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Report:

A sample cell for simultaneous control of temperature (T) and relative humidity (RH) has been constructed for diffraction studies of crystals that are unstable and may deteriorate easily, either by dehydration or deliquescence, depending on the RH of the environment. This cell has been used and further developed in diffraction experiments with Rochelle salt, an organic hydrate that becomes very unstable when exposed to humidities outside the safe range for a given T.

Rochelle salt (RS), $NaKC_4H_4O_6 \cdot 4H_2O$, is a well-known ferroic compound with two structural phase transitions involving water molecules. RS is paraelectric at $T > T_c^{high} = 297$ K and at $T < T_c^{low} = 255$ K, and is ferroelectric in the range $T_c^{high} > T > T_c^{low}$. This salt dehydrates easily at ambient conditions, thus, at 25 ^oC the lower limit in RH is about 40 %. Below this limit the crystals will begin to lose water and dehydrate. We have found that the dehydration is initiated and accelerates under exposure to X-rays. With the use of our new sample cell, however, excellent data could be collected for the paraelectric crystal at 308 K and have been used for structure refinement, *cf.* Experiment Report 01-02-231. In Experiment 01-02-343 we observed that the transition from high-T paraelectric ($P2_12_12$) to ferroelectric ($P2_111$) phase did not proceed as expected, at best only in part. In the follow-up Experiment 01-02-616 we found (*cf.* Report) that: I. Exposure to X-rays appears to affect crystals of RS such that they do not switch from the high-T paraelectric to the ferroelectric phase, or, when irradiated in the latter phase, they change back gradually to an orthorhombic symmetry. II. The formation of a multidomain structure in the crystal after the HT paraelectric $\rightarrow$ ferroelectric transition suggests that a permanent DC field must be applied to the crystal during data collection to avoid this.

In response to the requirement of II we have introduced in the sample cell a transparent and rotatable capacitor allowing a DC field to be applied in a fixed crystallographic direction. The aim of the present experiment was to test the new cell in the collection of diffraction data at about 276 K (3 ^{o}C) with a CCD detector. In order to monitor a possible radiation-induced reversal of the HT para- $\rightarrow$ ferroelectric transition, we intended to use a scintillation detector for measuring at regular intervals the phase-specific 0 5 0 reflection, a set of reflections h k ℓ with $\ell \neq 0$ that are split in a multidomain ferroelectric crystal, *cf.* Experiment Report 01-02-616, and as well reflections for scaling purposes.

Preliminary work: Prior to the diffraction work the operation of the Peltier element of the sample cell was checked over the temperature range 35 - 0 ^{o}C (308 - 273 K) and the relative flows of dry and moist N_2 gas were calibrated in this range in order to maintain the desired RH.

Crystallographic work: A single crystal of RS was mounted on the KUMA6 diffractometer, heated up to 30 ^{o}C, and from a few CCD exposures an orientation matrix was calculated for the paraelectric crystal. In the next step: positioning of the capacitor by rotation and tilting, prior to cooling the crystal down below T_c^{high}, we found that the assignment of the direction of the polar axis ***a*** relative to the diffractometer axes must be incorrect, and in disagreement with the assignment from the OM transformed to the scintillation detector geometry. The orientation of the capacitor was determined from the latter OM, and an electric DC field of 250 V/cm was applied along the ***a*** axis, during cooling of the crystal down to 4 ^{o}C. This field was then maintained throughout the data acquisition.

Data were collected in sets of 250 - 300 frames. For each frame ω was scanned 0.5^{o}, the exposure time was 10 sec. Frames receiving intensities above the saturation threshold of the detector were remeasured with successively reduced exposure times until no saturation occurred. At the end of about 19 hrs. 48800 reflections had been collected. The temperature was kept at 4.1 $\pm$ 0.3 ^{o}C during the measurements.

Unfortunately, there seemed to be an error in the transfer of the CCD OM to the scintillation detector geometry, or errors in the zero-points of some diffractometer axes. Therefore we were not able to do the monitoring with the point detector as had been planned. There were no signs of split peaks in the CCD frames. However, the resolution of this detector is not adequate to reveal the small degree of splitting expected in a multidomain crystal. The intensities of 0 -5 0 and 0 5 0 were measured with CCD at regular intervals along with several other reflections. As in our previous studies we observed that data for the ferroelectric crystal must be collected rapidly as radiation effects are only delayed but not eliminated even in a conditioned environment. A total data acquisition time of about 5 - 7 hrs. including a set of standard reflections for scaling seems appropriate. The radiation sensitivity of ferroelectric RS apparently has not been reported before. Clearly, it is important that the X-ray study is done without interruption because of the radiation-induced changes in the crystal. In the present experiment there was a delay of several hours between calculation of the first OM from CCD frames and start of the data collection, largely due to the unexpected difficulties related to the OM in the CCD mode. And for reasons explained above it is essential to follow a possible development of the structure by using a point detector for measurement of standard reflections and analyses of line profiles in combination with a CCD for fast data collection.

The performance of the sample cell was successful and we are very satisfied with this result.