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Micromechanics of domain switching in rhombohedral PZT ceramics

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Abstract

The lattice strain $\varepsilon\{2\ 0\ 0\}$ and diffraction peak intensity ratio $R\{1\ 1\ 1\}$ have been determined in soft rhombohedral PZT ceramics during the application of an electric field up to 2.5 MV m^{-1} and as a function of the grain orientation ψ, using high energy synchrotron X-ray diffraction. The magnitude of both $\varepsilon\{2\ 0\ 0\}$ and $R\{1\ 1\ 1\}$ increased sharply beyond a field level of 1 MV m^{-1} due to the onset of ferroelectric domain switching. $\varepsilon\{2\ 0\ 0\}$ exhibited a near linear dependence on $\cos^2\psi$, in agreement with previous studies of the remanent-poled state. In contrast, the $R\{1\ 1\ 1\}$–$\cos^2\psi$ plot showed evidence of saturation in ferroelectric domain switching, particularly for $\psi > 60^\circ$. The development of lattice strain during poling is discussed in terms of contributions from the intrinsic piezoelectric effect and from residual stress caused by differences in the poling strain of a grain, and the piezoelectric strain of a grain relative to its surroundings.

Keywords: B. X-ray methods; C. Ferroelectric properties; D. PZT; Residual stress

1. Introduction

The ferroelectric nature of PZT (lead zirconate titanate) ceramics has led to numerous applications in piezoelectric and pyroelectric devices [1]. Despite their widespread usage, some aspects of their behaviour are still relatively poorly understood. For example, the poling process itself, which is a necessary practical step in the fabrication of virtually all piezoelectric and pyroelectric components based on ferroelectric ceramics, introduces internal residual stresses on both the microscopic and macroscopic scales. The influence of these stresses on the functional properties of such components is often overlooked.

On the microscopic level, the poling strain of a grain, $\bar{\varepsilon}^{\mathrm{P}}$, caused by ferroelectric domain switching, depends on its orientation, ψ, relative to the direction of the applied electric field. Each grain experiences a misfit strain, $\bar{\varepsilon}^{*}$, and hence residual stress given by the difference between its individual poling strain, $\bar{\varepsilon}^{\mathrm{P}}$, and the macroscopic strain of the polycrystal, $\langle\varepsilon\rangle$:

$$\bar{\varepsilon}^{*} = \bar{\varepsilon}^{\mathrm{P}} - \langle\varepsilon\rangle \tag{1}$$

In piezoelectric actuators, cyclic variations in residual stress under high field conditions can lead eventually to device failure by electromechanical fatigue [2].

Through recent experiments, conducted using high energy X-ray diffraction (XRD), the present authors have shown that in single phase PZT ceramics both the elastic lattice strain and the ferroelectric domain fractions, represented by the diffraction peak intensity ratios, exhibit a linear dependence on $\cos^2\psi$ [3]; these relationships were found to be valid for PZT ceramics with both tetragonal and rhombohedral structures. The results indicate the occurrence of a tensile residual stress for tetragonal $\{1\ 1\ 1\}_{\mathrm{T}}$ or rhombohedral $\{1\ 0\ 0\}_{\mathrm{R}}$ grain families along the macroscopic poling direction. This behaviour was explained in terms of a micromechanical model based on the Eshelby inclusion theory [4,5].

