ESRF	**Experiment title:** Diffraction studies of ferroelectric thin films under electric field	**Experiment number**: 01-02-839
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Overview

Periodic domains arise in ferroelectric materials as a compromise in energy associated with various external forces such as depolarizing field, substrate-induced strain and applied electric field. The occurence of domains, their topologies and dynamic behaviour in response to an external electric field are issues of crucial importance for the design and application of these materials in electromechanical and optoelectronic devices.

The coercive field E_c required to reverse the polarization and create a monodomain state increases with decreasing film thickness d as $E_c(d) \propto d^{-2/3}$. For a 100 nm film of $PbTiO_3$ the local coercive field is of the order 200 kV/cm. In the present work we have studied an epitaxial film of thickness 20.7 nm, both under zero field and under weak fields $E << E_c$ in order to investigate the impact of field strength and direction on the domain structure. The diffuse scattered intensity near the Bragg reflections gives information both on the average domain periodicity and orientation.

Experimental

Our samples in these studies are epitaxial films of $PbTiO_3$ (PTO) deposited by RF magnetron sputtering onto (001) oriented insulating $SrTiO_3$ (STO) single crystal plates of dimension $a \times a \times 0.5$ mm, a = 5–7 mm. The nearly perfect lattice match between cubic STO and the *ab*-plane of tetragonal PTO ensures that the polar *c*-axis of PTO will be well aligned in the growth direction of the film, favouring the formation of *c*-oriented domains. In the present work a PTO film of thickness 50 unit cells (uc), corresponding to $d \sim 20.7$ nm, was studied by SR X-ray scattering, using a specially designed sample holder for applying an electric field along the polar axis. [1] The 500 μm thick tablet-shaped sample was fixed to the lower capacitor plate, a 0.5 mm thick copper plate with the same lateral dimensions as the sample, 7 x 7 mm. The upper capacitor plate was a 50 μm thick Kapton foil with a thin layer of gold deposited on the surface facing the sample. The distance between the capacitor plates was 2 mm. A single reflection 1 0 3 and the associated diffuse scattering were examined by scans in ω with step length 0.01° over a range of 2.5°. Scans were made without field and under fields ranging up to ~ 6 kV/cm in magnitude. Scattered intensities were recorded using a CCD detector with pixel size 60.3 μm placed orthogonal to the X-ray beam at a distance of 360 mm from the sample. The data were

binned 2x2 giving an angular resolution ~ 0.02°. Imaging with an area detector is vastly superior to linear *Q*-scans with a point detector for a complete survey of reciprocal space. Rectilinear reconstructions of reciprocal space were done with the CrysAlis software (Oxford Diffraction) and 3D visualization with new locally developed software allowing fine slicing in a selected rational direction for the subsequent construction of 3D images of the diffuse satellite intensities. A wavelength 0.9714 Å was used to avoid fluorescence from the heavy elements of the sample.

Results and brief discussion

In a previous experiment, 01-02-790, we studied three samples of different thickness *d* before application of field, under field, and again with the field switched off. In the following we refer to the parent Experiment Report 01-02-790, *cf.* also [2]. Fig 1 of the report shows various representations of reflection 1 0 3 for the 50 uc film before switching on a field. Of particular interest in the present study are intensity changes in the annular ring and in the diffuse film Bragg reflection which is part of the Bragg truncation rod, as a function of applied field strength and direction. We will define a positive field for the case that the copper plate of the capacitor has a positive charge, *i.e.* field direction is *out* from the dielectric STO substrate into the PTO film and the air gap. With this definition the field applied in Experiment 01-02-790 was negative.

Images have been recorded during cycling of the applied voltage in steps of 200 V between +1200 V and –1200 V, corresponding to nominal applied fields of +6 to –6 kV/cm. A selection of images of the same slice through the annular ring and the film Bragg reflection are collected in Fig. 1 in the Attachment. The annular ring is consistent with domain 'stripes' in a nearly random in-plane orientation. The images show the characteristic changes in diffuse scattering, reflecting changes in the domain structure. Under each figure is given the applied voltage with sign. The figures show the raw, uncorrected data, but suffice to provide a clear semi-quantitative interpretation.

