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Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

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Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

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Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** Stress-induced domain switching and ferroelectric-antiferroelectric phase transformations in PZT ceramics	**Experiment number**: ME-1014
Beamline: ID11	**Date of experiment**: from: 24/6/2005 to: 28/6/2005	**Date of report**:
Shifts:12	**Local contact(s)**: Dr. Jon Wright	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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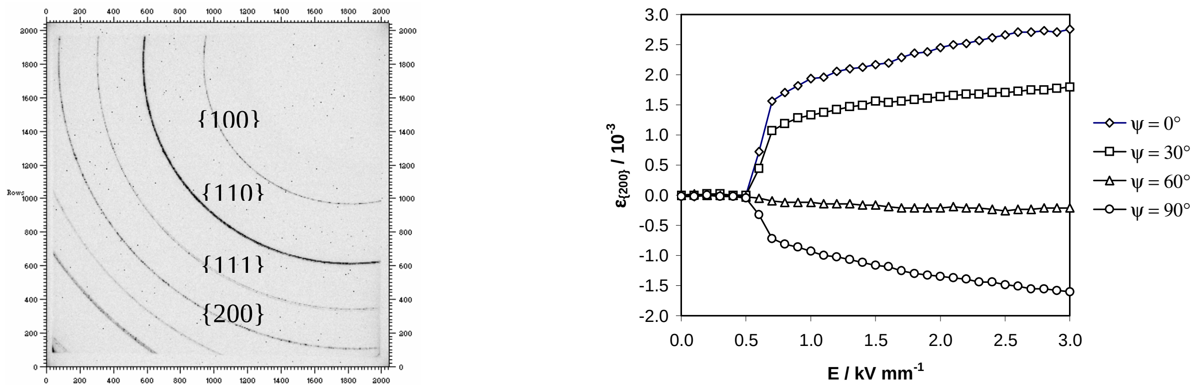
The purpose of the experiment was to evaluate the structural changes induced in PZT (Lead Zirconate Titanate) ceramics under combined electrical and mechanical loading. Ceramic specimens having compositions lying on both sides of the morphotropic phase boundary at Zr/Ti ≈ 53/47 were examined using high energy XRD on ID11. Several rhombohedral (Zr/Ti = 60/40) and tetragonal (Zr/Ti = 47.5/52.5, 50/50 and 52/48) materials were investigated. One composition close to the AFE-FE (Antiferroelectric-Ferroelectric) phase boundary at Zr/Ti ≈ 95/5 was also studied in order to determine the changes in structure caused by the stress-induced rhombohedral (FE) to orthorhombic (AFE) phase transformation. An electric field of up to 4 kV mm^{-1} and a uniaxial compressive stress up to 300 MPa were applied along the polar axis of the specimen, perpendicular to the direction of the incident x-ray beam.

The electric field and mechanical load were both controlled remotely using a Chevin Research high voltage amplifier and a Deben Microtester respectively. 2-dimensional diffraction patterns were recorded using the *Frelon* CCD camera with an acquisition time of 20 s and with an x-ray photon energy of 80 keV. As an illustration of the results obtained during the experiment, a typical 2-D diffraction pattern obtained after poling a rhombohedral PZT 60/40 ceramic is shown in Fig. 1(a). Analysis of the diffraction patterns using *Fit2D* and *X-fit* (available from the CCP14 web site) demonstrated that after poling both the position of the {200} peak and the relative intensities of the (111) and $(\bar{1}11)$ peaks exhibited significant variations as a function of the grain orientation, ψ, due to the development of residual stress and ferroelectric domain switching respectively.

The lattice strain ε{200} and the ferroelectric domain fraction R(111) both exhibited abrupt changes at an electric field of 0.7 kV mm^{-1} due to ferroelectric domain switching, as shown in Fig. 1(b) for lattice strain. ε{200}was positive (tensile) along the poling direction, at ψ = 0°, and negative (compressive) in the transverse direction, at ψ = 90°, in agreement with previous studies.[1,2] The domain fraction R(111) also increased for {111} type grains oriented at ψ = 0° and reduced for grains oriented at ψ = 90° due to reorientation of ferroelectric domains along the direction of the applied electric field.



(a) (b)

Fig. 1. (a) Typical 2-D diffraction pattern for poled rhombohedral PZT ceramic and (b) change in lattice strain ε{200} during poling up to 3 kV mm^{-1}.

