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Investigation of domain switching in fractured ferroelectric ceramics by using imaging of X-ray diffraction

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Abstract

The paper describes a method to study ferroelastic domain switching during fracture of PZT ceramics, which is based on imaging of diffracted X-ray radiation using a position sensitive detector. It is shown that the high spatial resolution of the detector allows one to measure accurately the spatial distribution of domain switching near the fracture. The capabilities of this method are demonstrated in two experiments performed for ceramics with a composition PZT 60/40 + 2%La. In the first experiment, the distribution of the amount of domain switching is measured on the fracture surface, and the regions with stable and unstable crack growth can be separated. In the second experiment, the half-width of the process zone is determined. Its value, $w = 60 - 80$ μm, is in a good agreement with the estimate from fracture mechanics.

Keywords: Domain switching; Fracture; PZT; Toughness and toughening; X-ray methods

1. Introduction

Fracture behavior of ferroelectric ceramics, such as lead zirconate titanate $Pb(Zr_xTi_{1-x})O_3$ [PZT $x/(1-x)$], has recently become a popular topic in fracture mechanics, since it has been discovered that fracture toughness of these materials exhibits R-curve behavior.[1–3] It is believed that the major mechanism of an increasing resistance to crack growth in ferroelectrics is similar to that in materials with transformation toughening. A process zone develops ahead of the crack tip, where high tensile stresses cause ferroelastic switching of domains, which form in PZT below the Curie temperature.[3] As the crack propagates, residual compressive stresses developed after switching at the crack wake reduce tensile stresses at the crack tip (so-called shielding), and thus slow further crack growth.

The objective of the present study is to introduce a method which allows one to measure distribution of domain switching around the fracture surface, and therefore, obtain parameters necessary to study R-curve behavior,[4] such as volume fraction of domain switching at the fracture surface and the half-width of the process zone. The method is based on imaging of diffracted X-ray radiation using a position sensitive detector.[5] The advantage of using this method is that X-ray diffraction (XRD) provides a direct quantitative information about the distribution in population of domains with different crystallographic orientations, whereas, high spatial resolution of the detector provides accurate determination of domain switching within small areas of the sample.

2. Experimental

XRD was measured from samples which were initially fractured using four-point bending technique. Bar-shaped samples were employed with dimensions 3×4×45 mm^3, with a length of the notch equal to 1 mm. Bars were loaded at room temperature with a loading rate of 2–3 μm/min until fracture occurred. The composition investigated was PZT 60/40 + 2%La, which has a rhombohedral crystallographic modification of the ferroelectric phase. Ceramic samples were prepared by the conventional mixed-oxide route, as was described elsewhere.[6] The sintering was done at 1225°C for 2 h, and the density of

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the sintered bodies was higher than 99% of the theoretical density.

All XRD experiments reported here were performed using synchrotron radiation at the G3 beam station of HASYLAB (DESY, Hamburg). The diffractometer available at this station has a position sensitive detector, which consists of a CCD camera and a multichannel plate placed between the camera and the sample.[5] The plate consists of a large number of parallel tubes, each with 10 μm in diameter. When a wide parallel X-ray beam irradiates the sample surface, each tube selects diffracted radiation from a small spot of the sample and directs it to the CCD camera. The output signal from the camera is an image corresponding to the distribution of diffracted intensity over the sample surface. In the present experiments, each point in the image corresponded to the spot on the fracture surface with dimensions approximately equal to 15×15 μm^2, which determined the spatial resolution of the experiment.

The wavelength of the synchrotron radiation was equal to $\lambda = 1.5395$ Å. Since the studied material, PZT 60/40 + 2%La, has the rhombohedral modification of the ferroelectric phase, XRD was measured in $\theta-2\theta$ scans around the (222)/(2-22) reflection. Heights of these reflections, $I_{(222)}$ and $I_{(2\text{-}22)}$, are proportional to the domain population with different orientations: $I_{(222)}$ corresponds to the number of domains with their polar axis perpendicular to the fracture surface, whereas $I_{(2\text{-}22)}$ is proportional to the number of domains which polar axis is inclined at 71 or 109° with respect to the normal to the fracture surface. At each diffraction angle θ in the $\theta-2\theta$ scan, an image corresponding to the spatial distribution of diffracted intensity was recorded by the CCD camera of the detector. Two types of experiments were performed. In one experiment, the diffraction from the fracture surface was measured, in order to determine the amount of domain switching within regions of stable and unstable crack growth. In the second experiment, the XRD was measured from the surface orthogonal to the fracture, in order to determine the half-width of the process zone where the switching occurred during fracture.

