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Morphotropic Phase Indentification in single crystal piezoelectrics via in situ electrical, thermal and mechanical induced phase transitions.

Aims of the experiment and scientific background

The experiment involved using synchrotron x-rays to study for the first time the bipolar ferroelectric phase transformations and structure of single crystals of PMN-PT ($Pb[Mg_{1/3},Nb_{2/3}]O3$ – PbTiO3) under applied electric field. 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 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.

Experimental Detail and Results

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. The experiments were performed on PMN-32mol%PT single crystals supplied by TRS with a (110) cut and with the fields applied parallel to the [110] direction. This allowed us to study the phase and domain evolution in rhombohedral to orthorhombic field induced transformations. This experiment was the first in-situ high voltage experiment (3kV) ever performed on XMAS. We observed a hysteresis of the rhombohedral to orthorhombic phase transformation under in-situ bipolar electric fields, figure 1. By cycling the electric field we found that the transformation was 1st order and recoverable.

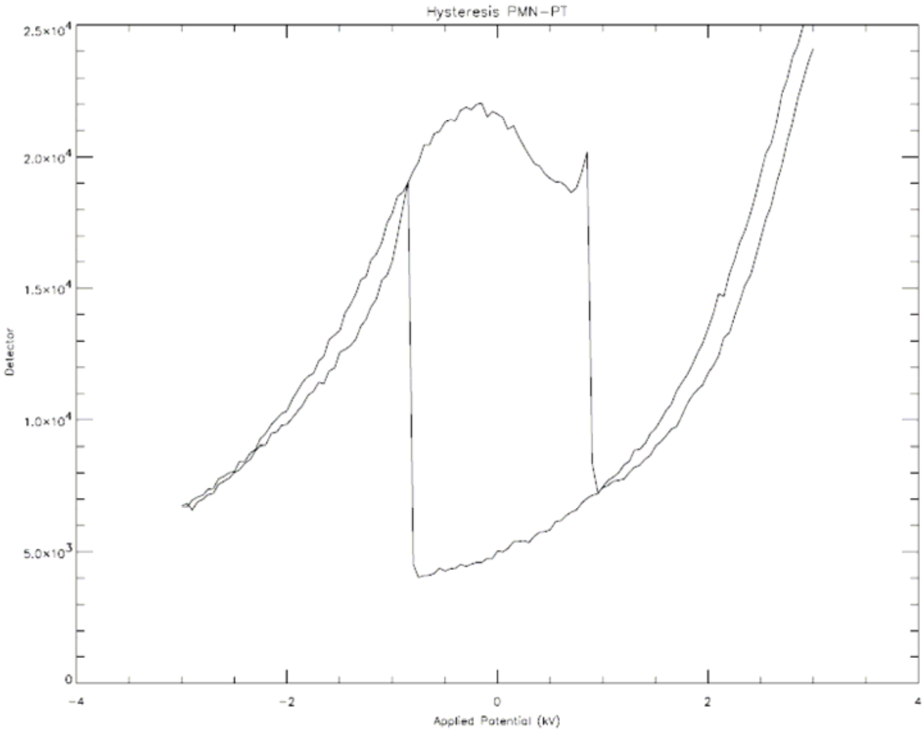
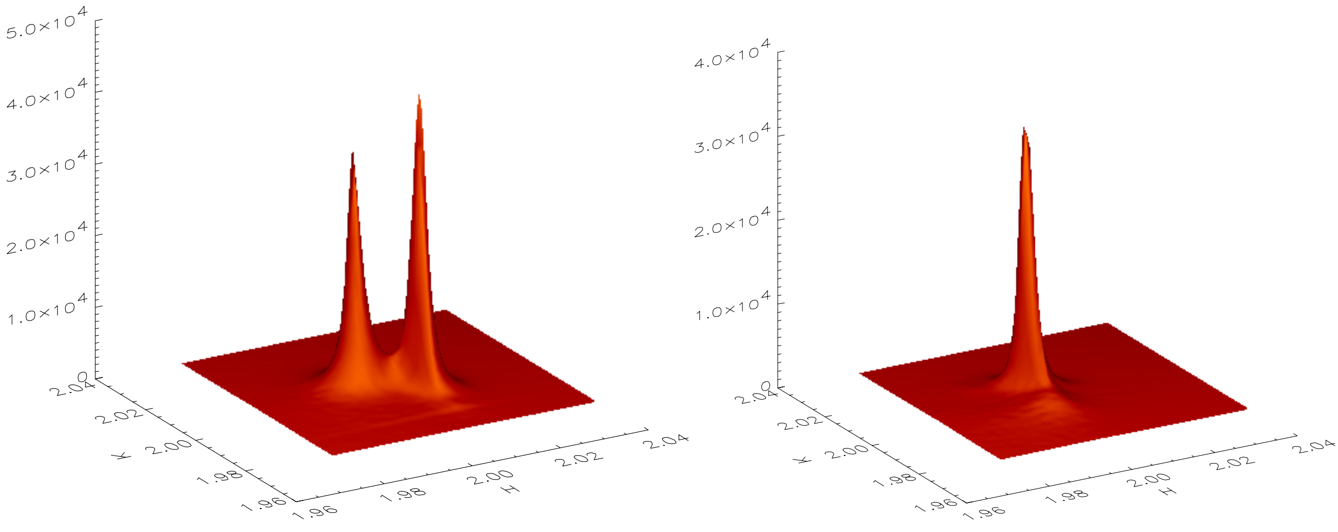


