ESRF	**Experiment title:** Coherent X-ray Imaging of Atomic-level Structure and Dynamics of Ferroelectric Domain Walls	**Experiment number**: ME302
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Report:

In the second allocation of beamtime for ME302, the first *in-situ* electric field poling experiments were conducted. The poling chamber was mounted on the goniometer head and a plexiglass domes, fabricated at ESRF, evacuated to between 10^{-5} and 10^{-6} torr (10^{-7} torr was obtained off-line using a glass dome). To avoid smearing of images due to the vibration of the vacuum pump, pumping had to cease during *in situ* poling and x-ray exposure, so the vacuum maintained during the poling was not as good as ideally required. This resulted in arcing across the crystals at lower fields than expected, a phenomenon deleterious to poling. The difficulty with maintaining vacuum and taking good images limited this experiment to samples that did not require the highest fields, principally $RbTiOAsO_4$ (RTA) and low-conductivity KTP (HKKTP). The samples were now coated with periodic electrodes for poling (unlike previous experiments on pre-poled crystals). Some tests were made to examine the contrast arising from periodic electrodes alone with (a) just periodic photoresist and (b) periodic photoresist + aluminium electrodes on both beam entry and exit surfaces. The contrast from these, whilst present in the near-surface regions on the periodic electrode side, was confirmed to be very weak and negligible for the majority of reflections of interest.

An (001) flux-grown RTA slice from Coherent Crystal Associates was patterned with a 38μm periodic grating in the [100] direction. With the crystal under vacuum conditions, white-beam section topographs were taken as a function of applied electric field in the sequence zero-field, positive voltage applied, negative voltage applied, zero-field *etc.*, for applied fields up to ±2.5 kV/mm. The field was delivered as a series of sinusoidal pulses of duration 16.5 ms (frequency 30 Hz). For each application, the actual voltage delivered to the crystal and the current (capacitative, ferroelectric switching or conductive contributions) were recorded. Examination of the images as a function of field showed a pronounced inflation effect of all sections captured as a function of field. The inflation occurred almost equally on application of both positive and negative fields. This effect is different from earlier findings for $LiNbO_3$ in which fields of opposite polarity produced alternately an expansion and a contraction of the sections. The effect in $LiNbO_3$ was explained by the generation of surface domains thus deforming planes in the near surface region. By a symmetry argument, it was reasoned that no such effect should be evident in Z-cut wafers of crystals of the KTP family (point symmetry *mm2*). However, in RTA, we clearly have an effect in the near-surface region producing a bending of the planes and expanding (only) the sections. The angle of distortion was calculated from measurements and plotted as a function of field. Fig 1 presents the "low-field" region, defined here as below the ferroelectric coercive field required for switching. The linear dependence on E^2 is impressive and suggests that the origin of the distortion of the planes ia an electrostrictive shear of the surface region under the high-voltage periodic electrode (the opposite electrode is at earth). Derivation of the effective electrostrictive coefficients from these plots gives a mean value (from a number of topographs and ± fields) of 3×10^{-17} m^2V^{-2}, which places the electrostrictive response of RTA as higher than quartz (10^{-18}) and lower than giant lead-based piezoelectric perovskites (10^{-16}), which seems reasonable. Data over the whole range fit to a polynomial, but with large errors on the coefficients. It is more likely that the data are separated into low, intermediate and high-field regions relative to the actual poling field (put at the estimated value from hysteresis measurements on Fig. 2). It is to be expected that data after the presence of periodic domains in the sample will differ from that before since there are now periodic interfaces (domain walls) in the surface. Further work is required to establish the complex dependence of the inhomogeneous surface on the field. The results of these studies will be presented as an invited talk (by P.A.Thomas) at the European Ferroelectrics Meeting, Cambridge, UK, August 2003 and a paper is in preparation.