3. Results and discussion

To measure the distribution of domain switching over fracture surface, the following procedure was adopted. After making a notch, the samples were annealed at 500°C (above the Curie temperature) for 4 h, in order to have a well-defined initial state of domain structure before fracture, with an isotropic domain orientation. Then the samples were fractured, and two XRD patterns were measured from the fracture surface. The first measurement was performed immediately after fracture. The second measurement was performed from the same sample after it was annealed for 4 h at 500°C. The purpose of annealing was to restore the isotropic domain orientation. Therefore, the difference between the diffraction patterns measured after fracture and after annealing should be directly related to the change of the domain structure induced during fracture. In each image of diffracted intensity, the measured intensity was integrated to increase the signal-to-noise ratio. Integration was performed within the regions with a width equal to the width of the sample and the length equal to 50 μm. The length was counted from the edge of the notch.

Fig. 1 shows diffraction patterns measured after fracture and after annealing from the two regions of the fracture surface: just behind the notch, where stable crack growth was expected, [Fig. 1(a)], and far from the notch, where crack growth proceeded in an unstable manner, [Fig. 1(b)]. The length of the region with stable crack growth was approximately equal to 500–600 μm for this sample. From the fit of the profiles of both reflections using two Gaussian functions, the peak heights, $I_{(222)}$ and $I_{(2\text{-}22)}$, were determined. From Fig. 1, one can see that the ratio, $I_{(222)}/I_{(2\text{-}22)}$, measured after

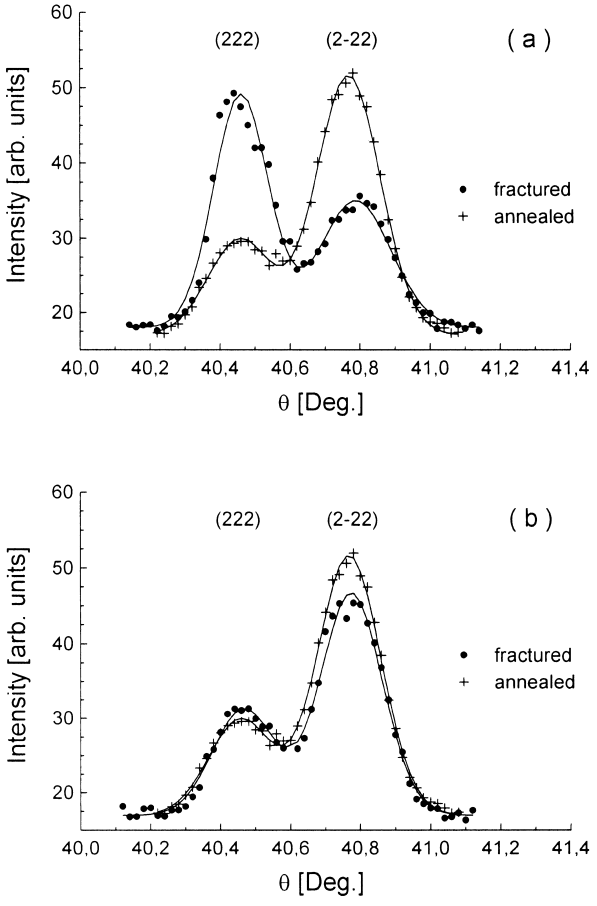

Fig. 1. Diffraction pattern measured from the fracture surface of the sample after fracture and after subsequent annealing. Data were measured (a) at the distance of 100 μm behind the notch, within the region of stable crack growth, and (b) far from the notch, within the region with unstable crack growth. Symbols show experimental data and lines correspond to the peak profile fit using two Gaussian functions.

fracture is higher than that after annealing. This corresponds to the increase in the number of domains with their polar axis directed perpendicular to the fracture surface since this domain orientation is favored by the tensile stresses acting at the crack tip, during application of an external load. It is also seen that the region with unstable crack growth shows a smaller change in the ratio of peak heights, $I_{(222)}/I_{(2\text{-}22)}$, with reference to the annealed sample than the region with stable crack growth. The reason for this difference is a higher rate of time variation of the tensile stress at the crack tip due to the higher crack growth velocity in the region with unstable growth. A higher rate of stress variation should result in a smaller amount of domain switching, due to the time dependence of domain switching in ferroelectrics.