For voltages up to about +800 V above the starting point V = 0, the intensity in the annular ring increases (observe anomalous result for +200 V) with a concomitant reduction of intensity in the Bragg truncation rod (BTR). The diameter of the ring translates into a mean domain period, $\Lambda \sim 22$ nm, that we have measured repeatedly for this film. Reducing the voltage from +1200 V does not change the picture significantly until at about 0 V, when a reversal of the intensity distribution begins. This process takes place and is nearly completed in the range –200 to –800 V. At the same time intensity migrates from the surrounding volume in reciprocal space into the BTR signifying a coalescence into larger domains. The magnitude of the average period Λ must be > ~ 55 nm, corresponding to the approximate diameter of the BTR. This distribution remains nearly unchanged for decreasing negative voltages from -1200 V to 0 V and further up to about +200 V when there is again a build-up of intensity in the characteristic annular ring and a depletion of intensity in the BTR. This process is over at about +800 V. The last picture included at +400 V, after reducing the voltage again below +1200 V, shows very little change, if any, in the intensity distribution. We observe that the result obtained in Experiment 01-02-790 , at –800 V, with the same film sample, is in very good agreement with the present more extensive observations.

What we have here is a hysteresis in domain size and order caused by the step-wise cycling in applied voltage between +1200 V and –1200 V. Within this range, increasing positive voltages favour a smaller domain size with *d*-specific average period ~ 22 nm. Reducing the voltage and reversal of polarity initiates a development, augmented and apparently completed in a certain range of increasing negative voltages, in which the characteristic annular ring disappears and the average domain size increases to the extent that the associated diffuse scattering is merged with the BTR. Cycling back to positive and increasing voltages brings about a complete reversal of the intensity distribution.

The graphs in Fig. 2 show the hysteresis using all measurements. The data have been approximately normalized against the integrated background intensity near the detector edge. The starting point in these plots, +200 V, is marked with a circle. In Fig. 2 *a*) points derived from the first cycle are marked with crosses. Upper and lower lobes correpond to symmetric cuts through the annular ring, Figs. 2 *a*) and *b*), respectively Fig. 2 *c*) depicts the intensity variation in Bragg and diffuse scattering in a cut through the BTR. The inverted hysteresis curve in Fig. 2 *c*) relative to those of Figs. 2 *a*) and *b*) illustrate the reversible migration of diffuse intensity associated with the field-driven changes in domain size.

Conclusions

1) We have shown that an applied field of the order 1 % of the estimated E_c for the domain structure in a 20.7 nm thick PTO film has a strong influence on the diffuse intensity distribution which is related to the domain size of the film. This is a surprising result.

2) Step-wise cycling of the voltage in the range +1200 to –1200 V, corresponding to nominal fields from +6 to –6 kV/cm, reveals an asymmetric hysteresis in the diffuse intensity distribution which must be related to a hysteretic response in domain size and order.

3) The asymmetry is linked to the field direction, the largest domain size arising when the field is directed from the air gap into the film and the underlying substrate.

4) More films must be studied, of particular interest are films with $d < 50$ uc, as the effect of a weak field is expected to decrease and, as we have shown in Exper. 01-02-790, will eventually become insignificant for films of sufficiently small thicknesses. Higher positive voltages should be applied to find out if the observed asymmetry of the hysteresis remains, or if further development is induced in the preferred *d*-specific domain size seen at +1200 V.

References

[1] F. Mo, K. Ramsøskar: A sample cell for diffraction studies with control of temperature, relative humidity and applied electric field. *J. Appl. Cryst.* (2009) **42**, 531-534.

[2] F. Mo, D. Chernyshov, L.S. Thoresen, D.W. Breiby, T. Tybell. *Acta Cryst.* (2008) **A64**, C520-521.

Attachment to report on Exper. No. 01-02-839

Fig. 1 Images of the same slice through the film Bragg reflection and the annular ring at selected applied voltages during cycling.

