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Fatigue induced effects on bipolar strain loops in PZN-PT piezoelectric single crystals

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Abstract Polarization and bipolar strain hysteresis (P-E and S-E) measurements were performed simultaneously during fatigue tests performed under ac fields with a triangular wave form. Rhombohedral (1-x)Pb($Zn_{1/3}Nb_{2/3}$)O_3−x$PbTiO_3$ (PZN-PT) piezo/ferroelectric single crystals demonstrate a wide variety of anisotropic behavior under bipolar electrical switching. Specifically, PZN-4.5 PT crystals demonstrate exceptional polarization switching fatigue resistance along $[001]_C$ (-c; pseudocubic), as opposed to normal fatigue in $[111]_C$ directions. This system provides an excellent opportunity to study fatigue induced effects in $[111]_C$ orientation in comparison with $[001]_C$. Studies in bulk ferroelectric ceramics have reported fatigue-associated strain hysteresis asymmetry. In this study, the evolution of bipolar strain loops was studied in both "fatiguing" $[111]_C$ and "fatigue-free" $[001]_C$ orientations. It was found that $[111]_C$ oriented PZN-4.5 PT crystals show the onset of a strain-field asymmetry displayed by shortage of one wing of the butterfly, which becomes more evident as cycling continues. In contrast, $[001]_C$ crystals show symmetrical strain-field curves throughout cycling. S-E hysteresis data obtained from different points in a fatigued crystal by gently moving it between the consecutive measurements show that the shorter wing switches side indicating the local character of fatigue. In comparison to the findings in polycrystalline ceramics this observation in a single crystal ferroelectric will be helpful for a better understanding of fatigue and related effects. Rejuvenation studies in fatigued crystals are also reported in this paper.

Keywords Piezo/ferroelectric single crystals · Polarization fatigue anisotropy · Switching asymmetry · Bipolar strain

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1 Introduction

Ferroelectrics, especially lead zirconate titanate (Pb(Zr,Ti)O_3) or its modifications, have been among the most popular materials of research for several decades due to their excellent piezoelectric and ferroelectric properties which offer potential for the development of many modern technological devices, such as microactuators, sensors, transducers, and memories [1–7]. A reliability problem limiting the extensive use of ferroelectrics is the suppression of switchable polarization, which is the defining characteristic of a ferroelectric material, after certain number of ac drive cycles [5, 6, 8, 9]. This is called polarization fatigue and popularly observed by polarization vs. electric field (P-E) hysteresis loop measurements. Electric field cycling, continuously reversing the polarity of the dipoles, induces certain changes in a ferroelectric and alters both P-E and bipolar strain vs. electric field (S-E) hysteresis loops. The S-E hysteresis loop, which resembles the shape of a butterfly, is due to three types of effects in ferroelectrics. One is the normal converse piezoelectric effect of the lattice, and the other two are due to switching and domain wall movement. There have been a large number of reports on the degradation of switchable polarization displayed by a decrease in P, and increase in E axis [5–9]. Recently studies focus on the changes in S-E loops or butterfly [10–12].

In bulk ferroelectric ceramics, fatigue-associated strain hysteresis asymmetry has been reported, and it was related to a preferred orientation set by the first poling state [13,14]. Nuffer et al. reported that by thermally annealing the samples before and after each cycling step, this preferred orientation due to first poling can be removed. Despite thermal treatments, one of the branches of the bipolar strain hysteresis degraded more strongly. An alternative explanation of the asymmetry in strain loops is the existence of a unidirectional frozen-in polarization [10]. In bulk lead zirconate titanate ceramics, bipolar strain asymmetry can be induced by either bipolar or unipolar cycling [11,15] Acoustic emission test results were thought as implying the fact that defect agglomerates hinder the domain wall mobility [11]. Polarization fatigue studies generally use bipolar cycling that results in loss of switchable polarization coupled with a reduced strain. It was reported that ceramics which are exposed to unipolar drive (3×10^8 cycles) also exhibit an asymmetric bipolar strain, but no loss of switchable polarization [15]. Verdier et al. reported that bipolar drive induced offsets are easily recovered by cycling at elevated electric fields but are fairly stable under thermal treatments up to 400°C. On the other hand, unipolar cycling induced bipolar strain asymmetry can be completely recovered at much lower temperatures, i.e., 250°C. High electric fields, though, are not very effective for regaining the symmetry. A large number of bipolar cycles at high field are needed to improve the unipolar cycling induced symmetry degradation. Similar to our earlier reported results in single crystal ferroelectrics [16], heterogeneous strain behavior is observed by Zhang et al. in polycrystalline lead zirconate titanate ceramics [12].

