ESRF	**Experiment title:** Diffraction studies of ferroic materials under non-ambient conditions	**Experiment number**: 01-02-754
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Report:

alpha-D-Glucose complex: Refinements on some of the data sets that had been collected previously indicated the presence of a third phase of this ferroelastic organic complex. Therefore, it was deemed necessary to collect data from a few more crystals in order to secure data of good quality for all phases.

Crystals of suitable size were cut from a larger specimen and checked by diffraction. Two crystals were mounted and centred in succession in our thermostat sample cell which was conditioned at t = 23 ^{o}C and relative humidity RH = 63 %. Crystals of the complex are sensitive to radiation, and dehydrate quickly in a too dry environment under exposure to X-rays. Intensity data were collected with a CCD, wavelength λ = 0.70915 Å.

Two sets of data comprising ~ 32900 (# 1) and ~ 26580 (# 2) reflections were collected to d_{min} ~ 0.59 Å. Merging excluding Friedel pairs gave ~ 14380 (# 1) and ~ 14775 (# 2) unique reflections, the parent R_{int} values based an all data were 0.040 and 0.033, respectively. Preliminary refinements yielded $R(F)$ ~ 0.039 and 0.045. We now have data of good quality for all phases.

Epitaxial ferroelectric films: Ferroelectric films constitute the major target for study in our programme on 'Diffraction studies of ferroic materials under non-ambient conditions'. Our samples were epitaxial films of $PbTiO_3$ (PTO) deposited by RF magnetron sputtering onto substrates of $SrTiO_3$ (STO). Ferroelectric $PbTiO_3$ is tetragonal, its (0 0 1) plane forms a nearly perfect match with the base plane of cubic paraelectric $SrTiO_3$. Hence, the polar ***c*** axis of the $PbTiO_3$ film will be oriented along the growth direction, parallel to one of the main axes of the $SrTiO_3$ substrate.

The samples having area 7 x 7 mm and thickness 500 μm were mounted horizontally between two transparent capacitor plates made from Kapton with a thin layer of gold deposited by evaporation. They were mounted lying flat on a vertical glass rod with end diameter 2 mm sticking through a hole in the centre of the bottom capacitor plate. With this mount the sample is completely detached from the capacitor plates, thereby eliminating possible displacements caused by the charged capacitor (*cf.* Report 01-02-746).

Horizontal alignment of the sample was made by small angular adjustments of the goniometer head to obtain a constant deflection geometry for a laser beam being reflected from the sample surface, independent of rotation about the sample normal. Centring in the beam was achieved by monitoring the intensity of the direct beam under a stepwise vertical translation of the sample into the beam, followed by a fine tilting of the sample about a horizontal axis orthogonal to the X-ray beam. This alignment procedure was suggested to us by Dr. Eric Dooryhée, CNRS, and we found it very efficient. Problems encountered in the centring part are due to an inadequate slit system giving an asymmetric, nonhomogenous beam profile on the sample.

In the previous experiment, 01-02-746, we used a point detector for the 1- and 2-dim. *q*-scans to explore substrate and film Bragg reflections and satellite peaks in the vicinity of the latter reflections. In order to reduce the long times required for the 2-dim. *q*-scans we now employed a CCD detector with a pixel size of 60.3 μm placed orthogonal to the X-ray beam at a distance of 360 mm from the sample. For most scans data were binned 2x2 giving an angular resolution ~ 0.02^o. The wavelength of the radiation, 0.9626 Å, was selected to avoid fluorescence from the heavy elements of the sample.

Two samples with nominal film thicknesses ~ 21 nm (50 unit cells), N60101, and ~ 5 nm (12 unit cells), N60801, were studied by ω-scans to map out some substrate and film Bragg reflections of the types 0 0 *l* , *h* 0 *l* and *h k* 0 as well as satellite peaks in the vicinity of some of the film reflections. The satellite peaks relay a short-range order that can be attributed to the average domain periodicity in the ferroelectric film. The measurements with field were corrupted due to a faulty lead to one of the capacitor plates. All scans were made with a nominal aperture ~ 150 x 300 μm The results from the scans were transformed to rectilinear reconstructions of reciprocal space using programs from the CrysAlis package (Oxford Diffraction).