Figure 1: Hysteresis observed during the electric field induced rhombohedral to orthorhombic phase transition. The detector signal is from the pseudo-cubic (222) peak.

Interpretation of figure 1 may be summarised:- an increase in the detector signal with an increasing applied positive field was due to the piezoelectric effect of the material witnessed as a gradual shift away from our fixed diffraction geometry set-up. As the field was then reduced, at approximately –1kV, a sudden jump in intensity was observed. This was due to a crystallographic phase transformation that resulted in enhanced diffraction. The sample continued to contract with an increasing negative voltage, and upon reversal of the sign of the applied field, we once again observed the phase transition, this time at a net positive electric field. The hysteretic behaviour indicates it was a first order transformation, with the possibility of co-existence of both rhombohedral and orthorhombic phases present at the phase boundary [5].

In this experiment we imaged diffraction around the (222) pseudo-cubic reflection. Two example HK mesh plots (around (222)) taken at +3kV and –3kV are shown in figure 2a) and 2b) respectively. It is observed that the pseudo-cubic (222) is split at high positive fields (positive indicates in the direction of original poling) and that at high negative fields (i.e. depoling fields) a single peak is observed. This indicates that at high positive electric fields the rhombohedral phase exists as two equivalent twin variants (out of a potential maximum of four for this symmetry). As the voltage is reversed a transformation to the orthorhombic phase is then observed. Previous work has suggested that an electric field induced phase transition to an orthorhombic phase occurs [6].



a) b)

Figure 2 (a) rhombohedral variants at +3kV and (b) orthorhombic variants at -3kV.

The rhombohedral twinned splitting was calculated from figure 2a) to be ± 0.21° which corresponds to α=0.105°. This is in close agreement with the rhombohedral distortion of α=89.88° [7] corresponding to an equivalent angular deviation of 0.12°.

The results from this experiment have provided the first direct information on the phase of PMN-PT single crystals with in-situ bipolar electric fields. This exploratory experiment has successfully proven the ability to monitor in-situ the electric field induced phase transformations and twin structure of single crystal piezoelectric materials. Future work will continue the exploration of the complex dynamics of these materials with particular emphasis on mapping the phase and domain meso-microstructure as a function of field, stress and temperature. XMAS is ideally suited to this task because of its collimated beam geometry and high voltage sample enclosure developed during this experiment. These results will form the basis of a future publication.

Acknowledgements

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