For rhombohedral PZT, the lattice strain in a grain along the $\langle 1\ 0\ 0\rangle$ direction, expressed in a reference frame Z inclined at an angle ψ to the macroscopic polar axis, was related to the macroscopic poling strain $\langle\varepsilon\rangle$ by the following expression [5]:

$$\bar{\varepsilon}_{33}(Z,\{1\,0\,0\}) = \frac{7-5\nu}{15(1-\nu)}\left\langle\varepsilon\right\rangle\left(\frac{3}{2}\cos^2\psi - \frac{1}{2}\right) \tag{2}$$

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A similar relation was obtained to express the fraction of domains aligned along the polar (1 1 1) direction in terms of the poling strain in the reference frame X at $\psi = 0^\circ$, the grain orientation ψ, and the transformation shear strain of the rhombohedral structure γ.

$$f(\psi, 1\,1\,1) = \frac{1}{4} + \frac{3\bar{\varepsilon}_{33}^{\mathrm{P}}(X, 1\,1\,1)}{8\gamma}\left(\frac{3}{2}\cos^2\psi - \frac{1}{2}\right) \qquad (3)$$

The aim of the present study was to determine the distribution of elastic strain and the ferroelectric domain fractions in soft rhombohedral PZT ceramics as a function of the grain orientation ψ during poling under an applied electric field up to saturation. Furthermore, by monitoring the lattice parameters during the poling process, the validity of the argument used previously to determine the unstrained lattice parameters, and hence the absolute value of the elastic strain can be evaluated.

Previous studies have reported the use of diffraction methods to determine the degree of ferroelectric domain switching and lattice strain in PZT ceramics in response to an applied electric field [6,8]. In these publications, it was assumed that the observed lattice strain could be attributed solely to the intrinsic piezoelectric effect. According to our interpretation, such an argument is flawed because the contribution from elastic strain due to residual stress in a polycrystalline ferroelectric ceramic has been neglected. Also, with the exception of recent work conducted using neutron diffraction [9,10], previous investigations have generally employed low energy XRD to study the lattice strain and crystallographic texture in crystal planes oriented parallel to the specimen surface [6–8]. Such methods provide only a limited view of the ferroelectric domain switching behaviour in the near-surface region, which is subject to a lower level of mechanical constraint than that in the bulk, and do not provide key information on the influence of grain orientation. These limitations are overcome in the present study by the use of high-energy synchrotron XRD.

2. Experimental procedure

PZT ceramics doped with both lanthanum and strontium were prepared according to the composition $(\mathrm{Pb}_{1-x-1.5y}\mathrm{Sr}_x\mathrm{La}_y)(\mathrm{Zr}_z\mathrm{Ti}_{1-z})\mathrm{O}_3$, with $x = 0.05$, $y = 0.03$ and $z = 0.58$, using the standard solid state reaction method [3]. The resulting materials had grain sizes in the range of 2–5 μm and possessed a rhombohedrally distorted perovskite crystal structure with a rhombohedral angle, α, of approximately 89.80° [5]. The coercive field for this composition, E_c, was measured as 0.82 MV m^{-1}, while the remanent and saturation polarization values, P_r and P_s, were determined as 0.35 C m^{-2} and 0.40 C m^{-2}, respectively [3]. Square ended beam specimens with dimensions of 1 mm × 1 mm × 10 mm were prepared by diamond machining, with Ag/Pd electrodes applied to the top and bottom faces, as described previously [3].

High-energy XRD experiments were carried out on station ID11 at the European synchrotron radiation facility (ESRF), using monochromatic X-rays with a wavelength of 0.1771 Å [3]. A static electric field with a value up to a maximum of 2.5 MV m^{-1} was applied to the specimens using a Chevin Research HVA1B high voltage amplifier, controlled remotely by means of a Hewlett-Packard HP33120A function generator. Connections to the specimen electrodes were made by attaching PVC-insulated wires using a conductive epoxy-based adhesive.

XRD patterns were obtained by scanning the point detector over a range of diffraction angles, with 2θ from 4° to 5°, corresponding to the {1 1 1} and {2 0 0} reflections. In addition, for each level of the applied electric field the specimen was rotated successively about the X-ray beam axis in order to monitor the range of grain orientations ψ from 0° to 90°. The time required to measure the XRD patterns in this way at a fixed value of the applied electric field was approximately 90 min.

