Experimental report

20/08/2021

Proposal: **DIR-191** **Council:** 10/2019

Title: HIGH-TEMPERATURE PHASE OF FERROELECTRIC DABCO PERRHENATE

Research area: Materials

This proposal is a new proposal

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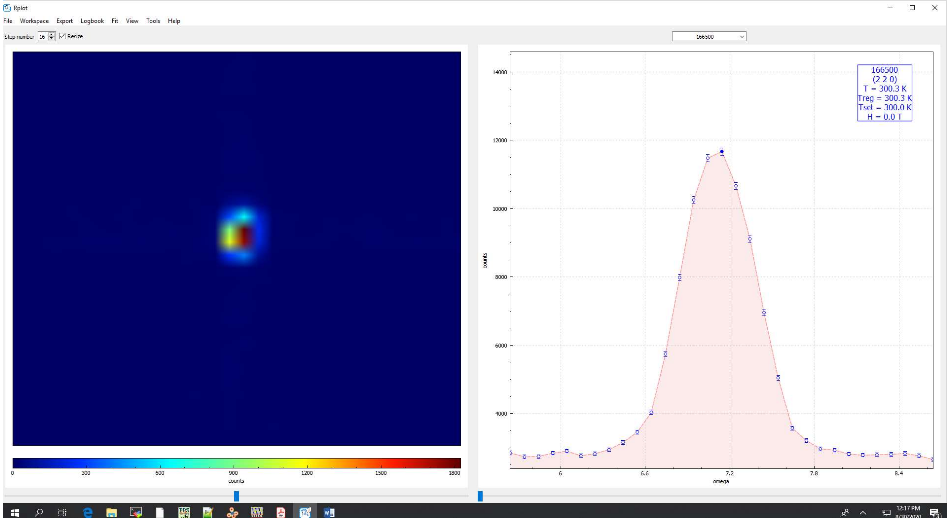
Samples: 1,4-diazabicyclo[2.2.2.]octane perrhenate/C6H13N2ReO4

Instrument	Requested days	Allocated days	From	To
D9	4	4	27/08/2020	31/08/2020

Abstract:

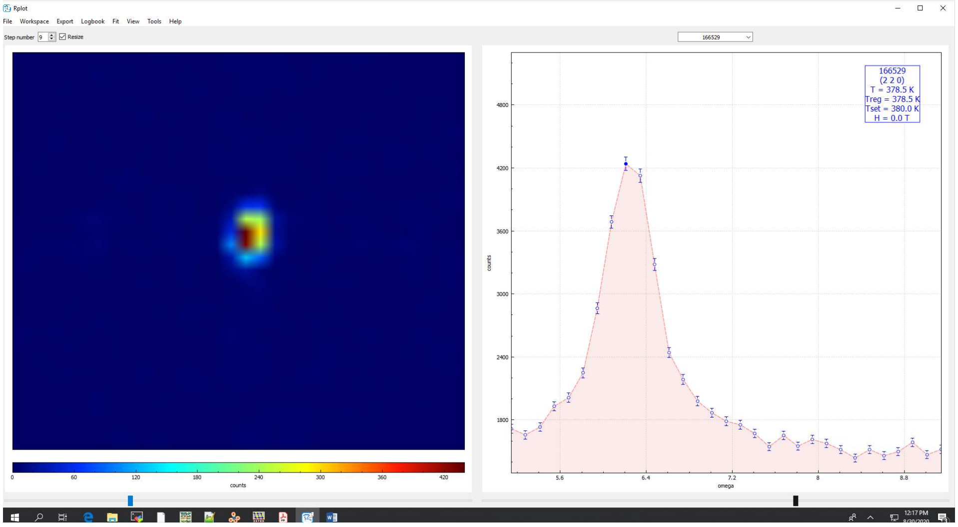
In this project we propose to collect the lacking single-crystal neutron diffraction data of dabcoHReO4 in the high-temperature phase II at 380 K. At room temperature this ferroelectric crystal is built of H-bonded polarized linear polycationic chains arranged parallel, which substantially contribute to the total polarization of the crystal. The structure determination with neutrons is essential for a better insight into the protons behavior in N{H¡P¡P¡PN hydrogen bonds and possible crystal disorder in phase II. Moreover, this experiment should be helpful in determination of the true crystal symmetry and resolving the long-standing debate on this issue.

