Study of global and local crystallography at the domain boundaries of Lead Zirconate Titanate piezoelectric ceramics

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Abstract. Reliable automated orientation mapping of 90° domains in a tetragonal perovskite has been achieved for the first time using both EBSD and TEM-Kikuchi pattern analysis. This has been used to compare local measurements of c/a ratios in PZT with global measurements by X-ray diffraction. The local c/a ratios are in broad agreement with the global measurements, but further work is needed to determine whether the small discrepancies are real local variations or are caused by experimental factors.

1. Introduction

Lead Zirconate Titanate (PZT), Pb(ZrₓTi₁₋ₓ)O₃, based piezoelectric ceramics are used in wide range of applications including sensors, transducers, actuators, multilayer capacitors, and ferroelectric memory devices. Piezoelectrics develop a spontaneous electrical polarisation below the Curie temperature associated with a crystallographic distortion; in order to minimise both strain and electrostatic energies, domains are formed in the grains with different polarisation orientations [1, 2]. Below the Curie temperature, PZT ceramics with x < 52.5% adopt a tetragonally distorted perovskite crystal structure and this results in lamellar domain structures with the domain boundaries on stress-free {101} planes. At junctions of different lamellar structures very high (GPa) stress concentrations can result, which will have a significant influence on the properties of these ceramics [3]. Additionally, there is some evidence that the composition and structure of such materials is not always homogeneous, and therefore methods for assessing local (sub-micron scale) crystallography will also be very useful. Both stress concentrations and local crystallography can be assessed using orientation mapping in electron microscopy, provided the accuracy of orientation determination is sufficient (~ 0.1°). The present paper concentrates on developing automated methods for accurate and unambiguous indexing of domain orientations in PZT ceramics using both electron backscatter diffraction (EBSD) and transmission electron microscopy (TEM) Kikuchi patterns, and using these to compare local with bulk crystallography.
2. Experimental

The material for investigation was received in the as-sintered state in the shape of cylinders with a diameter of about 9 mm. The samples for microstructural investigations were prepared by sectioning the pieces vertically as shown in Figure 1. The thickness of sections cut for TEM and EBSD analysis was 1 and 2 mm, respectively. Specimens for EBSD were ground on 1000 grit silicon carbide papers and polished using 6, 3 and 1 μm diamond paste, followed by a final polish with colloidal silica to remove strains and provide a high quality surface finish; a light etch of 100 ml H₂O, 5 ml HCl and five drops HF was applied for 11 seconds to reveal a slight amount of domain topography and finally a thin coat of carbon was evaporated onto the sample to minimise charging. The starting material for TEM specimens was also the rectangular section shown in Figure 1. Four smaller disks were cut out from each slice. These were then ground to about 150 μm and then dimpled to a thickness of about 20 μm in the centre. The samples were ion milled in a Gatan PIPS using 4 kV Ar⁺ ions and a 4° incidence angle from top and bottom, and finally coated with a thin film of carbon to minimise charging. The TEM investigations were carried out in a FEI Tecnai T20 TEM operated at 200 kV equipped with an Olympus-SIS Megaview III CCD camera for recording the diffraction patterns, typical spot sizes for the analysis were in the range 25-40 nm; and these were recorded using a convergent beam at a relatively low camera length so that the majority of the Kikuchi pattern is projected onto the CCD. Crystallographic orientations were determined from the Kikuchi patterns using the Euclid’s Phantasies (EP) software [4]. The EBSD data was obtained using a FEI Quanta 200F environmental SEM equipped with an EDAX Digiview II camera to capture the EBSD patterns. For EBSD pattern acquisition the microscope was operated at 25 kV accelerating voltage and 13 mm working distance using OIM EBSD data acquisition and data analysis software from EDAX. The X-ray diffraction was performed using a Siemens D500 diffractometer with Cu Kα radiation using an angular range from 20° to 72.5° and a step size of 0.02°.

3. Strategy for the unambiguous indexing of EBSD patterns

The non-conducting nature of PZT materials makes it very difficult to obtain high-resolution orientation data. Orientation mapping an area of less than 1 μm² is similar to a stationary electron beam. These conditions lead to problems like sample charging, image drift and sample surface contamination under the electron beam making long exposures and large maps almost impossible. Therefore, a strategy had to be devised to minimize these problems as well as to obtain the best quality data. To minimize charging an area adjacent to the area of interest was used to focus and set the mapping conditions. Using the fastest possible scans and the lowest possible spot size minimized the drift problem without compromising the quality of the patterns to any great extent. Our longest scanning times did not exceed 5-6 minutes. A 4×4 binning of the patterns reduced the acquisition time considerably without compromising the quality of the patterns needed for our work. An accelerating voltage of 25 kV was used to more accurately measure the narrow bands and a convolution mask of 5×5 pixels was used to enhance and identify peaks in the Hough transform of the EBSD patterns.