In this paper, the evolution of bipolar strain loops was studied in both “fatiguing” $[111]_C$ and “fatigue-free” $[001]_C$ orientations [17]. Use of single crystals provides the opportunity to study electrical switching within “a single grain” (in contrast to work on polycrystalline ceramics) and allows the crystallographic orientation dependence to be investigated. Furthermore, unlike thin films deposited by vapor deposition methods or sol-gel, the symmetry is not influenced by the substrate or the thermal processes used in growth, crystallization, and electroding of the films [18–22].

2 Experimental procedure

Single crystals of 0.955 $Pb(Zn_{1/3}Nb_{2/3})O_3$–$0.045PbTiO_3$ (PZN-4.5PT) solid solutions grown by a high temperature flux technique [23] were used in this study. The crystals of this composition have a perovskite structure and are rhombohedral (pseudocubic) at room temperature. The crystals were oriented either along the $[111]_C$ or along the $[001]_C$ axes to within ±2° by using a Laue Camera (Multiwire Laboratories Ltd., real-time Laue machine). For electrical characterization, plate-shaped samples were cut from the oriented crystals and prepared by polishing with silicon carbide and alumina polishing powders (down to ~1 μm) to achieve flat and parallel surfaces onto which silver paste electrodes were applied. Silver paste electrodes were preferred because they can be removed easily by washing with acetone without changing the nature of the crystal/electrode interface after the electrode removal. A set of samples were also electroded with sputtered Pt or Au to check if air dried silver electrode has any adverse effect on electrical tests. After a positive verification all the results reported in this paper are from air dried silver electroded samples. The thickness of samples used in this study ranged from 450 to 600 μm. Coercive fields (measured at 20 kV/cm and 0.1 Hz) for the crystals are about 3 and 5 kV/cm in <001> and <111> directions, respectively.

Polarization and bipolar strain hysteresis (P-E and S-E) measurements were performed simultaneously by using a modified Sawyer–Tower circuit and linear variable differential transducer (LVDT) driven by a lock-in amplifier (Stanford Research Systems, Model SR830). A high voltage amplifier (Trek Model 609C-6) was used in both poling and polarization fatigue measurements. Fatigue tests were performed under ac fields with a triangular wave

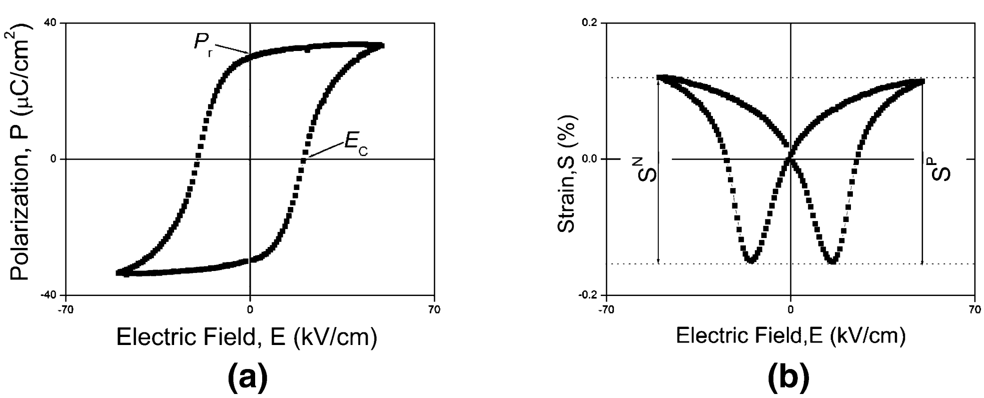


Fig. 1 Bipolar polarization (**a**), and strain (butterfly) loop (**b**). (S^P; positive strain, S^N; negative strain)