The ε{200}-cos^{2}ψ plot derived from these results, Fig. 2(a), was approximately linear, in agreement with previous results and in accordance with our micromechanical model.(2) In contrast, the R(111)-cos^{2}ψ plot became distinctly nonlinear and showed evidence of saturation of domain switching near ψ = 0° and for ψ > 60°. These data confirm the observations made in our earlier in-situ study of rhombohedral PZT ceramics.(3)

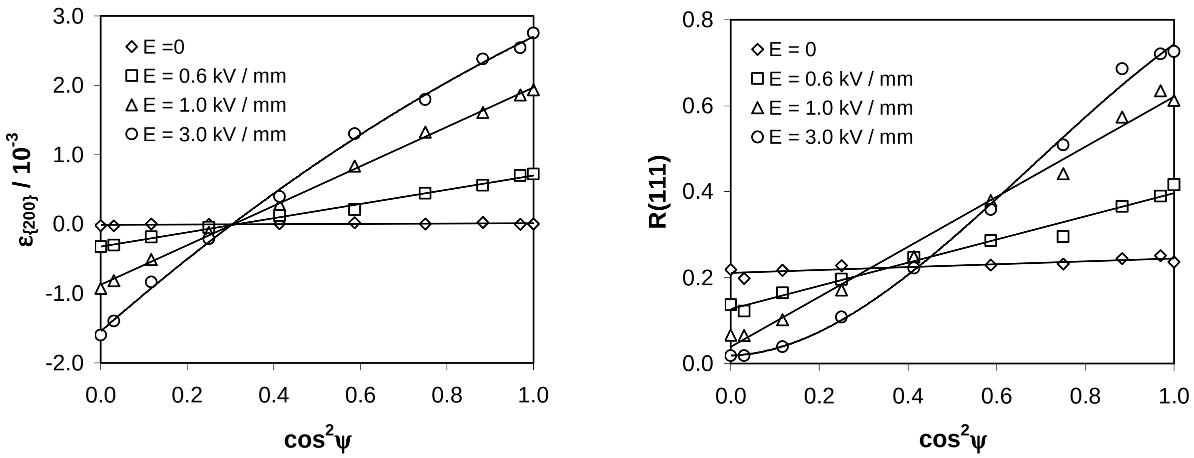


Fig. 2. (a) ε{200}-cos^{2}ψ and (b) R(111)- cos^{2}ψ relationships for rhombohedral PZT ceramics under various electric field levels.

The application of a uniaxial compressive stress to a previously poled specimen gave rise to a gradual reversal of the lattice strain from tensile to compressive for ψ = 0° and caused ferroelastic domain switching away from the polar axis, as shown in Fig. 3(a). Various experiments were also carried out to explore the combined influence of an applied electric field and a uniaxial compressive stress. It is shown in Fig. 3(b) that under a static compressive stress of 100 MPa, the anisotropy in lattice strain was gradually reduced by an applied electric field until an almost uniform state of strain was obtained at a field of 3 kV mm^{-1}.

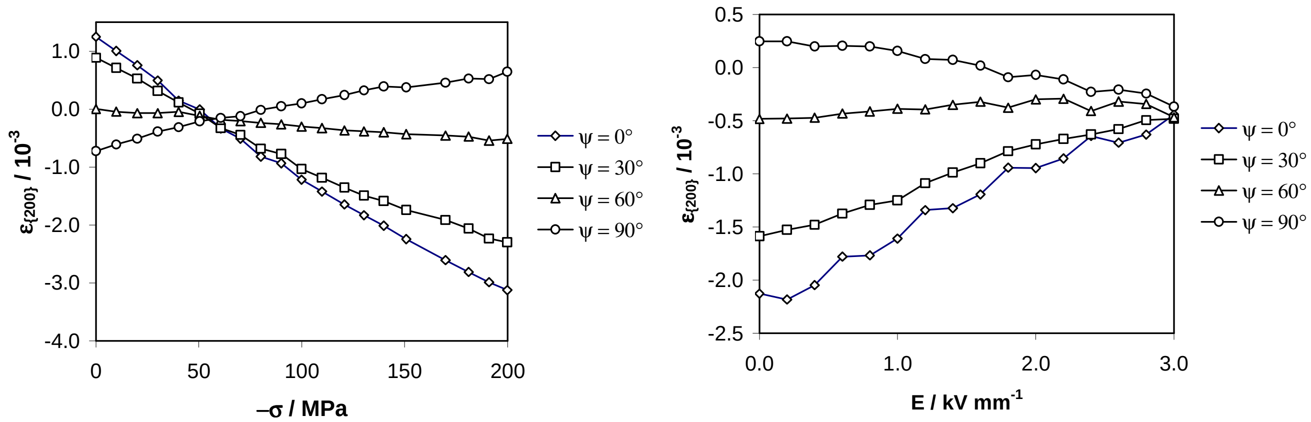
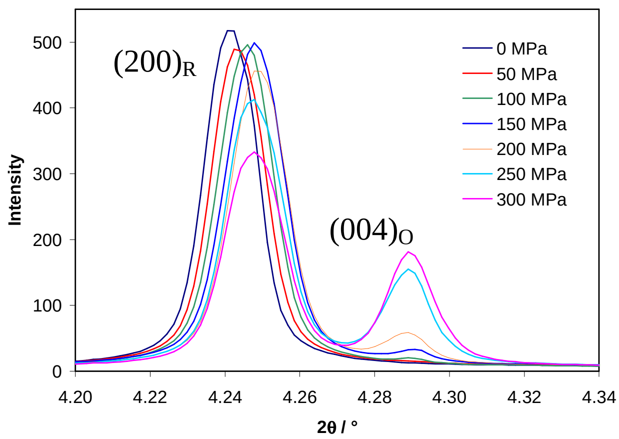
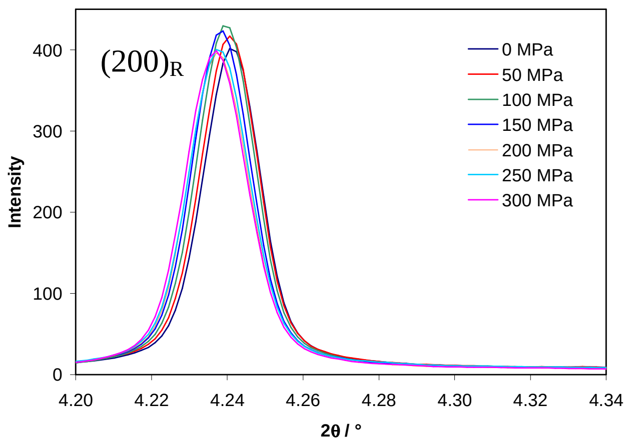


