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Fatigue anisotropy in lead-zirconate-titanate

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Abstract

Bipolar fatigue in bulk lead-zirconate-titanate ceramics is known to induce a severe loss of switchable polarization and strong asymmetries of strain hysteresis in cycling direction. An investigation into the transverse functional dependencies is conducted here. The polarization hysteresis perpendicular to the cycling direction only loses 35% amplitude after $2{\cdot}10^7$ cycles (compared to 80% in cycling direction). The strain in this field direction is symmetric and only reduced in amplitude (−8%). The transverse strain in the original cycling direction does exhibit pronounced asymmetries. Constant volume due to domain switching is no longer valid.

Keywords: Fatigue; Ferroelectric properties; Piezoelectric properties; PZT

1. Introduction

The ferroelectric polarization hysteresis is the macroscopic image of the reorientation of local polarization between a finite number of permitted orientations in the ferroelectric crystal as a function of the externally applied electric field.[1,2] So far, the modification of this hysteresis by cyclic external electrical loading has been a puzzling and only partly understood process limiting the use of polycrystalline ferroelectrics for ferroelectric memories as well as actuators.[3,4] The switching of polarization is a nucleation and growth process of domains[5] attempting to match the constraints imposed by external and local electric fields and stresses.[6] In polycrystalline pervoskite ferroelectrics domain wall motion is the dominant mechanism of polarization reorientation[2] because sufficient numbers of domains are generated during sample cooling from the paraelectric phase.[7,8] The domain wall mobility is in large part determined by the interaction with structural imperfections like the outer perimeter of a crystal, grain boundaries, inclusions, point defects, or their agglomerates.[1] As a result, the shape of the hysteresis loop is altered[2,7] and an enhanced emission of ferroelectric Barkhausen-pulses and acoustic emissions has been found.[1,9,10]

Thin films for practical reasons only allow for the observation of fatigue along the cycling axis which is the thickness direction of the film. In bulk ferroelectrics orientations perpendicular to the cycling direction are accessible. Pan et al. recognized that fatigue in bulk ferroelectrics induces a highly textured loss in switchable polarization.[11,12] The polarization in their experiment dropped to about 25% of the unfatigued value in PLZT (7/62.5/37.5). Perpendicular to the fatiguing direction the polarization hysteresis was unaltered. They then cycled in the perpendicular direction and observed that fatigue along this axis occurred earlier than in a virgin sample. An intermediate angle yielded an average of both directions. They also determined that fatigue is predominantly a bulk effect in ceramic PZTs independent of the electrode material by sectioning the sample in the thickness direction and measuring the individual slices for fatigue.

In order to understand the coupling between the different axes in a fatigue-textured sample, the complete longitudinal and transverse strains are determined here simultaneously yielding the full multiaxial information for yield directions both along and perpendicular to the cycling direction. The results are discussed in the framework of the previously observed texture of defect agglomerates.[10,13] Local stresses inducing microcracking[13] are macroscopically reflected in the effective Poisson's ratio displaying incomplete 90° switching.

2. Experimental

Commercial disc-shaped samples (10 mm diameter, 1 mm thick) in the tetragonal vicinity of the morphotropic

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phase boundary of soft doped lead-zirconate-titanate were used ($Pb_{0.99}[Zr_{0.45}Ti_{0.47}(Ni_{0.33}Sb_{0.67})_{0.08}O_3]$, PIC 151, PI Ceramics). Fired silver (720 °C) served as electrode. The samples were cycled at 1.96 kV/mm peak value ($2E_c$) sinusoidal. Measuring fields were applied at 0.02 Hz (details in [10,13]). One bipolar cycle was applied before the actual measurement. This polarisation (- P_r) was set as the initial zero in all figures. For the measurements in perpendicular direction the electrodes were removed using sandpaper, rectangular bars were cut from the disc shaped samples and silver paste electrodes were applied perpendicular to the original cycling direction.

3. Results

Fig. 1 displays the material behaviour for measuring fields applied along the cycling direction after $2{\cdot}10^7$ cycles, (a) through (f), and in a virgin sample, (g) to (l). It is clear that the longitudinal (b) as well as the transverse strain (c) suffer serious losses and asymmetries due to cycling. Constant volume as in the virgin sample (strain ratio-1/2, which is the effective Poisson's ratio, dashed line) is only maintained for the less fatigued wing of the strain hysteresis and even there the slope is not exactly -1/2. Effectively only negative polarization values are reached as displayed in the electrostrictive hysteresis (e), where one wing is entirely missing for the fatigued sample. Absolute polarization values are only accessible via the electrostrictive hysteresis, (e) and (f), or (k) and (l), because leakage currents defeat monitoring the cumulative charge during cycling. The charge values are set to an arbitrary zero before measurement. The transverse strain (f) behaves analogously.