According to the convention employed in the previous studies [3–5], crystal planes oriented at $\psi = 0^\circ$ have their scattering vectors parallel to the direction of the applied electric field, while planes oriented at $\psi = 90^\circ$ have their scattering vectors in the transverse direction. Therefore, a shift in lattice spacing measured at $\psi = 0^\circ$ corresponds to a component of lattice strain along the direction of the applied electric field, while a shift in lattice spacing measured at $\psi = 90^\circ$ provides the component of strain in the transverse direction.

3. Results and discussion

A selected set of the XRD patterns obtained during the experiment is presented in Fig. 1. These results illustrate the occurrence of 71°/109° ferroelectric domain switching, from the changes in the relative intensities of the $(1\,1\,1)/(\bar{1}\,1\,1)$ pair of diffraction peaks, and anisotropic lattice strain, from the shifts in the position of the {2 0 0} diffraction peak, during poling up to a maximum electric field of 2.5 kV mm^{-1}. Complementary information is provided by the XRD patterns recorded at $\psi = 0$ and 90°.

The reorientation of the spontaneous polarization, through an angle of either 71 or 109°, results in an increase in the fraction of ferroelectric domains oriented along the electric field direction. Consequently, the relative intensity of the (1 1 1) diffraction peak increased relative to that of the $(\bar{1}\,1\,1)$ peak in the XRD patterns recorded at $\psi = 0^\circ$. The opposite effect was observed in the patterns obtained at $\psi = 90^\circ$.

The fraction of ferroelectric domains oriented along the [1 1 1] direction can be quantified in terms of the diffraction peak intensity ratio, $R\{1\,1\,1\}$, where

$$R\{1\,1\,1\} = \frac{I(1\,1\,1)}{I(1\,1\,1) + I(\bar{1}\,1\,1) + I(1\,\bar{1}\,1) + I(1\,1\,\bar{1})} \qquad (4)$$

Here, $I_{(hkl)}$ represents the integrated intensity of the (hkl) diffraction peak.

The value of $R\{1\,1\,1\}$ prior to poling was approximately 0.25, as expected for an initial statistically random distribution of the different domain variants. During poling, the value of $R\{1\,1\,1\}$ changed to a maximum of 0.95 at $\psi = 0^\circ$ and a minimum of 0.01 at $\psi = 90^\circ$, indicating that the domain