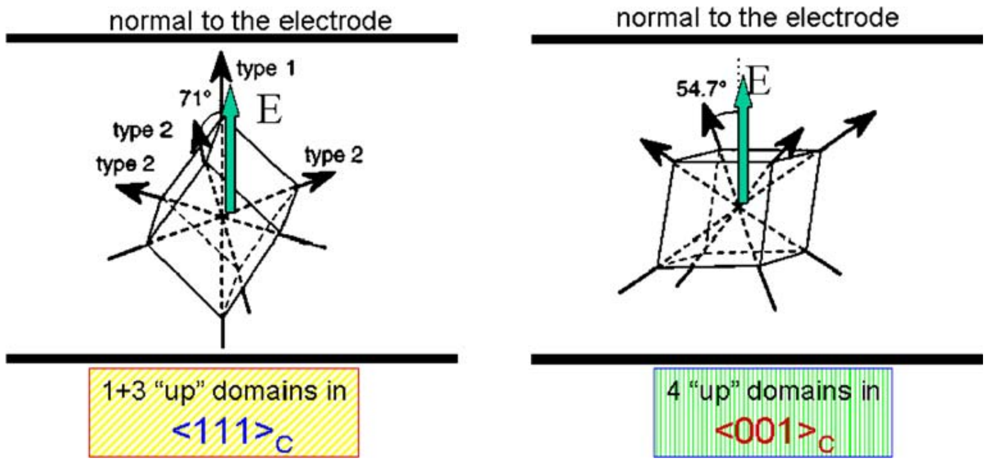


Fig. 2 Domain orientations in rhombohedral PZN_4.5 PT single crystals along the $[111]_C$ and $[001]_C$ orientations (after Damjanovic)

form. The applied field amplitudes for the fatigue tests were 15 or 20 kV/cm at 10 Hz for <001> and <111> crystals, respectively. The fatigue tests were interrupted for *P-E and S-E* measurements at varying electric field and frequencies after 10^1, 10^2,10^3, 10^4, and 10^5 switching cycles. Higher electric fields (40 kV/cm) were applied for $[111]_C$ samples after fatigue (10^5 cycles) to ensure full switching due to the increasing coercive field. During measurements, the samples were submerged in Fluorinert®, an insulating liquid, to prevent arcing.

3 Results and discussion

3.1 Effects of polarization switching fatigue on bipolar strain loops

Strain-field switching was successfully utilized by Kholkin et al.[24, 25] to study fatigue processes in ferroelectric thin films. This is a useful tool, since the presence of an internal electric field strongly perturbs the strain-field switching curves. In other words the local electric field in a ferroelectric is predominantly determined by the local polarization. Figure 1 shows spontaneously measured typical P-E and S-E hysteresis loops for the ferroelectric materials. Remanent polarization (P_r) which remains after a material has been fully polarized and then had the field removed and coercive field (E_C), a specific field which results in zero net polarization, are marked on P-E hysteresis loop. The right and the left wings of S-E (butterfly) loop is denoted as S^P and S^N respectively indicating strain values on the positive and negative sides of electric field axis. The Polarization switching fatigue is a common problem for all the ferroelectrics either in bulk or thin film form and it is observed by modifications of both P-E and S-E loops. Comparable measurements were made on PZN-PT crystals in this work for different crystallographic directions as a function of bipolar cycling. Figure 2 shows domain orientations in rhombohedral PZN-4.5PT single crystals along the $[111]_C$ and $[001]_C$ crystallographic directions, where electric field is applied parallel to the respective directions. Fatigue induced loss of remanent polarization and strain values (strain is

