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Observation of crack growth in a polycrystalline ferroelectric by synchrotron X-ray diffraction

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Abstract

Pre-cracked samples of unpoled, polycrystalline, soft ferroelectric lead zirconate titanate were subjected to electrical and mechanical loading whilst using synchrotron X-ray diffraction to map strain-fields. Clear evidence is found of switching around the crack tip and development of a crack-wake. A J -integral estimate based on strain-field data provided a sensitive measure of strain changes during loading. Electrical loading did not cause crack advance or crack-tip switching; this provides evidence for electrically permeable crack models. There was also enhancement of electrically-driven switching in the crack-wake region. The results provide improved understanding and a resource for testing fracture models in ferroelectrics.

Crack growth in ferroelectric polycrystals has remained a puzzling phenomenon for decades. Typically, several effects may be in play simultaneously: in addition to mechanical stress intensity causing material separation when a crack grows, electrical energy is expected to contribute to the energy release rate, while ferroelectric and ferroelastic switching can dissipate energy and affect crack-tip fields [1]. The situation is further complicated by uncertainty over the electrical boundary conditions at crack surfaces [2]. It is well established that polycrystalline ferroelectric ceramics can show R-curve behaviour [3–6], and this is associated with switching processes in the vicinity of the crack tip. However, there is still a need for convincing evidence to identify the switching processes that occur as a crack grows, and to identify the effect of electric fields on crack growth.

Synchrotron X-ray diffraction offers a powerful analytical tool for the study of fracture in ferroelectrics. By providing full-field measurements of interatomic spacing it allows the construction of strain-field data without additional electromechanical loading. A variety of studies have exploited this approach. Pojprapai et al. [7] mapped switching zone growth in poled PZT under mechanical loading and showed that the switching zone grows with increasing loading. The process zone size was evaluated by Glazounov and Hoffmann [8]. Similarly, Jones et al. [9] examined crack tip fields around a loaded static crack in soft PZT, and compared these fields with the elastic K_I fields and with the predictions of a Ramberg-Osgood type power-law stress-strain relation. They noted both reversal of switching on unloading, far from the crack tip, and a permanently switched region near the crack. Recently, Vögler et al. [10] examined the fracture surface of an NBT-BT relaxor ferroelectric and were able to correlate the lack of a process zone at the fracture surface with an absence of transformation induced toughening. In common, these studies applied

mechanical loads to cracked ferroelectric ceramics and exploited X-ray methods to examine structural changes near the crack. However, none of these studies used the technique to investigate the interaction of electric fields with cracks.

In the present work, we use synchrotron X-ray diffraction to map strain in pre-cracked samples of a soft PZT ferroelectric, with applied loading in the form of crack opening displacement and electric field. This enables observation of the crack-tip strain fields, local ferroelectric/ferroelastic switching, crack wake effects, and residual strain upon unloading. We observe little or no crack tip intensification of electric field, as detected by the strains due to local ferroelectric switching. This is consistent with an electrically permeable model of fine cracks. Also evident is a strained crack wake, indicating a toughening contribution due to ferroelastic switching. Using the strain field maps, we make an estimate of the J -integral and show that this provides a sensitive parameter for the assessment of strain-fields around the crack.

The experiment used samples 4 x 4 mm² square and 1.0mm thick, cut from soft PZT-5H in the unpoled state. A 2 mm long notch of approximately 0.5 mm width was machined into one side of the sample to serve as a starting point for propagation of a straight crack (see Fig. 1). Cracking at the notch tip was initiated by running a razor blade over the notch root. This resulted in local damage and a sharp notch tip with an opening angle of approximately 30°. Surface electrodes were deposited on the upper and lower edges of the specimen using conductive silver paint, and voltages were controlled using a Trek 2200 amplifier connected to the surface electrodes via thin copper wires.

Mechanical loading was applied by inserting a zirconia wedge with 15° half angle into the pre-machined notch whilst supporting the opposite side of each specimen on zirconia disks. By displacing the wedge, a controlled notch opening displacement was imposed on the sample, driving propagation of a crack from the notch tip. A Deben loading rig (Microtest 5kN; 660 N loadcell) was used to control movement of the loading wedge with micron precision. The loading wedge and supporting disks were mechanically hard compared to PZT, and electrically insulating; they were mounted on insulating ceramic supports (Macor® Machinable Glass Ceramic).

X-ray diffraction measurements were carried out on beamline ID15 at the European Synchrotron Radiation Facility. A schematic of the diffraction setup and integration of the electro-mechanical sample loading is shown in Fig. 1. Monochromated light of wavelength 0.0178 nm (69.6 keV) was collimated to a beamspace of 100 x 100 μm². Powder diffraction patterns were recorded on a Perkin-Elmer area detector (2048 x 2048 pixels, 200 μm pixel size) placed 0.904 m downstream of the sample in transmission geometry. Calibration measurements on Ceria powder were used to determine the parameters of the experimental geometry. For analysis the experimental powder diffraction patterns were “caked”, by transforming the intensity from detector coordinates into polar coordinates of azimuthal angle χ versus magnitude of the scattering vector q (Fig. 1).