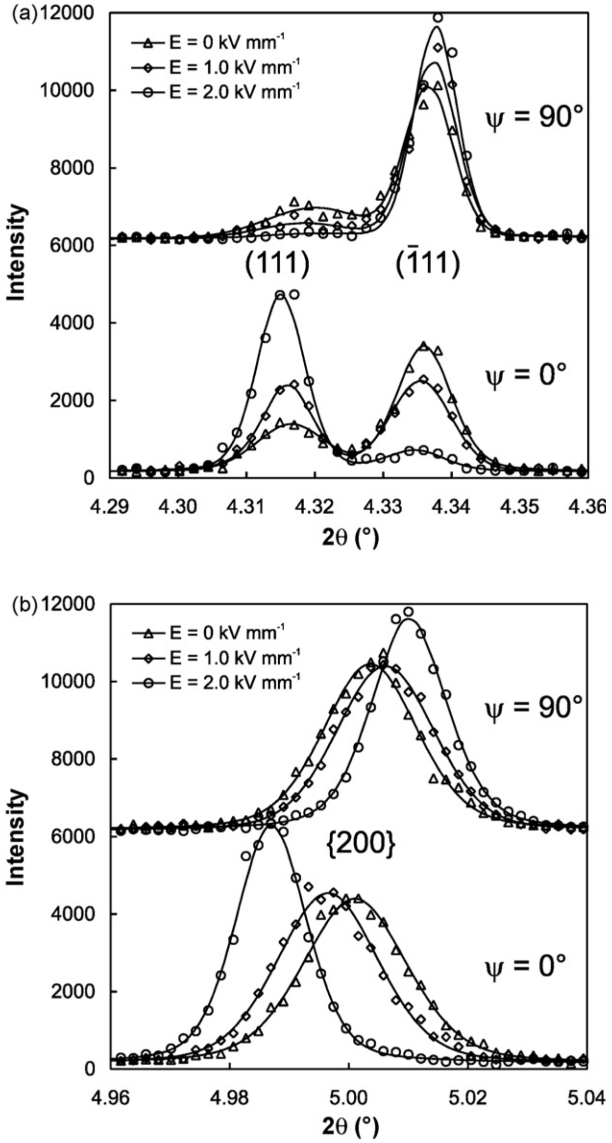

Fig. 1. Changes in XRD spectra for (a) {1 1 1} and (b) {2 0 0} reflections during poling.

switching process was almost complete for the {1 1 1} grain family at a field of 2.5 MV m^{-1}, as illustrated in Fig. 2(a).

Significant shifts in the positions of certain diffraction peaks were also observed during poling, indicating the development of a lattice strain along specific crystallographic directions. This effect was most pronounced for the (2 0 0) peak, as shown in Fig. 2(b). In contrast, the (1 1 1) and ($\bar{1}$ 1 1) peaks appeared to exhibit only minor shifts in position during poling.

Using the analysis method proposed previously [5], it is expected that both the ferroelectric domain fractions, given by the diffraction peak intensity ratio $R\{1\,1\,1\}$, and the lattice strain $\varepsilon\{2\,0\,0\}$ should depend on the grain orientation according to a $\cos^2\psi$ relationship. These relationships are evaluated in Fig. 3. It is apparent from these results that the $\cos^2\psi$ relation for the lattice strain remains approximately valid under a high electric field (Fig. 3(b)). For each level of the applied field, it was found that the lattice strain was close to zero at the critical grain orientation of $\psi = 54.7^\circ$, which corresponds to the angle at which $\cos^2\psi = 1/3$. This characteristic is in agreement with our previous analysis of the remanent-poled state in rhombohedral PZT ceramics [5] and indicates a strain free lattice parameter $d_{\{2\,0\,0\}}$ of 2.029 Å. The value of $d_{\{2\,0\,0\}}$ determined from the $\cos^2\psi$ plot is equal to the lattice parameter of the unpoled ceramic, which was also determined as 2.029 Å. This result confirms the principle of our previous analysis to determine the unstrained lattice parameter [3,5].

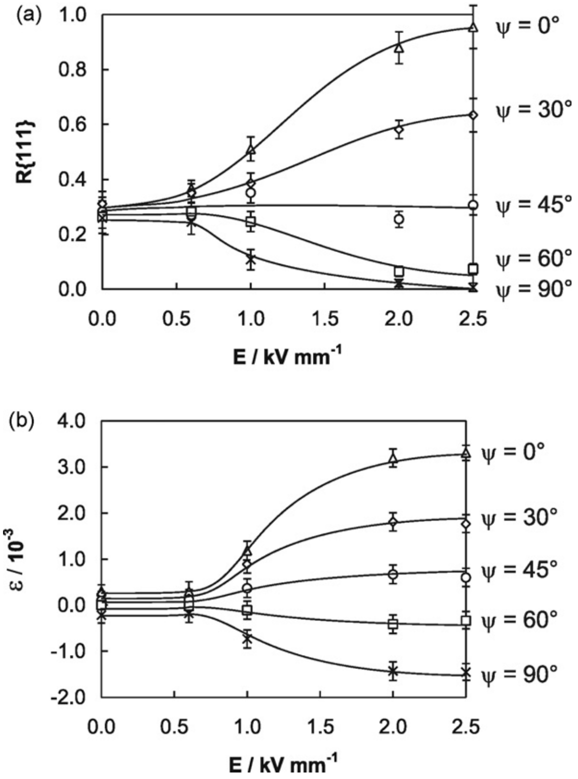

Fig. 2. Changes in (a) diffraction peak intensity ratio and (b) lattice strain $\varepsilon\{2\,0\,0\}$ during poling.