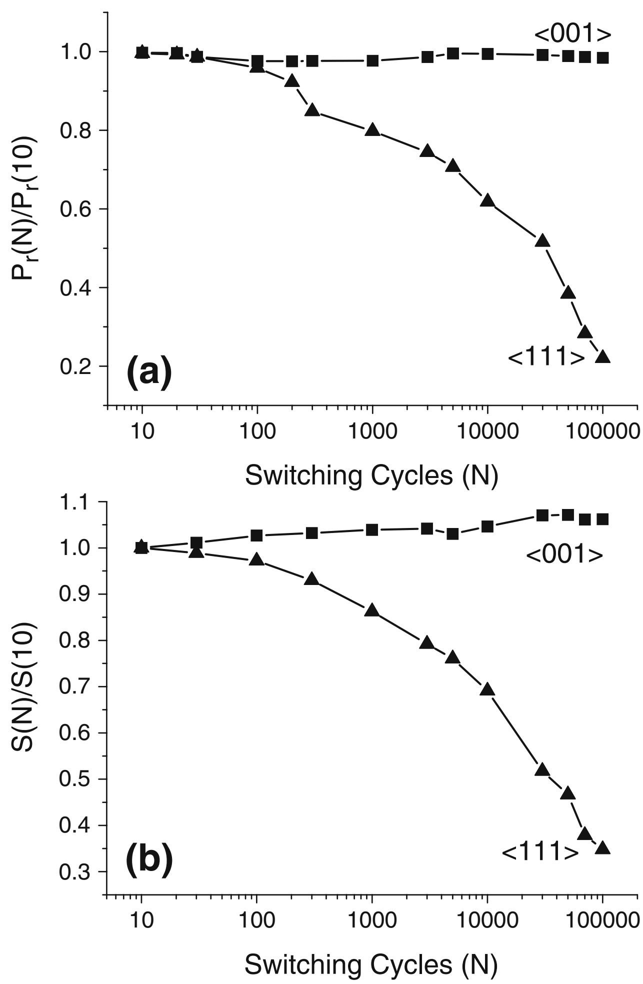
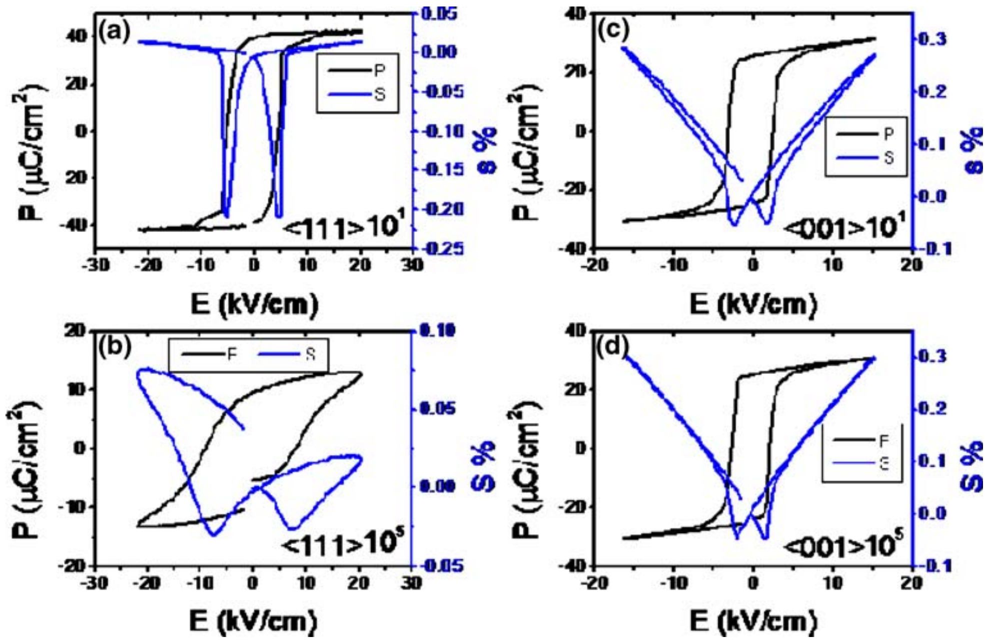


Fig. 3 Fatigue induced effects on polarization and strain behavior in PZN-4.5 PT single crystals for $[111]_C$, and $[001]_C$ directions, comparing remanent polarization (P_r) and Strain ($S=(S^P+S^N)/2$) values for *n*th cycle versus 10 switched case

Fig. 4 P-E and S-E loops of $[111]_C$, and $[001]_C$ oriented PZN-4.5 PT single crystals after 10^1 and 10^5 cycles



