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Application for beam time at ESRF – Experimental Method

Mapping of the Ferroelectric Phase and Domain Structure of PMN-PT
Single Crystals with In-Situ Electric Fields

Aims of the experiment and scientific background

The proposed experiment involves using synchrotron x-rays to image for the first time the ferroelectric phase and domain structure of single crystals of PMN-PT ($Pb[Mg_{1/3},Nb_{2/3}]O3$ – PbTiO3). These materials are of considerable technological interest because they have very large electromechanical coupling coefficients. Their enhanced properties are a consequence of electric field induced phase transformations. The proposed experiment follows on from an exploratory experiment performed on XMAS in October 05 in which we studied these transformations with in-situ electric fields. The work is part of an ongoing collaboration between Queen Mary University of London and The National Physical Laboratory.

Ferroelectric oxides have a spontaneous polarisation below their Curie point as a consequence of a noncentrosymmetric, displacive transformation of their prototype structure. This coupling of their structure and polarisation gives rise to their piezoelectric properties. The most commonly used ferroelectric materials are PZT ($Pb[Zr,Ti]O_3$) ceramics, which are based on the cubic perovskite structure. Most commercial materials are based on morphotropic phase boundary (mpb) compositions. A mpb separates solid solutions of the same prototype structure but with different structural distortions. The mpb in PZT separates rhombohedral and tetragonal phases. The phase diagram of PZT has recently had to been redrawn to include monoclinic intermediate phases [eg, 1]. The enhanced properties of these materials are produced by a mixing of these phases. Under the application of electric or mechanical fields the polarisation axis can rotate producing a "compliant" electromechanical behaviour. This interpretation has been backed up by ab-initio calculations by Fu and Cohen [2]. Using domain engineering in single crystals it is possible by the use of appropriate crystal cuts to maximise the piezoelectric properties. However, it is not possible to produce useful size single crystals of PZT because it melts incongruently. However, it is possible to grow large crystals of PMN-PT and PZN-PT ($Pb[Zn_{1/3},Nb_{2/3}]O3$ – PbTiO3) with mpb compositions. The pioneering work at Penn State by Tom Shrout [eg, 3] has shown that it is possible to achieve piezoelectric properties that are nearly an order of magnitude greater than those achievable with PZT ceramics. The field induced transformation of ferroelectrics is far from fully understood. For instance, it is not clear whether these transitions are continuous and reversible or irreversible and proceed by 1st order jumps in the polarisation.

In the case of PMN-PT the mpb also involves an orthorhombic intermediate phase [4]. The crystals are produced with compositions just on the rhombohedral side of the mpb. They are cut with their <111> spontaneous polarisation direction off-axis to the applied electric field direction. Under the application of an electric field the polarisation axis can rotate to the orthorhombic or tetragonal distortions depending on the crystal cut. In our exploratory experiment on XMAS we studied in-situ the electric field induced phase transformation of a PMN-32mol% PT single crystal with the field applied parallel to a <110> direction. We observed a hysteresis of the rhombohedral to orthorhombic phase transformation under in-situ bipolar electric fields. By cycling the electric field we found that the transformation was 1st order and recoverable (Figures 1).

The piezoelectric properties of the materials have contributions from the intrinsic linear response of the different phases, and the nonlinear contributions from the phase transformations and movement of the ferroelectric domains. Therefore, in order to model the behaviour of these materials it is necessary to understand the evolution of the phases and their domain structures under bipolar switching. At present this knowledge is not available, but could be provided by x-ray mapping. It is not possible to study this structure using other techniques, such as, optical microscopy, transmission or scanning electron microscopy. For instance, in optical microscopy it is not possible to identify the different phases.

Experimental method

The proposed experiments will be performed on PMN-32mol%PT single crystals supplied by TRS with (001), (110) and (1-10), and (001), (010) and (100) cuts and with the fields applied parallel to the [1-10] and [001] directions respectively. This will allow us to study the phase and domain evolution in rhombohedral to orthorhombic, and rhombohedral to tetragonal field induced transformations respectively. To do this study we will use the electric field stage developed for the exploratory study. This was, in fact, the first in-situ high voltage experiment (3kV) ever performed on XMAS. Using an xyz stage and tube slits, we will image the ferroelectric phases and their domain variants as a function of applied electric field. It has been shown that the separation of the twin boundaries of rhombohedral PMN-32mol%PT are >200 μm [5] and therefore resolvable by XRD mapping. This proposed experiment is demanding because of the presence of different phases and their domain variants. To assist us we will use the 2D-camera with a θ-scan to map volumes of reciprocal space. This will allows us to quickly identify appropriate reflections. The software required to analyse the 2-D data is currently being developed by the beamline scientists. If the technique works it will open up the possibility in future work of quantify the proportions of the different phases and their domain variants. This would provide valuable quantitative data to inform and test micromechanical models. It would allow the phase equilibrium diagrams as a function of temperature, electric field and mechanical stress to be quickly mapped.

Results expected

The results from this experiment will provide the first direct information on the phase and domain structure of PMN-PT single crystals with in-situ electric fields. The results from the experiment will improve our understanding of these technologically important materials and assist the development of microelectromechanical models.

References

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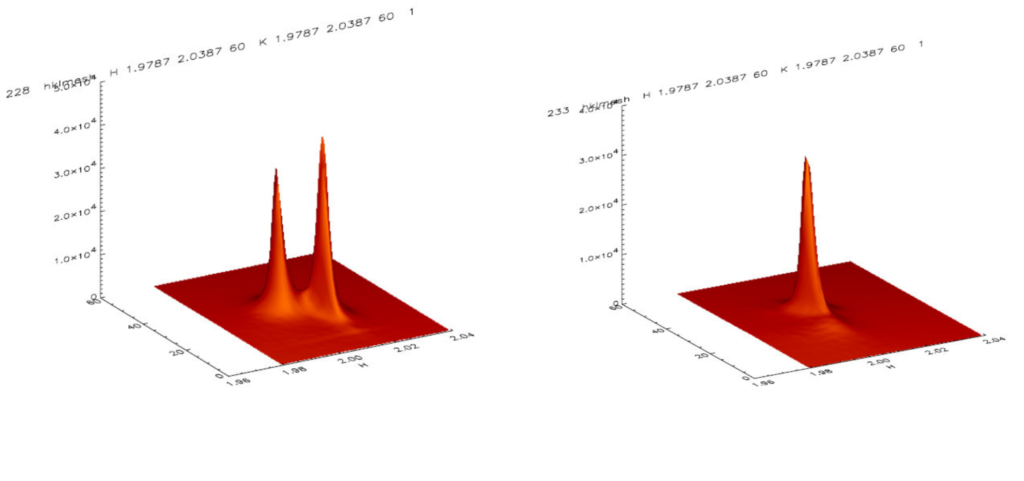

Figure 1 (a) rhombohedral variants at +3kV and (b) orthorhombic variants at -3kV.