ESRF	**Experiment title:** Residual Stress in PZT Ceramics	**Experiment number**: ME-441
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Report:

The main aim of the experiment was to determine the variations in lattice strain and crystallographic texture as a function of crystal orientation ψ (relative to the macroscopic polar axis) in poled tetragonal and rhombohedral PZT (lead zirconate titanate) ceramics. These data can then be used to determine the residual intergranular stress, which arises due to ferroelectric domain switching during poling. In addition, a preliminary study was conducted to evaluate the feasibility of "in-situ" electric field-induced ferroelectric domain switching experiments under high field levels up to 3 kV mm^{-1}.

A range of 'soft' PZT ceramics, modified with La and Sr dopants, were prepared at the Manchester Materials Science Centre, with Zr/Ti ratios from 50/50 (tetragonal) to 58/42 (rhombohedral). A mixed phase region was identified at Zr/Ti = 54/46, corresponding to the morphotropic phase boundary for this system. Small rectangular bars, measuring approximately 10 x 1 x 1 mm^3, were mounted on the KUMA 4-axis diffractometer, and investigated in transmission geometry using a monochromatic X-ray energy of 70 keV. The attenuation length at 70 keV in PZT is estimated as 0.5 mm, and so a specimen of 1 mm depth can be regarded as sufficiently homogeneously irradiated. By rotating the specimen about the beam axis, it was possible to obtain diffraction spectra over a range of crystal orientations, from ψ = -90° to +90°.

For poled tetragonal PZT ceramics, the {111} diffraction peak exhibited a significant shift as a function of ψ, as illustrated in Fig. 1(a), indicating a change in lattice strain as a function of crystal orientation. In addition, the {002} and {200} peaks showed the expected reversal in relative intensities associated with a preferred ferroelectric domain orientation, as shown in Fig 1(b). Poled rhombohedral PZT ceramics exhibited a similar behaviour, although in this case the most significant peak shifts were found for {200} and the preferred orientation was most evident in {111}.

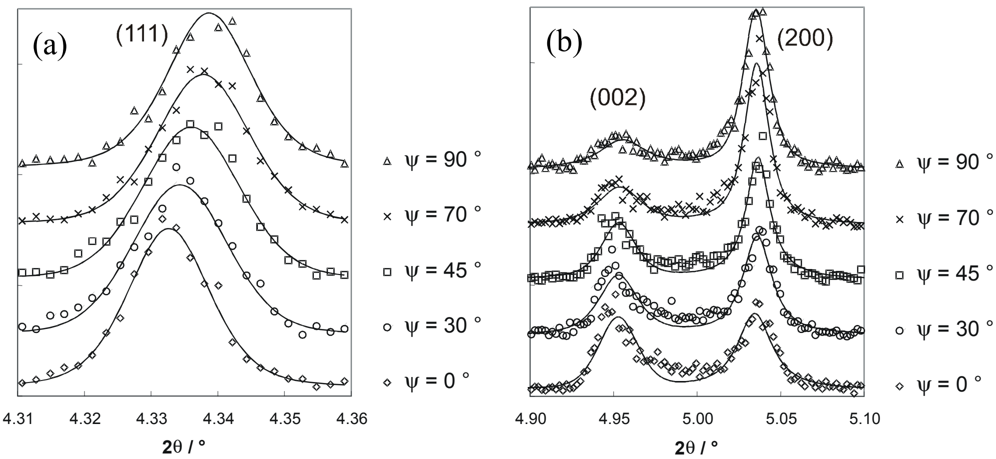

Fig. 1.

XRD scans over {111} and {200} reflections for tetragonal PZT ceramics (Zr/Ti = 52/48).

Further analysis of the data revealed that both the lattice spacing $d_{\{111\}}$ and the ferroelectric domain texture, quantified in terms of the intensity ratio $R_{\{200\}} = I_{\{002\}}/(I_{\{002\}}+I_{\{200\}})$, showed a linear dependence on $\sin^2\psi$, as illustrated in Fig. 2. Similar observations were made for $d_{\{200\}}$ and $R_{\{111\}} = I_{\{111\}}/(I_{\{111\}}+I_{\{11\text{-}1\}})$ in poled rhombohedral PZT ceramics.

