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:

The long-term project commenced with a survey of crystals periodically-poled off-line at Warwick. The purpose of this was to establish that crystals "home-poled" at Warwick using the rig designed for later *in-situ* poling would meet the quality demands of Bragg-Fresnel imaging of domains. The crystals examined were: **(i)** Rb-doped $KTiOPO_4$ (Rb:KTP), poled with grating vector along [100] (the conventional orientation) with grating period 60 μm; **(ii)** $RbTiOAsO_4$ (RTA) with grating vector [100] and period 38 μm; **(iii)** High-potassium stoichiometry, low-conductivity $KTiOPO_4$ (HKKTP) grating vector [100] and period 9 μm; **(iv)** HKKTP grating vector [100], period 60 μm. **(v)** HKKTP grating vector unconventional orientation [010] (reputedly difficult to achieve), period 60 μm; **(vi)** Stoichiometric $LiNbO_3$ (SLN), orientation [100], period 38 μm. **(vii)** Normal flux-grown KTP, poled at low temperature, grating vector [100], period 38 μm.

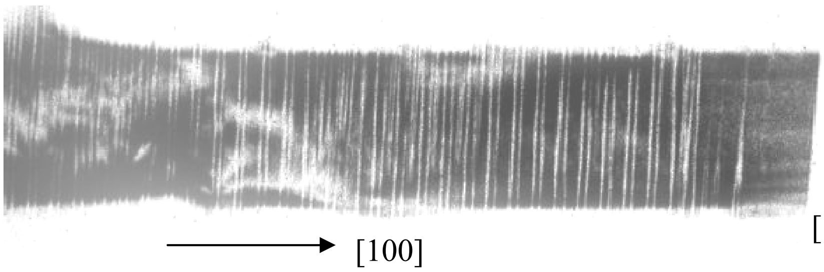
In summmary, the results indicated that periodic domain inversion had been successfully achieved in all but SLN, which showed no evidence of any grating. SLN is a relatively new variant of $LiNbO_3$ with a low coercive field (6 $kVmm^{-1}$) which is only 25% of the usual fields required to pole congruent $LiNbO_3$. Periodic poling is plagued by back-switching, a process in which the domains fail to pin and spontaneously relax back. This was most likely the case for the SLN examined here, which showed no sign of a periodic grating.

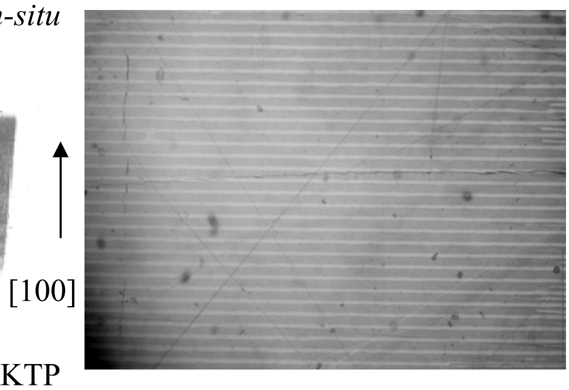
The evidence of being able to pole Rb:KTP, RTA and HKKTP well was particularly important for later experiments using the electric field in-situ. RTA, which is obtained from the commercial suppliers Coherent Crystal Associates, USA, is an insulator at room temperature and can be switched using relatively low coercive fields of 2.2 $kVmm^{-1}$. Rb:KTP[1] is a new low-conductivity material developed and patented by the Warwick/Oxford team. Periodic poling was successful in the [100] orientation but the 60 μm period posed a problem for coherent imaging since it approximates to the lateral coherence of the x-rays in the vertical direction (domain walls are always oriented horizontally for the most favourable diffraction geometry). Calculation of the first Fresnel zone at $\lambda = 0.4$ Å gives a radius of approximately 3 μm and, therefore, every domain wall at 30 μm intervals should be seen individually for a grating of 60 microns period. For Rb:KTP, features every 60 μm are seen with no intervening features at 30 μm. The absence of the intervening features has yet to be explained but may be the result of poor mask alignment during the photolithographic process for periodic poling. The sharp features at 60 μm intervals have the appearance of diffraction from a single phase step with a phase jump close to π.

