ESRF	**Experiment title:** Diffraction study of an alpha-D-glucose . NaCl . H_2O (6:3:3) complex - Structural changes at an isomorphous phase transition	**Experiment number**: 01-02-710
Beamline: BM01-A	**Date of experiment**: from: 07.09.05 08:00 to: 13.09.05 08:00	**Date of report**: 02.05.06
Shifts: 18	**Local contact(s)**: Dmitry Chernyshov	*Received at ESRF:*

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Report:

Preparing the optics for non-focussed beam, realignment of diffractometer and check of alignment with a crystal of ruby took 3 shifts.

alpha-D-Glucose complex: Crystals of suitable size were cut from a larger specimen and checked by diffraction. Two crystals were mounted and centred successively in our thermostat sample cell which was conditioned at t = 23°C and relative humidity (RH) = 65 %. Intensity data were collected with a CCD, wavelength λ = 0.6128 Å. Crystals of this complex are sensitive to radiation, and dehydrate in a too dry environment. In order to check the stability of the crystals at this RH, the profiles of a set of 5 reflections were examined by ω-scans with a point detector at the beginning and at certain intervals during the data collection.

Crystal #1: Two sets of data comprising ~ 32.400 reflections were collected to d_{min} ~ 0.60 Å. Merging gave a set of about 19500 unique reflections; R_{int} = 0.028 for all data. A preliminary refinement including H atoms converged at R(F^2) ~ 0.05, and revealed that this is a type CA crystal.

Crystal #2: Three data sets comprising ~ 35.200 reflections were collected to d_{min} ~ 0.61 Å. Due to problems with the integration programme the data has not been merged yet. However, refinement with one of the sets showed that this is also a type CA crystal.

The CCD data for both crystals will be reintegrated with a new programme featuring an improved algorithm for treating weak reflections. The stability check showed that the crystals remain stable for a period of about 12 hrs. under X-radiation with t = 23°C and RH = 65 %. Good quality data for the CA type crystal is now in hand. Data of comparable quality is still lacking for the other type (GE).

$NaAlF_4$: Powder data collected previously on SNBL-B for this compound have shown that the unit cell is not a simple tetragonal one, as has been proposed from diffraction studies with radiation from conventional X-ray tubes. Our SR data indicated larger cells of different symmetry, but with no definite preference among them. In order to resolve this indeterminacy, we have grown single crystals during the preparation of this compound from NaF and AlF_3, which involves deposition of solid material from the vapour phase. Two crystal forms were obtained: one tabular form (I) with a nearly square cross section, and very thin hairlike needles (II). Form I was identified from refinement of the intensity data as chiolite, $Na_5Al_3F_{14}$, a decomposition product of the metastable $NaAlF_4$. The latter crystallizes as form II. Several needle-shaped crystal were examined by diffraction. CCD data were collected for two specimens of dimensions, 3 x 13 x 190 μm and 5 x 6 x 225 μm, respectively. In both cases multiple reflections and/or diffuse intensities occur along one of the axes, indicating either a multiplication of this axis and/or disorder. The crystals split very easily along one of the faces. Even the small specimens used here consisted of 2-3 individuals, a fact which makes identification of a unit cell much more difficult. Several tentative cells of different symmetry are indicated. Single crystals of better quality, i.e. grown under a slower deposition rate at higher temperature, and handled with extreme care, are a prerequisite in order to address the structure problem.

Preliminary study of epitaxial ferroelectric films: The study of the alpha-D-Glucose complex is part of a larger programme entitled 'Diffraction studies of ferroic materials under non-ambient conditions' cf. proposals 01-02-746 and 01-02-754. Ferroelectric films constitute an important area within this programme. It was of great interest to carry out some simple exploratory experiments with one such sample, consisting of a 42 nm thick film of $PbTiO_3$ grown onto a matrix of $SrTiO_3$. Our sample cell that we have used successfully with single crystals of different organic ferroic hydrates, was modified to accomodate plate-shaped samples with the capacitor oriented to give a constant DC field normal to the film. The last two shifts of our beamtime was reserved for work on this sample.

Ferroelectric $PbTiO_3$ is tetragonal, its (0 0 1) plane forms a nearly perfect match with the base plane of cubic $SrTiO_3$. 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. We applied a DC field of 2000 V/cm on the sample, and studied the impact of field on position of single reflections as well as on reflection intensities from both film and substrate. The applied field brings about angular shifts, Fig.1 illustrates this for the reflections 0 0 1. Fig. 2 shows a reconstruction of the *h* -2 *l* lattice plane without field. Weak reflections from the film are seen below the stronger reflections from the substrate ($c^*_{PbTiO3} < c^*_{SrTiO3}$). Finally, Fig. 3 shows a reconstruction of the *h* -2 *l* plane, where the intensities are the differences between the recording without field and the one with a field applied. There are changes in the intensities evincing changes in structure.

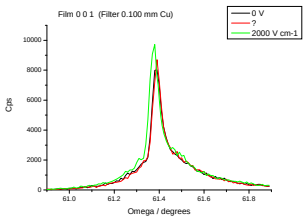

Fig. 1 a) 0 0 1 refl. from film

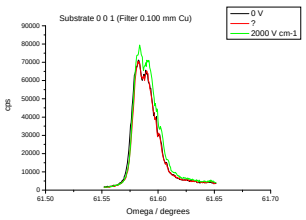

Fig. 1 b) 0 0 1 refl from substrate

Red and black curves recorded without field, green curve recorded under a field of 2000 V/cm.

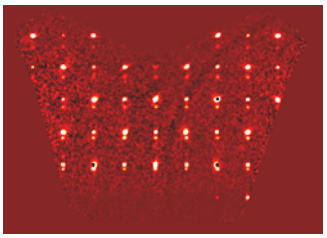

Fig. 2 Reconstruction of the *h* -2 *l* lattice plane with no field applied. Rows of weak reflections are from the film.

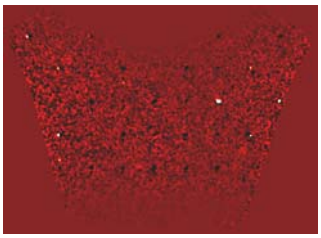

Fig. 3 Same reconstruction as in Fig. 2. Bright spots are residual intensities: I(no field) - I(field). Pattern of dark spots signify negative residuals.