The volume fraction of domain switching, N, induced during crack growth can be evaluated using the approach described by Subbarao et al.[7] By denoting the ratio $I_{(222)}/I_{(2\text{-}22)}$ before annealing as R, and after annealing as R', N can be written as:

$$N = \frac{R - R'}{(1 + R')(1 + R)}. \quad (1)$$

Fig. 2 shows the volume fraction of domain switching as a function of the distance from the notch tip. One can see that most of the domain switching occurred within a distance from the notch tip approximately equal to 600 μm, which corresponds to the stable crack growth. The average value of N measured from this region is approximately equal to (33 ± 2)%. It should be used to describe the toughness increment in the R-curve, ΔK_R, related with shielding of the tensile stresses around the crack tip. According to McMeeking et al.,[4] the toughness increment can be written as: $\Delta K_R \propto N \cdot \sqrt{w}$, where w is a half-width of the process zone where switching occurs. In the remaining part of the fracture surface, crack growth was unstable, and here the volume fraction of domain switching noticeably decreased to approximately (8 ± 2)%, due to the reasons discussed above.

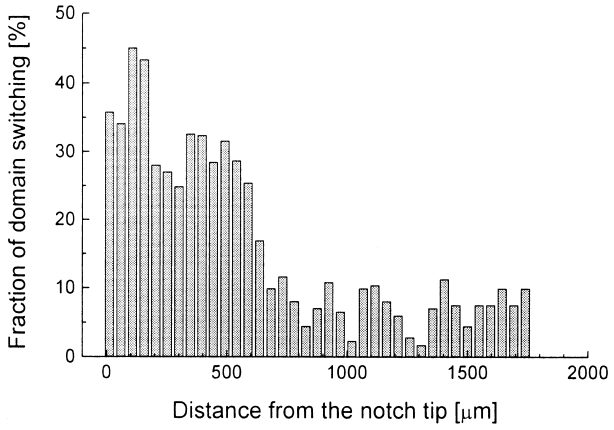

Fig. 2. Volume fraction of domain switching as a function of the distance from the notch.

The half-width of the process zone with domain switching was determined from the measurements of XRD from the surface orthogonal to the fracture. Similar to the previous experiment, the measured diffracted intensity was averaged to increase the signal-to-noise ratio. Averaging was performed along the direction parallel to the fracture surface within the distance of 1 mm behind the notch, which approximately corresponded to the region of stable crack growth.

Fig. 3(a) shows diffraction patterns measured in the bulk of the sample (at a distance about 2 cm from the fracture) and close to the fracture surface. In this plot, one can neglect the smaller values of peak heights, $I_{(222)}$ and $I_{(2\text{-}22)}$, near the fracture surface compared to those in the bulk. They are due to a smaller number of grains contributing to the diffraction near the fracture, because the fracture does not have a perfectly straight edge. The important point in this plot is a difference in the ratio $I_{(2\text{-}22)}/I_{(222)}$ in the bulk and near fracture surface, which should be related with the domain switching during crack