For fields applied perpendicular y to the cycling direction, z [see inset in (a)], the polarization hysteresis drops down to values around 80–65% of the unfatigued value depending on the individual sample. The right column in Fig. 2 displays a measurement with the field direction perpendicular to the cycling direction. The transverse strain (t) is along the original cycling direction, z. Again, constant volume is not maintained, even though at first sight both strain hysteresis loops seem intact. The splitting of the strain ratio in the one half-cycle indicates the deviations from constant volume for the more degraded wing of the transverse strain directions, one along the original cycling direction, z, (o), and the third non-cycled axis, x, (n). Their ratio (p) should be 1 which is also not observed.

The minima in the strain hysteresis (s) are more rounded than in a virgin sample (b). The electrostrictive curve (v) shows less hysteresis and more approaches the parabolic shape of pure electrostriction.

4. Discussion

A crucial question arising in fatigue studies is to how much certain domains, domain walls, or grains in polycrystals are affected by the overall fatigue phenomenon. It has long been known for polycrystalline materials that the remnant polarization only reaches values of about half the spontaneous polarization and fields higher than the single crystal coercive field have to be applied to fully pole the material.[2] Two effects contribute. First the projection of the oriented polarization onto the field direction is reduced directly explaining reduced remnant polarization values with respect to the spontaneous polarization of a single crystal. Secondly, not all domains switch under the external field projection onto the polarization direction, the reciprocal effect. The fatigue results can be understood in a similar manner. Switching in a certain cycling direction only affects certain grains and accordingly fatigue only occurs here. Thus, if fields are applied to the macroscopic sample in a perpendicular direction (Fig. 2 right column) other grains participate and the fatigue phenomenon is not as pronounced. On the other hand, those grains participating in both sets of switchable grains do communicate their fatigue state to the other field projection as seen in the transverse strain data (o) and (t). Domains constituting the polarization offset in Fig. 1 (e) no longer participate in the switching process. Evidently, some surrounding grains or domains still do participate in switching. Locally and globally stresses are induced, which is macroscopically well visible in the deviation from constant volume, Fig. 1 (d), and Fig. 2 (p), and (u), representing elastic stresses in the material. This is also well reflected in the previously observed occurrence of microcracks in fatigued samples.[13] The fact that the electrostrictive hysteresis more approaches a pure parabola in the transverse direction shows that the ferroelastic contribution to strain is reduced with respect to the piezoelectric contribution.[14] The resulting argument on the fatigue mechanism is that domain switching is reduced, but piezoelectric contributions to strain are maintained.

A second approach to the macroscopic anisotropy stems from a different set of arguments. We previously observed that the microscopic damage is highly anisotropic. We found etch grooves in fatigued samples after chemical etching non existent in virgin samples.[10] These were extended defects which occurred regularly, but not frequently in a cut parallel to the electrodes. In a perpendicular cut the etch grooves were numerous, but not extended.[13] Altogether, these etch grooves were associated with agglomerated point defects forming platelet structures predominantly perpendicular to the cycling field.[15] If such agglomerates are highly oriented within one grain their interaction with the domain system of this grain may also become highly anisotropic. At this