The PZT powder diffraction patterns contained more than 15 diffraction rings; the most intense peaks ({ 100}, { 110}, { 111}, { 200}, { 210}, { 211}, { 220}, { 310}, { 222}, { 321},

{411}) were selected for analysis. There was no appreciable splitting of {100} peaks due to tetragonality of the PZT unit cell [9] as, at the selected sample to detector distance, broadening due to the projected sample thickness was of similar magnitude to the peak splitting expected due to tetragonality. Changes in peak position were used to measure strain.

For each diffraction peak arising from {hkl} crystal planes, the spacing of lattice planes d_{hkl} was determined by Gaussian fitting of diffraction peaks, and strain $\epsilon_{hkl} (d_{hkl} - d_{0hkl})/d_{0hkl}$ was calculated. Here d_{0hkl} is the lattice plane spacing, measured in a strain-free reference PZT sample. Experimental elastic strains determined as a function of χ , $\epsilon_{\text{exp}}(\chi)$ were computed by two methods. To give an overall average strain, an intensity weighted average was conducted over all diffraction peaks, $\epsilon_{\text{all}}(\chi)$. To identify switching in the tetragonal phase, an intensity weighted average over the {100} and {200} peaks was used, $\epsilon_{\{100\}}(\chi)$.

The 2D in-plane strain tensor components, ϵ_{xx} , ϵ_{yy} and ϵ_{xy} were found from $\epsilon_{\text{exp}}(\chi)$ by a least squares fit to Mohr's circle:

$$\epsilon_{\text{exp}}(\chi) = \frac{\epsilon_{xx} + \epsilon_{yy}}{2} + \frac{\epsilon_{xx} - \epsilon_{yy}}{2} \cos(2\chi) + \epsilon_{xy} \sin(2\chi). \quad (1)$$

Here, the x - y co-ordinate axes correspond to directions parallel to the crack, in the sample plane (x direction) and perpendicular to the crack (y direction) as shown in Fig. 1. Note that these co-ordinates are useful for identifying residual strain in the crack wake, but do not necessarily correspond to principal strain directions elsewhere in the sample. Values of $\epsilon_{\text{exp}}(\chi)$ were determined for slices 6° wide in χ , providing a compromise between signal to noise ratio for diffraction data fitting and azimuthal angular resolution for Mohr's circle fitting. The resulting strain maps are shown in Figs. 2 and 3.

The strain fields were characterised using an approximate measure of the strain energy release rate of crack propagation, which was evaluated using a method derived from the JMAN approach [11] that allows direct calculation of the J -integral from measured displacement fields. In coupled piezoelectrics and ferroelectrics the J -integral formally includes energy contributions due to electric fields [12,13], which could not be evaluated from the strain data in the present study. Therefore the measure was treated as an indication of mechanical strain energy release rate only: we do not attempt to relate this to fracture toughness in the electrical loading cases. The JMAN method, which solves for an equivalent displacement field from the diffraction strain data using strain compatibility conditions, is presented in detail in [11, 14]. Briefly, a finite element solution uses the measured strains (average for all diffraction peaks) to determine the missing components of the displacement field required for the J -integral, and in particular separates the measured strain ϵ_{xy} into the displacement gradients u_x/y and u_y/x required for the computation of J . Plane stress conditions were assumed and, for simplicity, the material behaviour was approximated as isotropic with Young's modulus of 60 GPa and Poisson's ratio of 0.38 [15, 16].

The mechanical J -integral was calculated for each strain map using 7 to 10 contours centred on the crack tip, up to a distance of 1.2 mm from the crack. The crack tip positions were

identified using the ϵ_{xy} strain maps, with an uncertainty of less than 0.1 mm. Data were excluded within a masked region of width 0.2 mm over the crack and 0.2 mm ahead of the crack tip to permit convergence of the J -integral estimate [14] which was achieved for all data. The uncertainty was estimated as the standard deviation over the contours, and was typically less than 1%. The resulting J -integral estimates are shown in Fig. 4.

The strain maps and J -integral estimates provide a means of interpreting the effect of electromechanical fields on the cracked electroceramic. In Fig. 2, the unpoled material is mechanically loaded and strain maps track the propagation of the crack. The average strain data clearly show the crack advancing under mechanical load and developing crack-tip strain fields. As the crack advances, a wake region of residual strains ϵ_{yy} of around 2×10^{-3} develops, with thickness of about 0.2 mm, consistent with estimates of Glazounov and Hoffmann [8].

