ESRF	**Experiment title:** Diffraction study of the high-*T* paraelectric phase of Rochelle salt with an area detector	**Experiment number**: 01-02-1009
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Report:

Background

Rochelle salt (RS), $NaKC_4H_4O_6 \cdot 4H_2O$, is the classical ferroelectric material. The term ferroelectricity was originally defined and for many years linked exclusively to this organic salt. RS has several unique physical properties, among them are two phase transitions and two Curie points. It is parealectric both at $T > 296$ K and $T < 255$ K, is ferroelectric in the range 255 K < T < 296 K, and has an extremely strong piezoelectric effect. The salt has been the target for a large number of investigations, both experimental and theoretical. Following the first structure study in 1941 [1], at least 17 more diffraction studies (X-rays or neutrons) of one or more of the three phases have been reported, the last one in 2008 [2] was of the low-*T* paraelectric form.

In spite of the efforts over 70 years the experimental data are not conclusive wrt. a nanoscale description of the phase transitions. Apparently, they comprise very small changes in structure, presumably involving dynamic or static shifts of several hydrogen atoms. Therefore, data of very good quality is needed to resolve the problem, but good data is not easily obtained, in part because the structure of RS is very sensitive to changes in relative humidity and temperature, secondly and more important it is extremely easily damaged by ionizing radiation like X-rays, in particular in the ferroelectric phase.

Previous work by us

We have previously collected diffraction data at SNBL-A both for the high-*T* paraelectric (PE) and the ferroelectric (FE) phases, at $T = 308$ K and $T = 276$ K, respectively. For the data collection we have developed a gas-stream thermostat sample cell with contol of relative humidity and the possibility to apply an electric DC field on the crystal in a selected crystallographic direction [3].

We have obtained data of excellent quality for the high-*T* PE phase and also very good data for the FE phase. Refinement of the PE structure is completed, for the FE structure refinement is at an advanced stage. The values of the crystallographic *R* indices and other indices for goodness-of-fit show that both structure models are superior to any of those reported previously.

Data for the FE phase was collected with a 2-dim. CCD detector. For the high-*T* PE phase a point detector was employed. This is the case in all previous studies of this structure, in which also radiation from conventional radiation sources was used. As a point detector will record only reflections in the pre-calculated positions in reciprocal space, one cannot exclude the possibility that there are additional weak reflections corresponding to a larger unit cell and probably also a different space group symmetery. If so, this would directly affect modelling of the high-*T* PE structure, and could possibly be the reason for the problems encountered in describing the phase transition in RS. It was therefore imperative, before completing work on the two stuctures, to ensure that unit cell and crystal symmetry were correct by doing a 2-dim. imaging of diffraction space with high-flux radiation for the high-*T* PE crystal

Results

Two series of measurements were made of a crystal at 308 K with a CCD detector using step length in angle /time per step 0.25^{o}/5 sec and 0.1^{o}/10 sec, respectively. Both series, in particular the second one, represent long exposures that would reveal even extremely weak additional reflections corresponding to a larger unit cell.

The images, however, show no new reflections, thus we can conclude that the unit cell and crystal symmetry are as have been assumed in all previous studies. With this knowledge we have completed the analysis of the high-*T* PE. The results indicate a mechanism of the phase transition different from those that have been proposed in the past. A draft of a paper to be published has been finished. The work on the FE structure is continued. A detailed picture of the latter structure is required to corroborate the suggested transition mechanism.

References

[1] Beevers, C.A. & Hughes, W. (1941). *Proc. Roy. Soc. (Lond.)* Ser.A **177**, 251-259.

[2] Görbitz, C.H. & Sagstuen, E. (2008). *Acta Cryst.* E**64**, m507-m 508

[3] Mo, F. & Ramsøskar, K. (2009). *J. Appl. Cryst.* **42**, 531-534.