defined here as the average of S^P and S^N) as a function of switching cycles are shown in Fig. 3. Here it is clearly seen that loss of polarization and strain follows a similar trend. It was observed that $[111]_C$ oriented crystals show the onset of a strain field asymmetry, which grows as cycling continues in contrast to symmetrical strain-field curves throughout cycling in $[001]_C$ crystals. Both P-E and S-E hysteresis loops are shown in Fig. 4 for PZN-4.5PT single crystals in two different orientations after 10 and 10^5 cycles. One side of the S-E loops becomes shorter in fatiguing $[111]_C$ crystals as the number of the switching cycles increases while both P-E and S-E loops remains unaltered in $[001]_C$ crystals. After 10^5 cycles, in both of the $[111]_C$ and $[001]_C$ crystals strain data were taken at different points of the same surface and also after the sample is flipped over. Actual strain data is presented in Fig. 5 with a sketched sample. Resistance of "fatigue free" $[001]_C$ crystals to asymmetry evolution suggests that no net internal fields develop in the $[001]_C$ non-fatiguing directions. Small and homogeneously distributed internal fields may exist. These, though, if they do exist, do not effectively stabilize domains and give rise to fatigue. A rather interesting observation is the region to region difference in strain behavior of $[111]_C$ oriented crystals [see Fig. 5(a)] which demonstrate substantial fatigue. It is believed that internal fields that develop in $[111]_C$ crystals are locally inhomogeneous, as deduced by positional changes across the surface of the PZN-PT crystal. These differences are sufficiently large that the asymmetry in the strain field switching can develop with either positive or negative bias. In some regions quite symmetrical strain loops were observed. The difference from one region to another is not only in terms of the polarity of the bias but also the magnitude of the maximum strain measured. This implies that local internal fields vary across the $[111]_C$ crystals, producing islands of frozen domains. Unlike earlier studies in polycrystalline materials, PZT, the asymmetry is

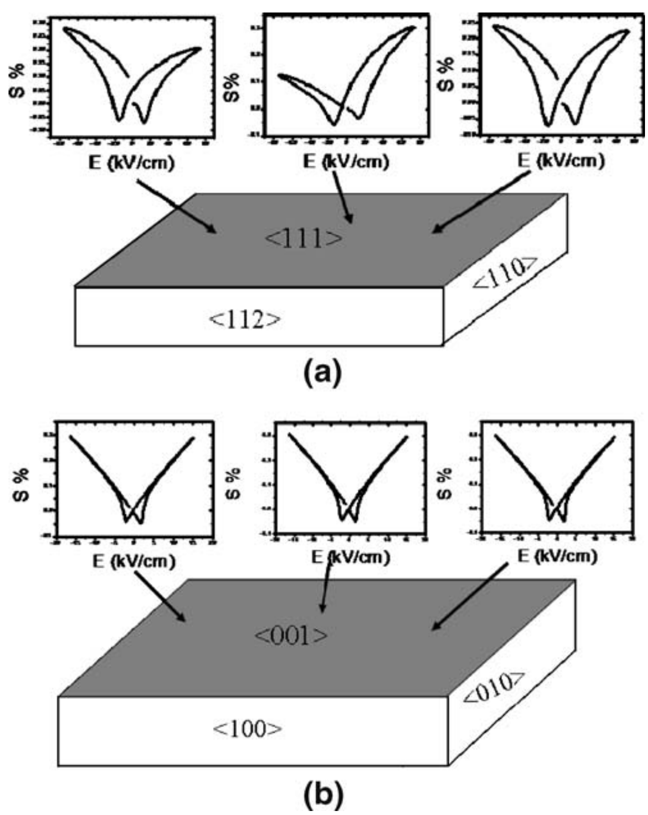


Fig. 5 Bipolar strain behavior of <111>- and <001>-oriented PZN-4.5 PT single crystals after 10^5 cycles on different spots of their respective surfaces