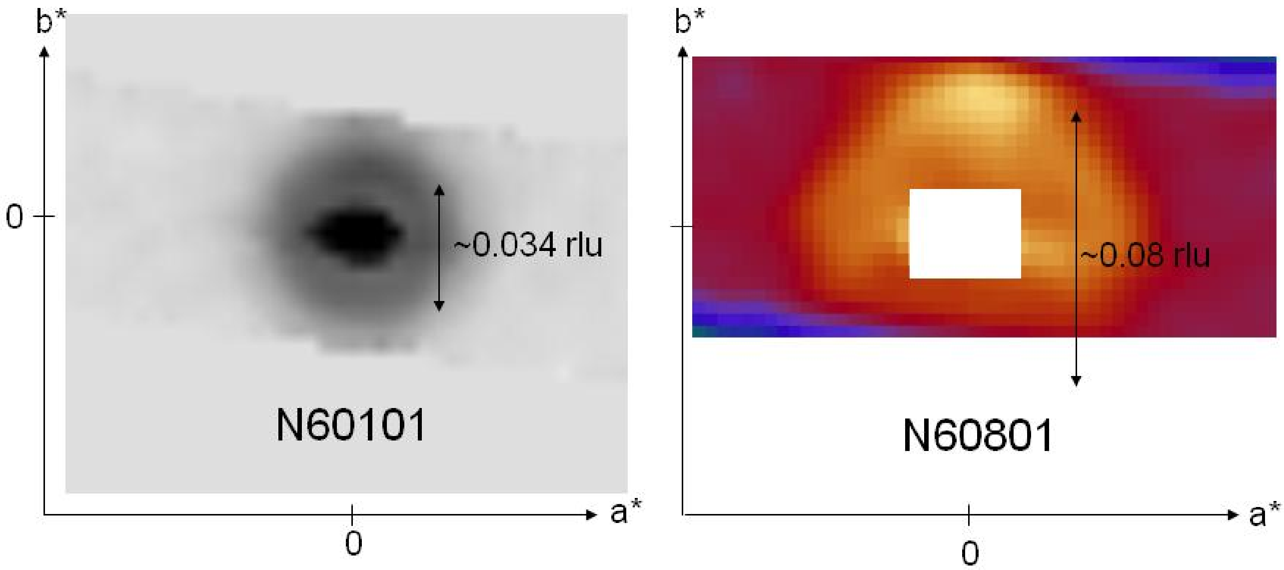

Fig. 1

Fig. 1 shows the 3-D distribution of diffuse intensity near the PTO (0 0 1) reflections for both samples. The annular ring distribution for N60101 should be compared with Fig. 1 of Report 01-02-746. The present results indicate an isotropic distribution of domains in the *ab*-plane with average periodicity 23.0 nm ($\Delta(h)$ = 0.017 x a^*, a^* = 3.905^{-1} Å^{-1}). The transversal q_x-scan made in 01-02-746 does not bring out this isotropy. The distribution for N60801 shows enhancement of diffuse intensity along the main reciprocal axes a^* and b^* corresponding to domain stripes of periodicity ~ 10 nm ($\Delta(h)$ ~ 0.04 x a^*) with preferred orientation along a^* and b^*. The signal/noise ratio for this reconstruction is rather poor, but can be improved by including more scans. These results demonstrate the superiority of 2-D detectors for collecting more information in a shorter time than can be done with a point detector.

From the present work we are able to identify limiting conditions and suggest modifications in procedures and instrumentation that are required to further improve the experimental conditions:

1) A slit system is needed much closer to the sample allowing a precise beam definition with the desired cross-section. With the present arrangement: four slits at a distance of ~ 3 m from the

sample, it is not possible to obtain a regular, homogenous beam with cross-section say 150 x 300 μm through the centre of the diffractometer.

2) The possibility to do psi-scans, i.e. scans about the diffraction vector, in the CCD detector mode. Psi-scans will locally improve the poor global orientation matrices usually obtained for these large plate-formed samples, thereby facilitating the localisation of e.g. *h* 0 *l* reflections, and permitting a more precise definition of the plane for scanning a given reflection.

3) Moving the CCD farther away from the sample than the present maximum 360 mm. A longer distance will improve the angular resolution, as will also a 1x1 pixel readout. A resolution $\sim 0.01^{o}$ appears adequate.

With these modifications implemented, at least points 1 and 2, we will be able to improve the quality of the data and at the same time reduce the reflection search and scan times significantly.