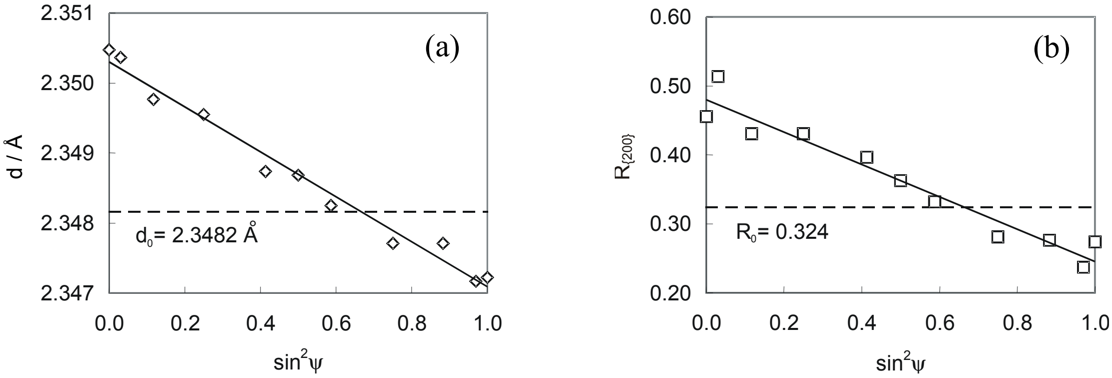

Fig. 2. Variations in (a) $d_{\{111\}}$ and (b) $R_{\{200\}}$ for poled tetragonal PZT ceramics (Zr/Ti = 52/48).

These observations can be understood in terms of the coupling between the intrinsic (lattice strain) and extrinsic (ferroelectric domain switching) mechanisms, as a result of intergranular stresses. Using an Eshelby-type micro-mechanical model, it can be shown that both $d_{\{111\}}$ and $R_{\{200\}}$ for poled tetragonal PZT ceramics should show a linear dependence on $\sin^2\psi$, in agreement with the observed relationships. Furthermore, it is predicted that $R_{\{200\}} = 1/3$ (or $R_{\{111\}}=1/4$ for rhombohedral ceramics) when $\sin^2\psi = 2/3$, which is also in agreement with the experimental results. This occurs because the macroscopic strain associated with ferroelectric domain switching is positive along the polar axis and negative in the orthogonal directions, falling to zero at $\sin^2\psi = 2/3$ ($\psi = 41.8$ °).

The feasibility exercise to monitor changes in lattice strain and ferroelectric domain texture in-situ as a function of an applied electric field was conducted successfully, using a high voltage (± 5 kV) amplifier in conjunction with a general purpose function generator (HP33120A). Preliminary results were obtained showing a gradual increase in lattice strain and texture for rhombohedral PZT ceramics in response to an applied electric field up to 2.5 kV mm^{-1}, as illustrated in Fig. 3.

The results obtained from the experiments are highly significant in that they provide direct evidence for coupling between the intrinsic and extrinsic contributions to the electro-mechanical response of ferroelectric ceramics, as a result of intergranular residual stresses. It is likely that a similar coupling also occurs at lower sub-switching electric fields, which are most relevant to the application of such materials in piezoelectric actuators. Therefore, these observations will help to clarify the origins of the nonlinear dielectric and piezoelectric responses in piezoelectric ceramics, since it has often been assumed in previous literature that the nonlinear component can be attributed solely to the extrinsic (domain switching) mechanism and that the intrinsic (lattice) strain is entirely linear. Further in-situ studies are necessary to confirm whether the type of coupling described above does indeed occur at lower (sub-switching) electric field strengths.

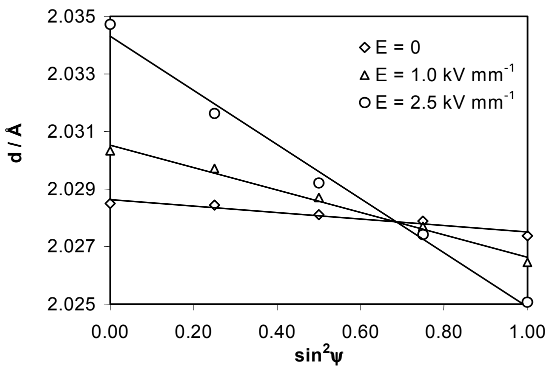

Fig. 3. Variation in $d_{\{002\}}$ for rhombohedral PZT ceramics (Zr/Ti=58/42) at various fields.

A detailed paper describing the results of the experiments on poled PZT ceramics has been completed and submitted recently to a leading journal.[1] A second paper, which develops further the micro-mechanical model for the observed inter-granular stresses in ferroelectric ceramics, is currently being prepared.[2]

1. *Synchrotron X-Ray Study of Crystallographic Texture and Lattice Strain in Poled and Unpoled Soft PZT Ceramics*, D.A. Hall, A. Steuwer, B. Cherdhirunkorn, T. Mori and P.J. Withers (submitted to Phys. Rev. B).
2. *Model for Coupling between Lattice Strain and Domain Switching in Ferroelectric Ceramics*, T. Mori, D.A. Hall, A. Steuwer and P.J. Withers (in preparation).