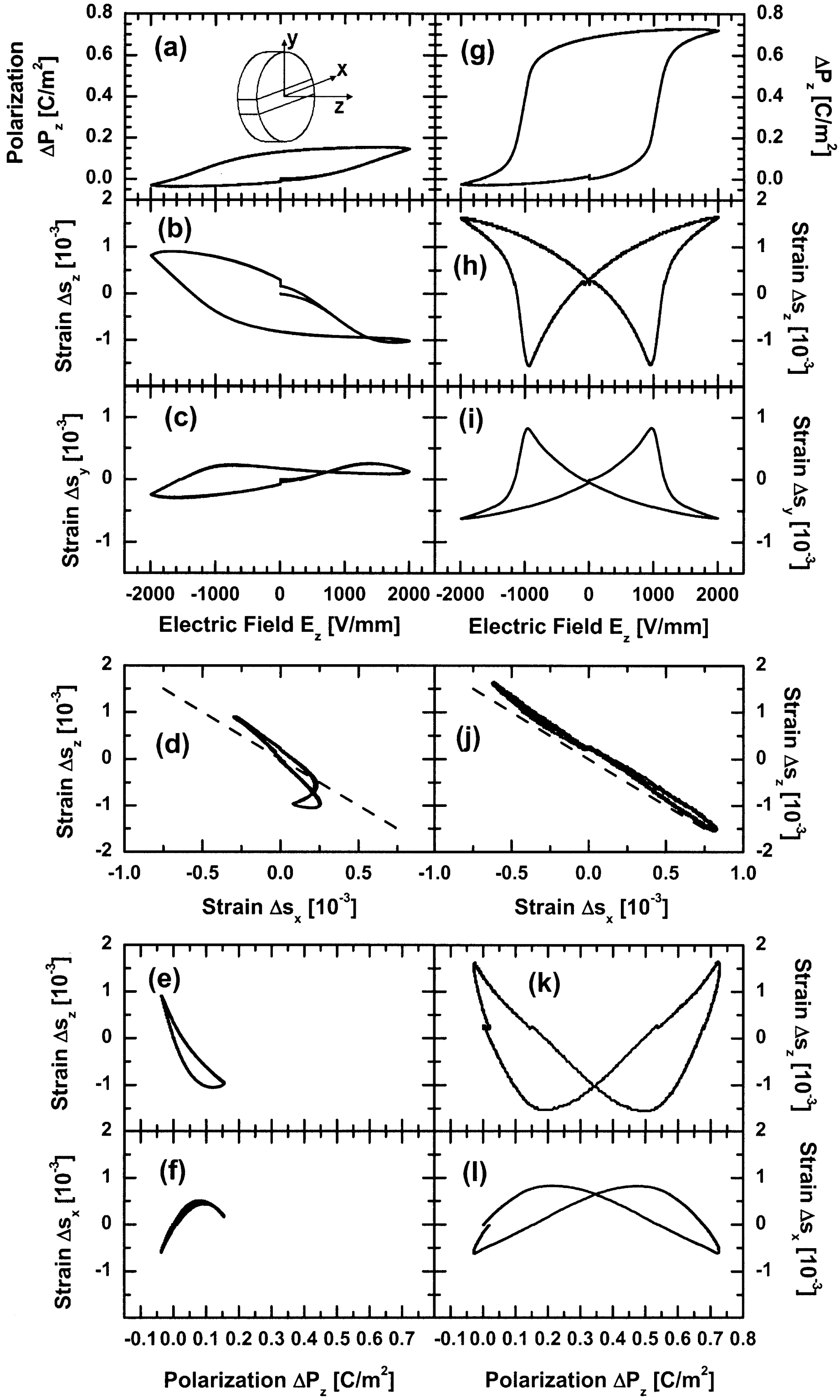

Fig. 1. Strain and polarization anisotropy with the external field applied *in cycling direction along z*, (a) through (f) after fatigue ($2{\cdot}10^7$ cycles) and (g) through (l) on a virgin sample.

point it is crucial to consider the degree of correlation of domains within the domain system of one grain. Arlt used symmetry arguments to determine the number of possible domain systems in a tetragonal crystal.[8] 24 (48) orientational configurations are permitted out of which 12 (24) contain charged 180° domain walls and 12 (24) do not.

Considering our previous results on the formation of platelet agglomerates, these induce needle domains in their immediate environment.[15] Such needles represent