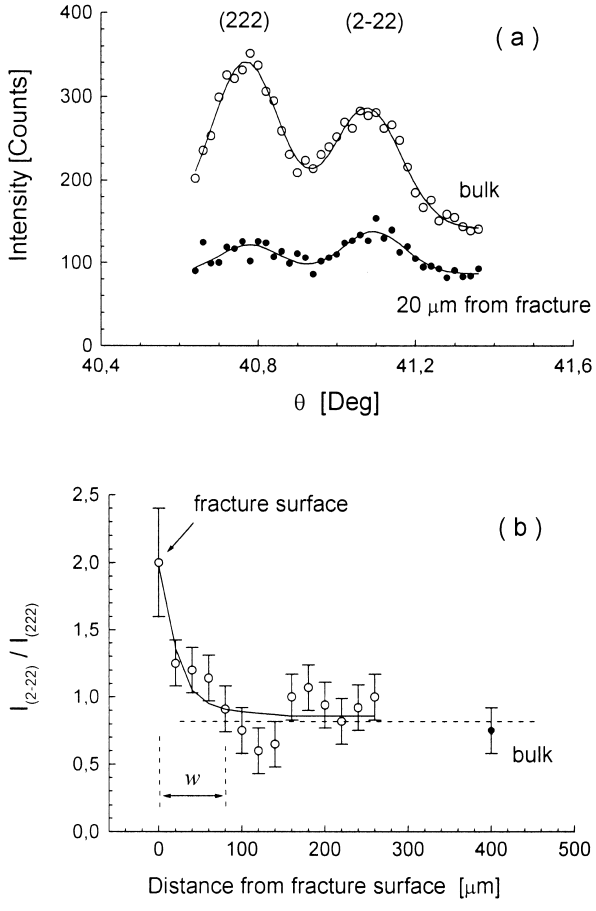

Fig. 3. (a) XRD patterns measured from the surface orthogonal to the fracture, far from the fracture (open circles) and near the fracture (closed circles). (b) The ratio of peak heights $I_{(2\text{-}22)}$ and $I_{(222)}$ as a function of the distance from the fracture surface. The point corresponding to the bulk (closed circle) was measured at the distance of 2 cm from the fracture. Also shown is the half-width, w, of the process zone, where the ferroelastic domain switching occurred during the crack growth.

growth. The ratio of peak heights calculated from the fitting of diffraction peaks, [Fig. 3(a)], using Gaussian functions, is plotted in Fig. 3(b) as a function of the distance from the fracture surface. One can see that as one moves away from the fracture, the ratio $I_{(2\text{-}22)}/I_{(222)}$ gradually reaches the value corresponding to the diffraction from the bulk. Within the present resolution limit, we can estimate that at distances larger than 80 μm, no switching occurred within the accuracy of peak intensity measurements. Therefore, for the studied composition, PZT 60/40 + 2%La, the half-width of the process zone can be estimated as $w = 60-80$ μm, as shown in Fig. 3(b).

The half-width of the process zone can be evaluated theoretically by using an approach similar to that which is used in fracture mechanics to describe transformation toughening in ceramics. It can be written as:[4,8]

$$w = A \cdot \left(\frac{K_R^{\infty}}{\sigma_c}\right)^2 \quad (2)$$

where A is a numerical constant, K_R^{∞} is the plateau value of the R-curve, and σ_c is the coercive stress necessary to cause ferroelastic domain switching. The value of the constant A depends upon the transformation criterion, and may vary between 0.17 and 0.23.[8] Coercive stress and R-curves were measured separately for the studied composition, PZT 60/40 + 2%La: $\sigma_c = 55$ MPa, and $K_R^{\infty} = 1.20$ MPa $\sqrt{\text{m}}$.[9] Using these values, Eq. (2) yields w within the range 80–120 μm, depending upon the value of the constant A. This estimate is in a reasonable agreement with the half-width of the process zone, $w = 60-80$ μm, determined in the present study using X-ray diffraction [Fig. 3(b)]. Two reasons may be responsible for the difference in the values of w measured directly and estimated using Eq. (2). First, Eq. (2) uses the plateau value K_R^{∞} corresponding to a steady state zone with domain switching.[4,8] This zone is unlikely to develop in the four-point bending tests used in this work, and therefore, in our experiment a smaller value of K_R^{∞} should be used to estimate w. Second, Eq. (2) describes the process zone developed during the crack growth, whereas in the present experiment we could only measure w of the fractured sample. The fast reverse domain switching which occurs in PZT samples after unloading may also lead to a smaller value of the process zone determined using XRD.

4. Conclusions

A method was proposed to study ferroelastic domain switching during fracture of PZT ceramics, which is based on imaging of diffracted X-ray radiation using a position sensitive detector. It was shown that the high spatial resolution of the detector allows one to measure accurately the spatial distribution of domain switching near the fracture. The capabilities of this method were demonstrated in two experiments performed for ceramics with a composition PZT 60/40 + 2%La. In the first experiment, the distribution of the amount of domain switching was measured on the fracture surface, and the regions with stable and unstable crack growth were separated. In the second experiment, the half-width of the process zone was determined. Its value, $w = 60 - 80$ μm, was in a good agreement with the estimate from fracture mechanics.

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