Figure 1. The sampling strategy for EBSD and TEM investigations
4. Results and Discussion

Figure 2a is a secondary electron image showing an overall distribution of domains across several grains in a PZT sample; the lamellar structure of the domains can be clearly seen across much of the surface, and it is also clear that multiple domain structures occur within each grain. A bright field image (Figure 2b) of parallel domains from a La-Sr doped 42.5\% Zr/57.5\% Ti sample depicts locations from where 8 Kikuchi patterns were obtained. These Kikuchi patterns were indexed using the EP software and the misorientations between adjacent points in the two domains are given in Table 1. It was found in both this case, and many others that provided suitable patterns are recorded with sufficient intensity to allow clear band detection to the edges of the image, that unambiguous indexing of the unit cell orientation (not just of the pseudocubic perovskite cell, but also including of the long c-axis direction) could routinely be achieved. In previous work, MacLaren et al. [3] showed that the \( c/a \) ratio should be related to the deviation of the misorientation angle from 90° by \( c/a = 1/\tan(90°-δ)/2 \) and this is used in Table 1 to evaluate the local \( c/a \) ratios from the measured misorientation angles. Three of the misorientations are very similar but the misorientation 1-2 taken close to the edge is significantly different; this is probably related to sample bending and does not reflect real local crystallography in these materials. It is thus clear that the Kikuchi diffraction patterns are best recorded in material that is thick enough to prevent significant local relaxation and bending or spurious results may be obtained.

Figure 2. (a) Domain structure of a composition 37.5\%Zr/62.5\%Ti PZT sample after etching. (b) Bright field image of domains in La-Sr-doped PZT 42.5\%Zr/57.5\%Ti with the locations of CBED patterns marked.

Figure 3a shows an EBSD orientation map of a lamellar domain structure in an undoped 50-50 PZT. Statistical distributions for the misorientation angles across the domain boundaries were obtained from the OIM software. Similar EBSD maps have also been obtained from other samples with various compositions. The values of \( c/a \) ratios were calculated from the misorientation angles using the formula given above and these are summarised in Table 2 together with the results from TEM-Kikuchi based measurements. For comparison with global measurements, \( c/a \) ratios
were also determined from X-ray diffractograms using simple comparison of the (200) and (002) peak positions with zero point correction; these are also summarised in Table 2.

Table 1. Misorientations calculated from the orientations of the regions marked in Figure 2b.

| Position pair | Misorientation (°) | c/a ratio |
|---------------|--------------------|-----------|
| 1-2           | 87.6               | 1.0427    |
| 3-4           | 88.74              | 1.0222    |
| 5-6           | 88.36              | 1.0290    |
| 7-8           | 88.32              | 1.0297    |

A comparison of the local c/a ratio measurements made by EBSD with the global measurements made by XRD seems to show a broad agreement between the two. However, local deviations from the average crystallographic distortions obtained from X-ray diffractograms are also evident in Table 2. These discrepancies could arise from real local changes in lattice parameters due to compositional inhomogeneities or internal stresses, or from experimental factors such as deformation or stress release (especially for thin TEM specimens) in sample preparation, or indexing errors due to poor quality patterns. Until further experiments on the estimation of the experimental errors have been completed, it is impossible to determine if these discrepancies arise from local variations in lattice parameters.

Table 2. Determination of c/a ratios by different techniques.

| Type of PZT  | Composition (%Zr/%Ti) | XRD c/a ratio | TEM - Kikuchi 90° - δ | Local c/a 90° - δ | EBSD Local c/a |
|--------------|-----------------------|---------------|------------------------|-------------------|----------------|
| La-Sr doped  | 42.5/57.5              | 1.0301        | 88.47 ± 0.232          | 0.004             | 0.34 ± 0.006   |
|              | 50/50                  | 1.0239        | 88.61 ± 0.377          | 0.007             | 0.12 ± 0.002   |
| Undoped      | 50/50                  | 1.0277        | 88.27 ± 0.08           | 1.031 ± 0.001     | 89.00 ± 0.32   |

5. Conclusions and further outlook

We have for the first time been able to unambiguously resolve 90° domain structures in a tetragonal perovskite structure using EBSD, which was only possible through a combination of advances in sample preparation, optimisation of SEM/EBSD operation, and of the EBSD indexing settings. We have also demonstrated that unambiguous automated indexing of Kikuchi patterns from TEM can routinely be achieved allowing straightforward determination of domain misorientations in the TEM. Misorientation measurements at domain boundaries have been used to determine local crystallographic distortions and in spite of small variations most measurements accord well with global measurements made by X-ray diffraction. Future work will concentrate on separating real variations in local misorientations from experimental errors, and on using these misorientation measurements to study the stress concentrations at boundaries between different domain structures and at grain boundaries.

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