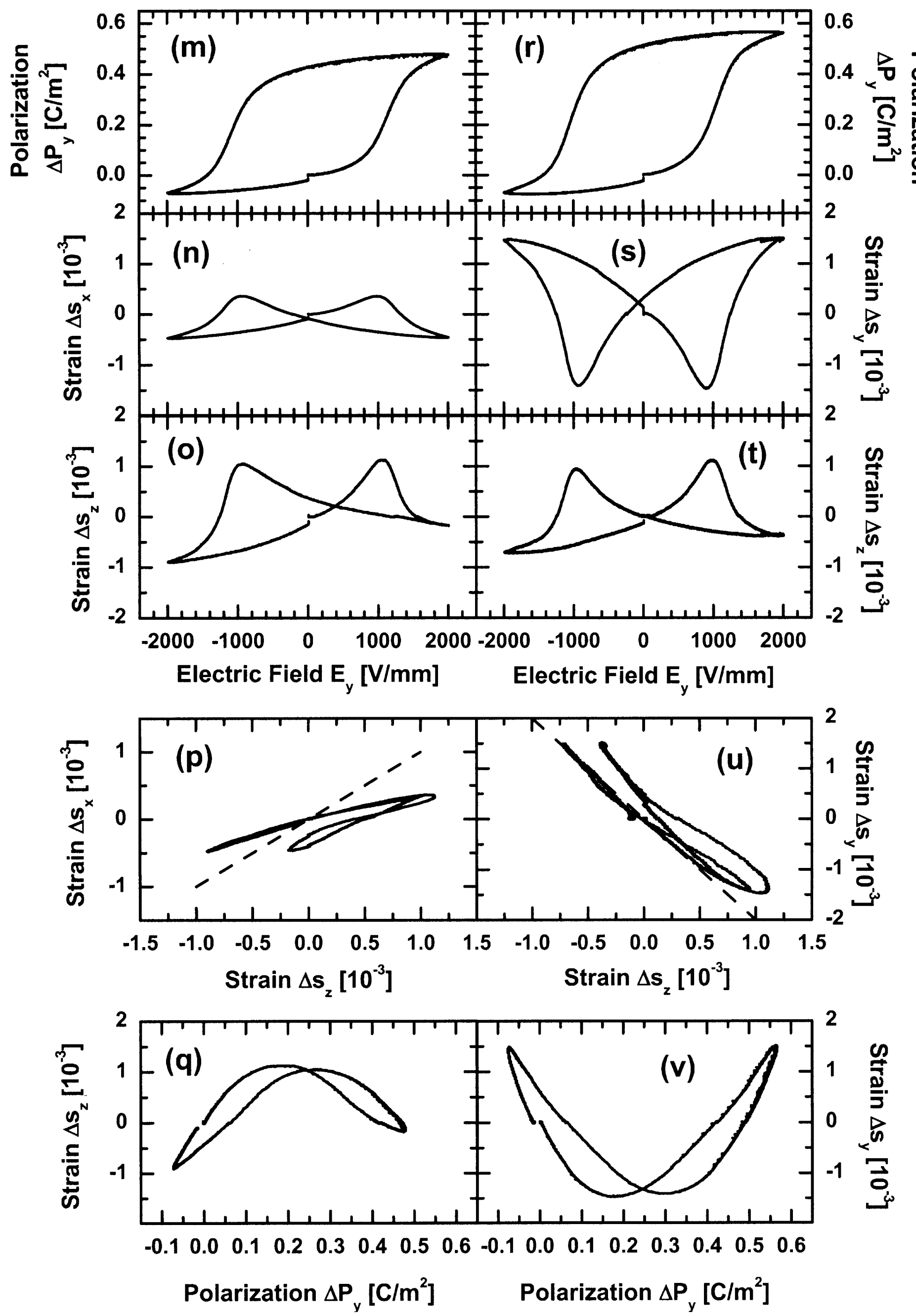

Fig. 2. Strain and polarization anisotropy after fatigue with the external field applied *perpendicular to the cycling direction, along y*. The two columns show two different samples. On the left, (n) through (q), both strains perpendicular to the measuring field direction, s_x and s_z, are compared. On the right, (r) through (v), the strain parallel to the measuring field direction, s_y and one transverse strain, s_z, are shown. The cycling direction was z.

significant barriers to the motion of 90° as well as 180° domain walls, which we were able to show by fatigue dependent acoustic emission studies.[10] Unfortunately, we have so far not been able to determine the differences in interaction strength between both types of domain walls and the observed agglomerates. Considering the high degree of correlation of the entire domain system within each crystallite, defects interfering with the domain wall motion of certain domain walls will strongly affect the entire domain system of that grain. If the domain system is blocked at some location, further charged domain walls will form and consume energy. Thus, as soon as some part of the domain system is affected by agglomerated defects the entire domain system of that grain should experience some significant mobility changes. Particularly frozen domains will block certain regions within the grain and strongly modify the boundary conditions for remaining domains in that grain. It seems more reasonable that different fractions of grains participate in the two different electric field directions.

5. Summary

The anisotropy of the fatigue effect was shown in bulk lead-zirconate-titanate. Macroscopic strain measurements yield a direct image of the local stresses developing in certain orientations of the sample and for certain 90° switching processes. The observed anisotropy correlates well with the anisotropic orientation of fatigue induced point defect agglomerates. The subsequent microcracking is an immediate consequence of the macroscopically reflected local stresses.

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