Low-conductivity HKKTP prepared for a 38 μm [010] grating was investigated under field. Striations traversing the sections commenced fields > 0.5 kV/mm. These black striations, which were reminiscent of those seen in normal flux-grown KTP[2] (which has a conductivity ~10^2 higher) at lower fields, could be the manifestation of conductivity in HKKTP at the higher applied fields used here. Although the conductivity is much suppressed in HKKTP relative to normal flux-grown material, it is nonlinear in the applied field[3,4] (the Poole-Frenkel effect). In normal flux grown KTP, it shoots up after a threshold field of 50 Vm^{-1} whereas in HKKTP, the threshold field is increased to ~1kVm^{-1}. The field was stepped up to ±2.3 kV/mm in an attempt to induce poling. However, there was arcing across the sample, which meant that the field could not be sustained. There was some evidence of domains, which were not faithful to the patterning of the grating, in the images after high-field treatment. This departure from the grating pattern is the result of the reported problems of poling in the unfavorable [010] direction. Black dots were not seen as a result of this *in-situ* poling experiment although it was noted that a 90-degree rotated domain viewed end-on *ie*, a domain created in the wrong orientation, with a wall normal to **a** instead of to **b**, might appear in an image as a dot. Therefore, the rotation of the domains observed here, if taken to the extreme (90 degree rotation) could explain the earlier black dot observations (see first report on ME302).

The HKKTP sample did not show inflation of the section topographs as for the RTA, despite their identical point symmetries and similar elastic/piezoelectric properties. This suggests that a special combination of circumstances is required for the surface distortion to occur. One obvious difference between the RTA and the HKKTP investigated here is the magnitude of the conductive effects, with RTA not showing conductive effects until much higher fields. In the absence of conductivity, the actual voltage sustained in the insulating near-surface region should be higher than in the case where there is a substantial conductivity and this may account for the different behaviours of these materials.

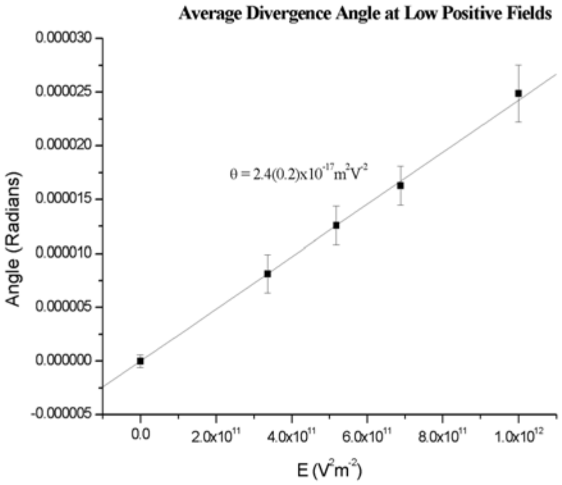

Fig. 1 Distortion vs square of applied field for positive applied field in low-field region (+ve fields)

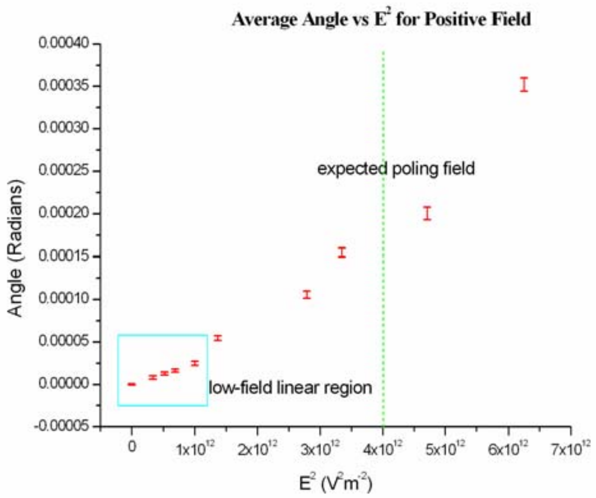

Fig. 2 As for Fig.1 but over whole range of fields investigated (first 5 points are shown in Fig. 1)

References

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