The strains inferred from $\{100\}$ reflection peaks highlight the switching between tetragonal variants. Ferroelectric or ferroelastic switching can promote a specific tetragonal variant, resulting in movement of the $\{100\}$ peak, which contains overlapping contributions from (100), (010) and (001) reflections. As discussed above, the experimental geometry here does not allow separation of the individual reflections. By comparison with the average strain data, the $\{100\}$ peak strain maps show a larger strained region suggesting a process zone in which there is tetragonal switching in some grains, constrained by elasticity in a surrounding majority of grains. The shear strains ϵ_{xy} give a particularly clear indication of the crack-tip location due to their anti-symmetric pattern centred on the crack-tip. The corresponding J -integral estimates in Fig. 4(a) suggest a steady mechanical energy release rate of around 100 Jm^{-2} , corresponding to a K_{IC} value of $2.5 \text{ MPa m}^{0.5}$. This toughness is somewhat higher than is typical in soft PZT ceramics but lies within the range reported for doped materials in the literature [17, 18]. In the present set of results no R-curve behaviour is observed; note, however, that the R-curve in polycrystalline ferroelectrics typically saturates within about 0.1 mm of crack extension [6, 19], which is less than the initial crack length in our experiment.

In Fig. 3, the strain maps for an unpoled, mechanically pre-cracked sample subjected to electrical loading show that the electrical loading does not advance the crack, even though the crack was at the point of propagation when electrical loading started. In this series of images, it is clear that as the electrical loading is increased, a strained region with ϵ_{yy} of about 2×10^{-3} spreads across the sample. The strain magnitude is consistent with 90° switching that aligns the tetragonal c -axis with the mean electric field direction. However, this switching does not initiate at the crack tip, spreading instead from the lower (0 V) electrode region. Using the J -integral estimate from the electrically unloaded case as a reference for crack opening displacement, and taking the assumption of an impermeable flaw at 2000 V electrical loading, the switching zone would then be about $400 \mu\text{m}$ in size. Thus the field concentration due to an impermeable crack would be clearly visible with our experimental resolution of $100 \mu\text{m}$. However, almost no change in the switched region around the crack tip is seen. This indicates that the crack is not acting as a field concentrator for electric field, which is evidence for a permeable model of fine cracks [2, 20]. In the later stages of poling (1800 V and 2000 V applied) the $\langle 100 \rangle$ strain maps show evidence that the

regions above and below the crack have greater straining, and hence a greater degree of switching, than those regions ahead of the crack. This may be attributed to the residual stress field behind the crack tip bringing the material close to the critical condition for 90° switching. The corresponding estimates of the J -integral, shown in Fig. 4(b) cannot be relied upon as measures of energy release rate because the JMAN calculation assumed linear elastic response. Notably, the initial value of the J -integral estimate is different from that in the mechanically loaded case. This may be due to some underlying texture in the sample in the initial condition. Nevertheless, the calculation does provide a sensitive measure of the developing strain fields around the crack: At 600 V and 1200 V electrical loading the changes to the strain fields near the crack are barely discernible by eye from the strain maps, but the J -integral estimate almost doubles over this range of loading. After unloading, the J -integral estimate remains high indicating that the residual strains due to switching remain upon unloading.

In conclusion, our results show strain maps for an unpoled, soft PZT ceramic experiencing crack growth due to mechanical loading, and switching without crack growth, due to electrical loading. The strain maps provide clear evidence of a switched crack-wake, and 90° switching around the crack. Electrical loading did not promote noticeable crack growth, even when the field was strong enough to cause poling. Additionally, the crack did not act as an electric field concentrator, suggesting that it is thin enough to be permeable to electric field, but the residual stresses in a region around and behind the crack tip did appear to enhance switching. This suggests that the ferroelastic and ferroelectric switching processes near crack tips are somewhat distinct, with not much 90° switching contribution to the electrically driven process. A J -integral estimate was used as a measure of the developing strain field, and this appeared very sensitive to small changes in the strain field around the crack.

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Figure 1. Schematic of the experimental setup.

The pre-notched sample is mechanically loaded by the loading wedge and subject to voltage V at surface electrodes (red and blue). An area detector downstream of the sample records powder diffraction patterns in transmission geometry.

Figure 2. Strain evolution due to mechanical loading.

Rows 1 to 3 show strain maps for 3 different crack lengths as the loading wedge is further inserted into the pre-notch. Columns 1 to 3 show the in-plane strain components computed based on all diffraction peaks. Columns 4 to 6 show the strain components calculated based on the $\langle 100 \rangle$ diffraction peak. Maps are $3 \times 3 \text{ mm}^2$ in size and sampling points outside the specimen are shown in black.

Figure 3. Strain evolution due to electrical loading.

Rows marked “electrical loading” and labelled 0 V – 2000 V show strain maps for increasing electrical loading of a pre-cracked specimen. The final row, marked “unloading” and labelled 0 V shows the strains in the specimen at 0 V following the electrical loading cycle. Maps of the in-plane strain components computed based on all diffraction peaks are provided in the columns labelled “average strain”. Strain components calculated based on the <100> diffraction peaks are labelled “<100> strain”. Maps are 3 x 3 mm² in size and sampling points outside the specimen are shown in black.

Figure 4. Mechanical J-integral estimates for the two loading cases.
(a) Mechanical loading. (b) Electrical loading.