Fig. 3. Changes in lattice strain ε{200} for poled PZT ceramics under (a) increasing compressive stress (zero field) and (b) increasing electric field at a static stress of 100 MPa.

The occurrence of a stress-induced ferroelectric to antiferroelectric phase transformation in rhombohedral PZT ceramics having a Zr/Ti ratio of approximately 95/5 was investigated by examining the changes in the diffraction patterns on increasing stress from 0 to 300 MPa. It was found that a new diffraction peak, which could be identified as the $(004)_O$ reflection of the antiferroelectric orthorhombic phase, appeared for stresses above 150 MPa, as illustrated in Fig. 4(a). Furthermore, the position of the rhombohedral $(200)_R$ reflection shifted progressively under stress up to 150 MPa, indicating an elastic strain, but then remained approximately constant as the rhombohedral (FE) to orthorhombic (AFE) phase transformation progressed. These results can be explained in terms of the occurrence of a gradually increasing tensile residual stress in the untransformed rhombohedral phase. The total stress, comprising the sum of the compressive applied stress and the tensile residual stress, remains approximately constant during the course of the transformation with the result that the lattice parameter of the untransformed rhombohedral phase is almost unchanged for stresses between 150 and 300 MPa.



(a)



(b)

Fig. 4. Changes in {200} diffraction patterns of PZT 95/5 ceramics under increasing compressive stress, for grain orientations at (a) $\psi = 0°$ and (b) $\psi = 90°$.

It was also found that the stress-induced orthorhombic (AFE) phase was strongly textured, with the shorter c-axis being oriented preferentially along the direction of the applied uniaxial compressive stress. As a result of this, the $(004)_O$ reflection was absent in the diffraction patterns for grains oriented at $\psi = 90°$, as shown in Fig. 4(b). The data obtained from this investigation confirm the results of our previous study of the rhombohedral (FE) to orthorhombic (AFE) phase transformation in PZT ceramics, which was carried out using neutron diffraction at ISIS.[(4)] Further analysis of the results will also be undertaken in order to quantify the fraction of orthorhombic phase for intermediate grain orientations between 0° and 90° and to demonstrate the suppression of the antiferroelectric phase by an applied electric field.

The experiments conducted were highly successful in that the ferroelectric domain switching behaviour and FE-AFE phase transformations in a range of PZT based ceramics were examined under the combined influence of an applied electric field and compressive stress. Some of the results obtained from the study have confirmed the findings of our previous work, while others have yielded new information on the competing effects of electric field and mechanical stress on the lattice strain or domain fractions. In comparison with our previous experiments (ME-441 and ME-881), which were carried out using the Kuma diffractometer, the use of the *Frelon* 2-D detector has improved the data acquisition rate by a factor of at least 50, with only a small reduction in angular resolution. The resulting combination of high energy synchrotron XRD with the *Frelon* detector on beamline ID11 at ESRF has been proven to provide an ideal facility for dynamic studies of domain switching and phase transformations in ferroelectrics.

References

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2. D.A. Hall, A. Steuwer, B. Cherdhirunkorn, P.J. Withers and T. Mori, Acta Materialia 54, 3075-3083 (2006).
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