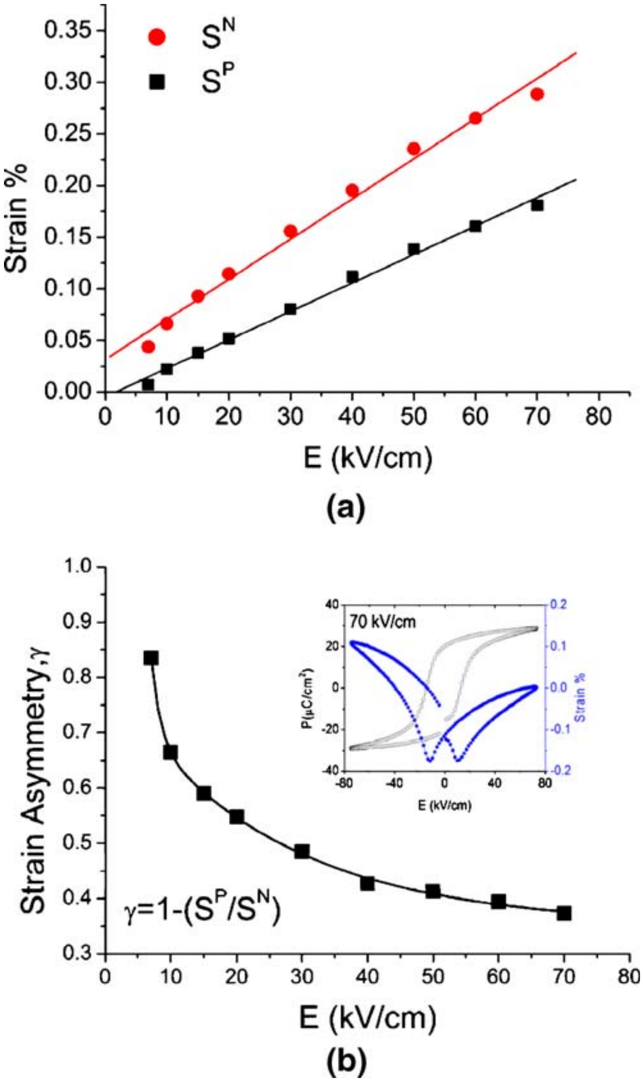


Fig. 6 Recovery of bipolar strain (**a**) S^P and S^N, and (**b**) asymmetry, γ. (insert in (**b**) shows asymmetric S-E)

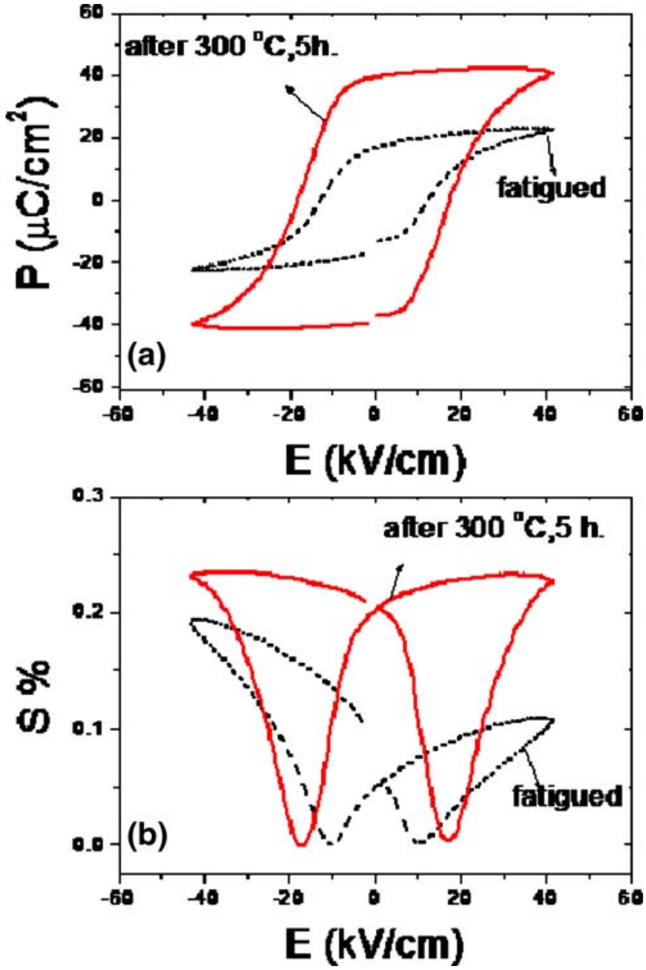


Fig. 7 Thermal rejuvenation of (**a**) polarization (P), and (**b**) strain (S) in fatigued crystals. (fatigued samples were held at 300°C, for 5 h)

not induced by the polarity of first switching. The lateral resolution of the LVDT used in this investigation was relatively coarse; given this, the scale of the islands is on a millimeter scale. The observation of island formation in PZT thin films undergoing fatigue was first reported by Colla et al. on a micron scale, as detected by atomic force microscopy [26]. The origin of the islands may be the same in both cases, but the difference in the size of the islands might be a result of the relative difference in thickness of the ferroelectrics or the spatial resolution of the probe utilized.

