![ESRF logo] ESRF	**Experiment title:** Micromechanics of Residual Stress in High Temperature Piezoelectric Ceramics	**Experiment number**: ME-881
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The requirement for piezoelectric ceramic materials suitable for use in high temperature (>200 °C) environments has stimulated the search for new compositions having ferroelectric Curie points substantially higher than those of conventional PZT (lead zirconate titanate) based materials (approximately 350 °C, depending on composition). To date, the most promising materials are based on $BiScO_3$-$PbTiO_3$ solid solutions, which exhibit T_c values in the region of 450 °C.[1] At present, there have been few reports of the durability or domain switching behaviour in such materials. This is a key issue for their practical performance, since a high T_c is usually associated with a high *spontaneous strain* i.e. the transformation strain from the high temperature cubic to the low temperature ferroelectric tetragonal or rhombohedral structures. This could lead to excessive residual stress and hence problems with electromechanical fatigue.

The aim of the experiment was to investigate the domain switching behaviour and the development of residual stress in high T_c ferroelectric ceramics, using the methods developed during the previous investigation of residual stress in PZT ceramics.[2,3] The materials used in the study were ceramics based on BSF-PT ($BiSc_{0.5}Fe_{0.5}$-$PbTiO_3$) solid solutions, prepared by I. Sterianou (University of Sheffield, UK).[4] The BSF/PT ratios of these materials were in the range from 45/55 to 55/45, spanning the tetragonal-rhombohedral MPB (morphotropic phase boundary) in this system. High energy X-ray diffraction patterns were obtained using the KUMA diffractometer on station ID11, with monochromatic X-rays having a wavelength of 0.2486 Å. Examination of the {111} and {200} diffraction peaks revealed that the 45/55 composition was single phase tetragonal, while the 50/50 and 55/45 compositions were single phase rhombohedral, as illustrated in Fig.1. The 47/53 composition appeared to be mixed phase tetragonal and rhombohedral, indicated by the splitting of both the {111} and {200} reflections. Quantitative analysis of the broad {200} diffraction peaks for the 45/55 and 47/53 compositions was hindered by the presence of an extraneous peak at approximately 6.73 ° 2θ (not shown in Fig. 1), which was attributed to the Au(200) reflection from the conductive electrodes on the specimen surfaces. For this reason, the study focused mainly on the rhombohedral materials.
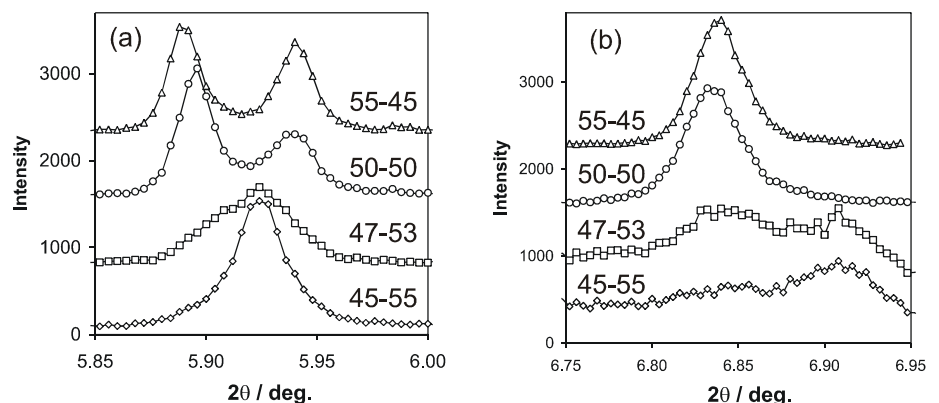

Fig. 1. XRD patterns for (a) {111} and (b) {200} reflections for BSF-PT ceramics poled at 4 kV mm^{-1}.