In contrast, the domain fraction $R\{1\,1\,1\}$ does not conform to a linear $\cos^2\psi$ relationship at high electric field levels and tends to saturate in the range from $\psi = 60^\circ$ to 90° (Fig. 3(a)). This indicates that the 71°/109° ferroelectric domain switching process is almost complete for {1 1 1} oriented grain with ψ in the range from 60° to 90°.

It is evident from Fig. 1(b) that the {2 0 0} diffraction peaks show not only a shift in position but also a significant reduction in peak width during poling. This is clarified in Fig. 4, where it is shown that the major reduction in peak width occurred during poling at an electric field strength above 1 MV m^{-1}. This effect can be understood in general terms as resulting from the growth of favourably oriented ferroelectric domains, increasing the average domain size, and the elimination of short-range fluctuations in strain associated with planar domain boundaries and triple junctions (disclinations) between domains [11].

In previous publications, the observed differences in the lattice strain along different crystallographic directions have been interpreted as providing direct evidence of intrinsic piezoelectric anisotropy [6–8,12]. However, according to our

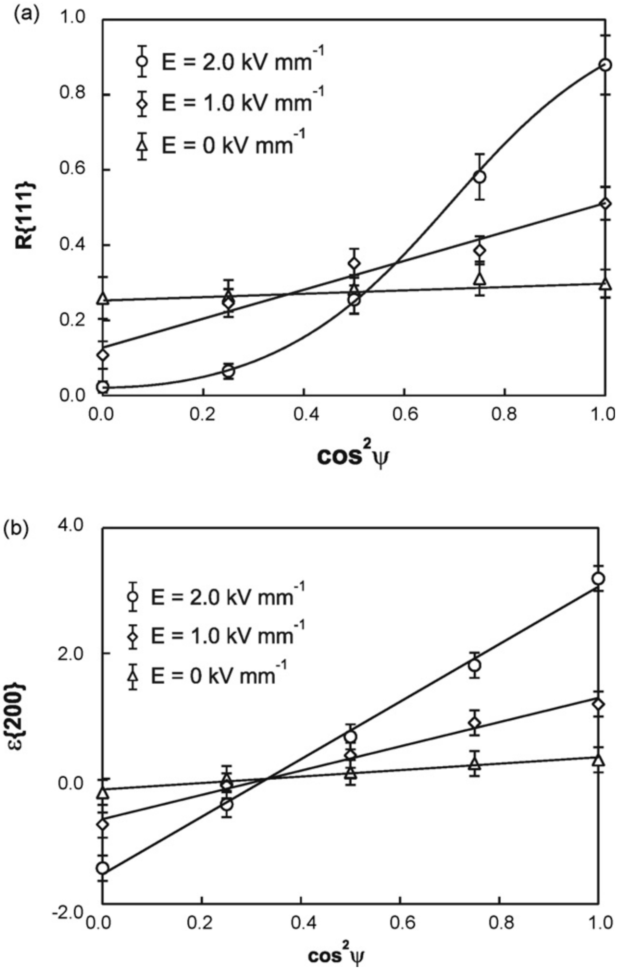

Fig. 3. Changes in (a) $R(1\ 1\ 1)$–$\cos^2\psi$ and (b) $\varepsilon\{2\ 0\ 0\}$–$\cos^2\psi$ plots during poling.

previous investigation of the lattice strain in poled rhombohedral PZT ceramics, it is important to consider also the influence of residual stress caused by variations in the transformation strain due to domain switching in differently oriented grain families.

In our earlier studies [3,5], we identified the rhombohedral $\langle 2\ 0\ 0\rangle_R$ directions as unique in the sense that they exhibit zero transformation strain for domain switching during poling. As a result, they act as an elastic strain sensor in the remanent-poled state. The elastic strain is a result of residual stress induced by ferroelectric domain switching in the surrounding, different-oriented grains and occurs even in the absence of an applied electric field. Therefore, it is certainly not a result of piezoelectric anisotropy, although elastic anisotropy must play an important role.