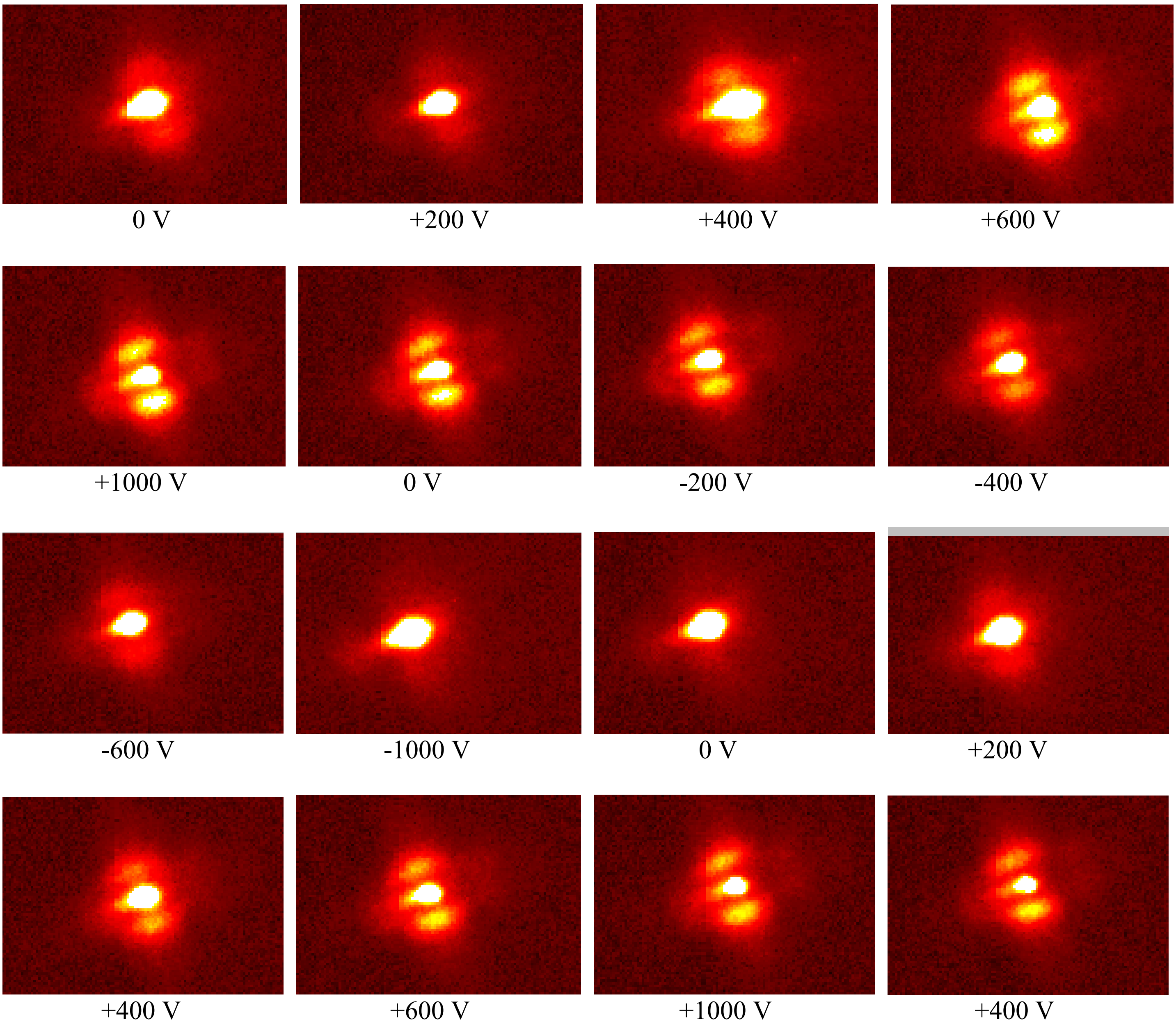
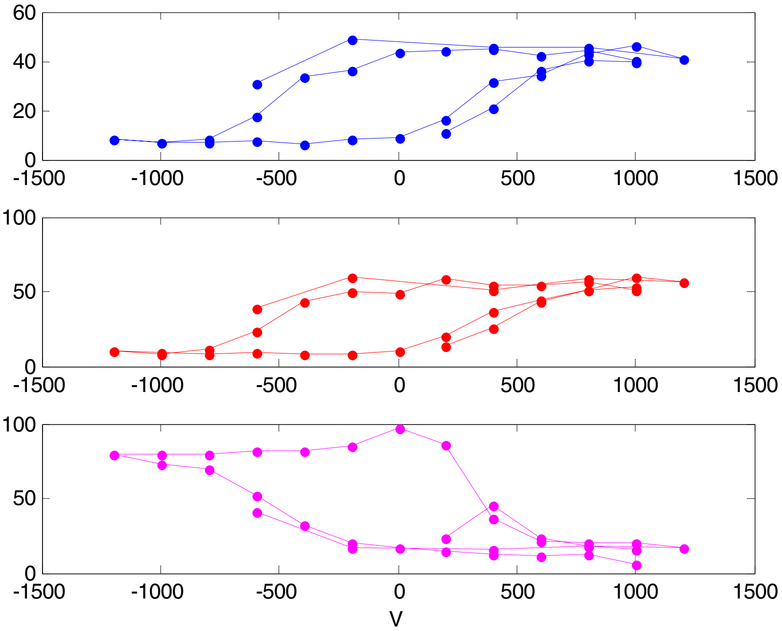


Fig. 2 Hysteresis observed in the diffuse and Bragg scattered intensities relating to changes in size and order of the domain structure. Intensities have been summed over 3 x 3 pixels. Note difference in relative intensity scale in Fig. 2 *a*) vs. 2 *b*) and *c*)



a) Diffuse intensity, upper lobe

b) Diffuse intensity, lower lobe

c) Bragg scattered and diffuse intensity in truncation rod.