The elastic strain, $\varepsilon\{200\}$, and ferroelectric domain texture, represented by the peak intensity ratio $R(111) = I(111)/(I(111)+I(\bar{1}11))$, were determined as a function of the grain orientation ψ relative to the direction of poling by rotating the specimen about the x-ray beam axis. It was found that both $\varepsilon\{200\}$ and $R(111)$ exhibited a linear dependence on $\cos^2\psi$, as shown in Fig. 2, similar to that observed for rhombohedral PZT ceramics.[2,3] This behaviour can be understood using a micromechanical model for poled rhombohedral ferroelectric ceramics, developed recently by the authors.[5] The gradient of the $R(111)$-$\cos^2\psi$ plots was similar for the 50/50 and 55/45 compositions, indicating that a similar degree of ferroelectric domain switching occurred during poling. However, the elastic strain $\varepsilon\{200\}$ was significantly higher for the 50/50 composition. The latter result is unexpected, since it was anticipated that the 55/45 composition, having a slightly larger rhombohedral distortion, would exhibit the higher elastic strain, as explained below.
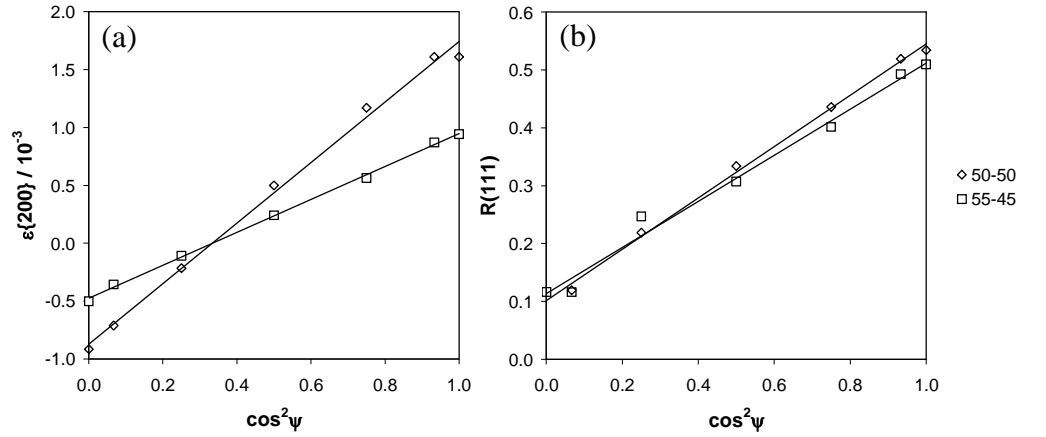
Fig. 2. Analysis of (a) elastic strain $\varepsilon\{200\}$ and (b) domain fraction $R(111)$ for rhombohedral BSF-PT ceramics poled at 4 kV mm^{-1}.

For {111} oriented grains, the domain fraction, $\overline{f_1} = R(111)$, is related to the average strain along the poling direction, $\bar{\varepsilon}_{33}^P(X,111)$, by the following expression

$$\frac{2\gamma}{3}(4\overline{f_1}-1) = \bar{\varepsilon}_{33}^P(X,111)\left(\frac{3}{2}\cos^2\psi - \frac{1}{2}\right), \tag{1}$$

where γ is the shear strain for the cubic to rhombohedral transformation.[5]

The elastic strain $\varepsilon\{200\}$ is related to the macroscopic strain along the poling direction, $<\varepsilon>$, as follows:

$$\bar{\varepsilon}_{33}(Z,\{200\}) = \frac{(7-5\nu)}{15(1-\nu)}<\varepsilon>\left(\frac{3}{2}\cos^2\psi - \frac{1}{2}\right). \tag{2}$$

If the lattice elastic strain $\varepsilon\{111\}$ is small, then the poling strain $\bar{\varepsilon}_{33}^P(X,111)$ is approximately equal to the macroscopic strain $<\varepsilon>$ and is proportional to both $R(111)$ and γ. Therefore, we expect that if $R(111)$ is approximately equal for the two compositions, the elastic strain $\varepsilon\{200\}$ should be determined by the transformation shear strain γ. In the present case, the γ values for the 50/50 and 55/45 compositions were determined from the $d(111)$ and $d(\bar{1}11)$ lattice spacings as 0.0027 and 0.0032 respectively. The fact that the elastic strain is significantly higher for the 50/50 composition, which exhibits the lower transformation shear strain, indicates that an important additional factor has not yet been considered. The most likely cause of this discrepancy is the vicinity of the 50/50 composition to the MPB, which could lead to some tetragonal phase being present. Changes in the relative intensities of the (002) and (200) diffraction peaks for this phase during poling would lead to an apparent shift of the rhombohedral {200} peak, which could explain the large elastic strain of the 50/50 composition in Fig. 2(a) above.

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