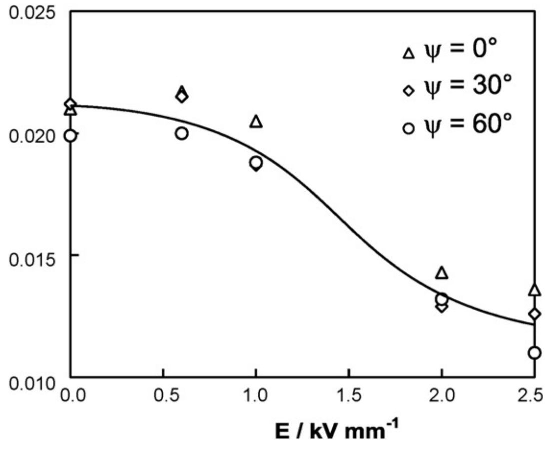

Fig. 4. Reduction in peak width for {2 0 0} reflection during poling.

When the lattice strain of a grain ε is measured under an electric field, as in the present investigation, we must consider it as comprising a sum of the intrinsic piezoelectric strain, $\varepsilon^{\text{piezo}}$, and elastic strain due to residual stress, ε^{el}:

$$\bar{\varepsilon} = \bar{\varepsilon}^{\text{piezo}} + \bar{\varepsilon}^{\text{el}} \tag{5}$$

Here, the overbar indicates that the strain is averaged over a grain, according to the convention used in our previous analysis [5].

Furthermore, the elastic strain caused by residual stress can be attributed to two factors, which are the difference in transformation (domain switching) strain and the difference in intrinsic piezoelectric strain of a grain relative to its surroundings. In our previous analysis of the remanent-poled state, we were able to neglect the piezoelectric contributions and thus determine the contribution from residual stress due to domain switching directly [5]. The separation of the three contributions to lattice strain under the influence of an electric field is a non-trivial matter, which will require further in situ studies and modelling effort.

The saturation of ferroelectric domain switching at high electric fields, in the region of 3–5 MV m^{-1}, offers one possible means of determining the piezoelectric contribution, which is assumed to be linear to the electric field. However, the contribution from residual stress due to the effects of piezoelectric anisotropy and the constraint of the surrounding grains remains as an important factor at high fields. In this case, we anticipate that the residual stress should have a negative (compressive) character for the {1 0 0} grain family at $\psi = 0^\circ$, since it is predicted that the magnitude of the piezoelectric coefficient reaches a maximum along $\langle 1\ 0\ 0\rangle$ [12].

4. Conclusions

The lattice strain $\varepsilon\{2\ 0\ 0\}$ and peak intensity ratio $R\{1\ 1\ 1\}$ exhibited a sharp increase at an applied electric field above 1 MV m^{-1}, corresponding to the coercive field for initial poling of the rhombohedral PZT ceramics used in the present study. The $\varepsilon\{2\ 0\ 0\}$–$\cos^2\psi$ plot remained approximately linear under an applied electric field up to 2.5 MV m^{-1}, consistent with previous measurements in the remanent-poled state. In contrast, the $R\{1\ 1\ 1\}$–$\cos^2\psi$ plot exhibited pronounced non-linearity due to the saturation of ferroelectric domain switching in the {1 1 1} grain family for $\psi > 60^\circ$. The width of the {2 0 0} diffraction peaks reduced significantly during poling due to a combination of an increase in the average domain size and elimination of the short-range fluctuations in strain associated with planar domain boundaries and disclinations. The present study demonstrates the significant contributions of residual stress to lattice strain in polycrystalline ferroelectrics, which should be included in future discussions of piezoelectric anisotropy.

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