In HKKTP sample iv), which was grown by the Oxford team, individual features are seen at intervals of 40 and 20 μm throughout most of the sections (Fig 1a) and the pattern has period of 60 μm. This suggests that the duty cycle (relative size of up and down domains) achieved in poling was not 1:1 as ideally desired, but 2:1 (Fig 1b). Simulations of the patterns were made assuming matching of domains through the P(1) atom[2] and starting from duty cycles of 1:1 and progressively altering the ratio. A satisfactory fit was obtained for up and down domains of widths 18 and 42 μm, respectively, *ie* close to the duty cycle suggested by the x-ray images and etching. This result shows that KTP of different origin, with different potassium stoichiometry and poled at different temperatures and fields, gives structurally identical domain walls to those previously investigated[2]. Sample (vii), was also successfully poled but since this was a low-temperature process, it is not practical for later *in-situ* studies, low-temperature being an unwanted additional complication to high-electric fields *in vacuo* in the x-ray beam.

Sample (v), HKKTP with a grating in the unorthodox [010] direction, was the most interesting. First, evidence of poling throughout the whole 0.5 mm thickness of the sample was shown in the topograph[3].Secondly, interesting contrast arose at short crystal-to-film distances, which was added to by genuine phase contrast at distances > 1m. The contrast is in the form of separated black "dots" (Fig 2) within domains at various points in the thickness of the crystal. We suggest that these show the poling history. For example, when poling starts, a highly deformed region is created under the electrode. Somehow, the growing domain must propagate to the other side – it may do this in one clean sweep of a front through the crystal or perhaps it achieves this stepwise. If we take the dots to represent the progress of a deformed region, we can suppose that domain propagation, in some domains at least, takes a stepwise form. We suggest that propagation halts for enough time to produce a non-recoverable deformation within the domain, perhaps because a pre-existing small defect is met, thus leaving the dot behind before the domain either does or does not continue through to the other side. It is observed that the domain propagation sometimes ceases at a dot (domain inversion incomplete) or continues after a dot. An argument against the deformation interpretation is that it is very difficult to deform crystalline materials, e.g. silicon, plastically. The elastic constants of Si and KTP are similar: c_{11}'s are 166 and 165.7 GPa, respectively, c_{33} for KTP is 169 GPa, suggesting that KTP might be similarly resistant to unrecoverable deformation. However, we note that the black dots appear only on the 60 μm period sample with poling in the "difficult" [010] direction. The domain walls move approximately 100 times more slowly for this direction than the conventional [100] direction and, therefore, we can suppose they "stop" for long enough to cause local damage. Further *in-situ* experiments to monitor the poling in this direction are required and these are waiting upon the availability of new HKKTP samples.

Off-line at Warwick, a poling rig, capable of sustaining a vacuum to 10^{-6} torr and of providing fields up to 8 kV/mm safely, whilst allowing x-ray access in and out, was constructed. This rig, which was designed to fit into the goniometer head on the ID19 diffractometer, was to interface to previously-constructed computer-controlled switching boxes for the *in-situ* experiments.





Figs 1 a & b Section topograph of the 451 reflection from HKKTP [100] poled, d_{CF}=127 cm, λ=0.411Å, showing periodic contrast as pairs of white lines separated by 20 and 40 μm. Etch pattern from the grating on the same crystal showing that the duty cycle is not 1:1. Alternating domains are shown by the dark and light stripes.

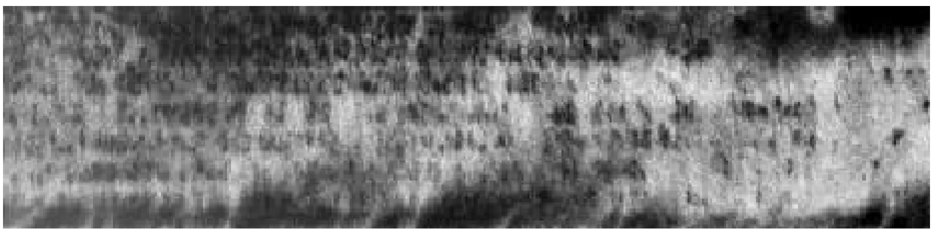


Fig. 2 A reflection from the HKKTP [010] grating showing the black dot phenomenon. The domain walls were arranged parallel to the section (unlike Fig 1a, which has walls orthogonal to the section)

References

[1] Q.Jiang, P.A.Thomas, R.C.C.Ward & K.B.Hutton J.Appl.Phys, **92**(5), 2717-2723 (2002): [2] P.Pernot, P.A.Thomas, P.Cloetens, T.S.Lyford & J.Baruchel Accepted fo J.Phys.C. February 2003: [3] Q.Jiang, P.A.Thomas, D.Walker, K.B.Hutton, R.C.C.Ward, P.Pernot & J.Baruchel, with JPhysD, Feb 2003.