_{33} values as a function of position, at different reversal times for two fatigue states (**a**) 1.8×10^5 cycles, (**b**) 3.8×10^6 cycles sample center to sample edge. To the contrary, in the case of the sample after 3.8×10^6 cycles, the d_{33} value along one diameter direction remains virtually unchanged. The results of similar experiments carried out at other diameter directions show the same tendency for the two fatigue states. The variation of d_{33} values for the sample of 1.8×10^5 cycles shows that fatigue occurred earlier at the sample center than at the sample edge. The center of the sample is moderately fatigued but the edge is nearly non-fatigued. Moreover, it has also been shown that the d_{33} values from center to edge changed almost linearly so that the fatigue rate decreases linearly from center to edge. For the sample of 3.8×10^6 cycles, the d_{33} values along one diameter direction from the edge to center are nearly equal, showing that the switching is highly retarded and so all of the sample is seriously fatigued.

A pronounced feature of our d_{33} measurements is the occurrence of obvious heterogeneity behavior, which is particularly obvious for different fatigue states. This behavior has been observed by several groups in case of ferroelectric thin films [12, 16], and in the case of different measuring para meters [13, 17]. This effect can be explained by the cascading of the switching process across the sample thickness.

Since the switching retardation of highly fatigued samples is in the range of hours, our d_{33} measurements for switching are compatible with the polarization switching experiments. Certain local regions at the sample edge reproducibly switch faster than others, which were shown in Fig. 4. Thus, the retardation variation occurs in each column of the sample. The laterally distributed regions have different switching speeds and were retarded in their own switching process. Alternatively, the switching speed is associated with the fatigue states of the corresponding regions. When the sample was moderately fatigued, the fatigue states vary greatly from the sample center to the sample edge (Fig. 4(a)). This variation may be related with the boundry effect in PZT sample and the mechanical constraint at the contact point during fatigue. The nature of this difference between the center and the edge is not presently clear and is under ongoing research.

Another particular behavior we have observed in our d_{33} measurements is the decrease of fatigue heterogeneity with increasing cycle number. Compared to the moderately fatigued samples, nonuniformly distributed fatigue regions disappear in seriously fatigued samples after 3.8×10^6 cycles. There is thus a large reduction of switching capability in the fatigued regions.

4 Conclusions

Experimental studies of the fatigue behavior of piezoelectric PZT ceramics were tested using a quasi-static d_{33} measurement based on switching experiments. The results demonstrate that apparent fatigue heterogeneity exists down to the millimeter scale across disc shaped samples 20 mm in diameter. The d_{33} contour plots on sample surface point to a strongly heterogeneous behavior. The switching behavior as a function of fatigue cycles indicates that the switching retardation exists in the different fatigue stages and increases with increasing cycle number. The observed fatigue heterogeneity is alleviated after serious fatigue.

Acknowledgements This work was supported by National Natural Science Foundation of China (Grant No. 50672042) and the Ministry of Sciences and Technology of China through 973-Project under Grant No. 2009CB623306.

References

1. A.K. Tagantsev, I. Stolichnov, E.L. Colla, N. Setter, J. Appl. Phys. **90**, 1387–1402 (2001)
2. J. Nuffer, D.C. Lupascu, J. Roedel, Acta Mater. **48**, 3783–3794 (2000)
3. D.C. Lupascu, J. Roedel, Adv. Eng. Mater. **7**, 882–898 (2005)
4. P.M. Chaplya, G.P. Carman, J. Appl. Phys. **90**, 5278–5286 (2001)
5. A.K. Tagantsev, I. Stolichnov, N. Setter, J.S. Cross, M. Tsukada, Phys. Rev. B **66**, 214109 (2002)
6. O. Lohse, M. Grossmann, U. Boettger, D. Bolten, R. Waser, J. Appl. Phys. **89**, 2332–2336 (2001)
7. A. Jiang, M. Dawber, J.F. Scott, C. Wang, P. Migliorato, M. Gregg, Jpn. J. Appl. Phys. **42**, 6973–6982 (2003)
8. S.C. Hwang, G. Arlt, J. Appl. Phys. **87**, 869–875 (2000)
9. D.C. Lupascu, U. Rabe, Phys. Rev. Lett. **89**, 187601 (2002)
10. J.J. Lee, C.L. Thio, S.B. Desu, J. Appl. Phys. **78**, 5073–5078 (1995)
11. E.L. Colla, I. Stolichnov, P.E. Bradely, N. Setter, Appl. Phys. Lett. **82**, 1604–1606 (2003)
12. E.L. Colla, S.B. Hong, D.V. Taylor, A.K. Tagantsev, N. Setter, K. No, Appl. Phys. Lett. **72**, 2763–2765 (1998)
13. Y. Zhang, D.C. Lupascu, E. Aulbach, I. Baturin, A. Bell, R. Roedel, Acta Mater. **53**, 2203–2213 (2005)
14. H. Yu, V. Gopalan, J. Sindel, C.A. Randall, J. Appl. Phys. **89**, 561–567 (2001)
15. D.C. Lupascu, S. Fedosov, C. Verdier, J. Roedel, H. von Seggern, J. Appl. Phys. **95**, 1386–1390 (2004)
16. D. Ricinschi, M. Okuyama, Appl. Phys. Lett. **81**, 4040–4042 (2002)
17. M. Ozgul, S. Trolier-Mckinstry, C.A. Randall, J. Electroceram. **20**, 133–138 (2008)