3.2 Recovery of fatigue induced effects

As reported by many earlier studies on fatigue in ferroelectric bulk and thin films, fatigue can often be rejuvenated either by annealing the material above the Curie temperature or applying larger electric fields to overcome internal fields [10]. Both of the two different strategies were applied to recover fatigue induced effects in <111> oriented PZN-4.5 PT single crystals in the present study. The magnitude of the applied field was increased from 20 kV/cm up to 70 kV/cm in

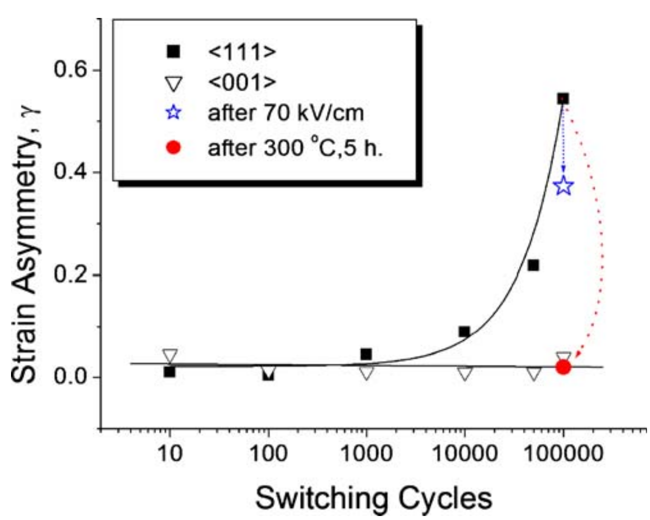


Fig. 8 Rejuvenation of fatigue induced asymmetry by higher electric field (up to 70 kV/cm), and thermal annealing at 300°C for 5 h

an attempt to recover the symmetry, but only partial success was obtained even at the highest electric fields applied here as shown in Fig. 6. Here asymmetry (γ is defined as the ratio between the shorter and larger wing of the butterfly loop subtracted from 1 (one). So it is concluded that in $[111]_C$ directions, fatigue cannot be recovered by simply applying higher field. This is consistent with local regions having frozen in domain structures clamped by an internal bias. However, thermal annealing at 300°C for 5 h in air completely recovers both the magnitude of the switchable polarization and symmetry in the bipolar strain hysteresis loops in fatigued crystals, as shown in Fig. 7. This can be attributed to re-distribution of the accumulated defects that can control freezing of domains. However, the coercive field remains large; the defects, although now randomized in space throughout the ferroelectric, limit domain motion and increase the coercive field. Even if their concentration is increased, homogeneous distribution may prevent effective pinning of the domain walls resulting in the suppression of polarization switching and fatigue effects, such as decreased polarization, strain, and asymmetry. As shown in Fig. 8, fatigue induced asymmetry in <111> oriented crystals can be completely recovered by heating the crystals above the Curie temperature.

4 Conclusions

Bipolar electrical field cycling induced effects, in PZN-PT crystals in $[111]_C$ and $[001]_C$ orientations has been studied. Single crystals of this composition demonstrate highly anisotropic switching behavior. Especially in contrast to <111> oriented crystals, <001> oriented crystals exhibit a very high resistance to ac cycling fatigue. Through measurement of strain electric field switching, an asymmetry in $[111]_C$ fatiguing crystals was observed. This is considered to be the result of an internal electric field. No net internal fields are found in $[001]_C$ oriented crystals, even after large numbers of cycles. Local changes in the amount of asymmetry and also reversal in the asymmetry across the same crystal indicates the internal field is the result of statistical events and not broken by symmetry from the first injection process. Once the asymmetry evolves, it can not be recovered by stronger electric fields up to 70 kV/cm. However, thermally annealed crystals regain symmetry in the strain-field curves if the driving electric field is high enough to give polarization saturation, $E \geq 2 \times E_c$. It is believed that the thermal annealing randomizes the defects. In $[111]_C$ orientation, rejuvenation anneals yield a symmetrical hysteresis, but with enhanced coercive fields.

In light of the observations in fatigued <111> crystals it can be inferred that polarization fatigue has local effect changing from region to region. That is fatigued crystals posses areas with different level of domain wall pinning producing regions biased in certain directions. When probed by strain measurements such local differences were revealed. The collapse of the bipolar strain loop which means the deterioration of piezoelectric properties was studied in single crystals eliminating the complication of grain boundaries and random orientation effects of polycrystalline ceramics and thin films. These results all together give insight into the understanding of polarization switching and fatigue induced effects in ferroelectrics and will contribute to the reliability of many microelectronic devices utilizing polarization reorientation.

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