The experiment was aimed at determining the symmetry and structure of 1,4-diazabicyclo [2.2.2]octane perrhenate, $[C_6H_{13}N_2]^+ReO_4^-$, hereafter dabcoHReO$_4$, in its phase II above 374 K. DabcoHReO$_4$ is a prototypic NH$^+$--N bonded ferroelectric at normal conditions, and the knowledge about the structure and symmetry of its paraelectric phase is essential and evokes lots of controversy. One of the fundamental questions to solve is whether phase II is polar (ferroelectric) or it is nonpolar (paraelectric). We have planned the high-temperature single-crystal diffraction measurements on D9 to resolve this problem. The large single crystals of dabcoHReO$_4$ were grown for the purpose of this experiment and their quality was checked with the photographs performed on OrientExpress at normal conditions. The high quality of the selected crystal is testified by the CCD image and the profile of reflection 220 measured at 300 K (Fig. 1).


Step number 16 ☑ Resize

166500
(2 2 0)
T = 300.3 K
Treg = 300.3 K
Tset = 300.0 K
H = 0.0 T

Fig. 1. Reflection 220 of dabcoHReO$_4$ in phase III at 300 K, recorded as the 2D-detector image on D9 and shown as the ω-scan profile.


Step number 9 ☑ Resize

166529
(2 2 0)
T = 378.5 K
Treg = 378.5 K
Tset = 380.0 K
H = 0.0 T

Fig. 2. Reflection 220 of dabcoHReO$_4$ in phase III at 378.5 K, recorded as the 2D-detector image on D9 and shown as the ω-scan profile.

The crystal sample and its reflections remained fine till the transition temperature. As illustrated in Fig. 2, at 378.5 K the crystal was still in the ferroelectric phase III and generated Bragg reflections of good profiles. However, few tenths of K higher in the temperature, the reflections became broadened and split, as can be seen in the image taken at 378.9 K (Fig. 3), testifying for the occurrence of phase transition. The transition temperature is 4-5 K higher than observed previously [1], probably because of some temperature gradient between the sample and the temperature sensor and the sample. In the next step we tried to anneal the crystal in phase II at 390 K, but without any noticeable improvement of the diffraction pattern (Fig. 4).

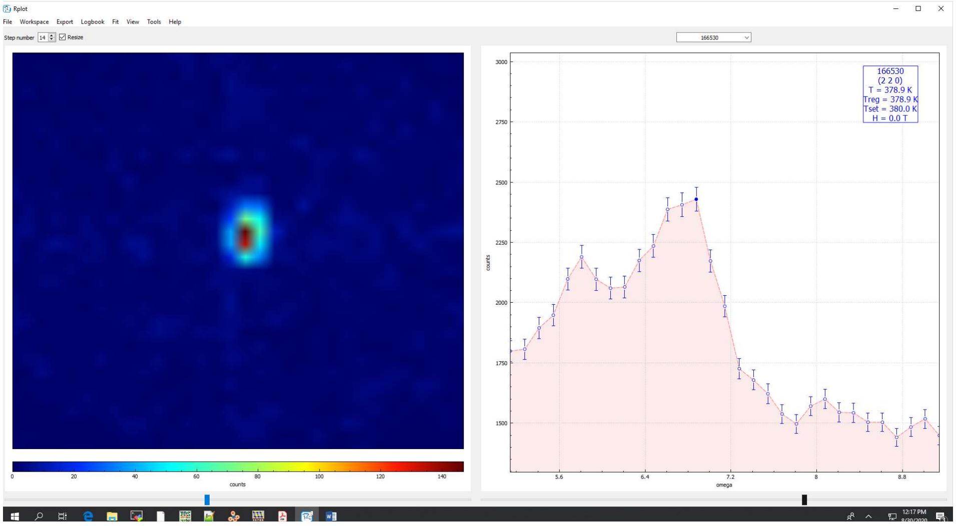


Fig. 3. Reflection 220 of dabcoHReO$_4$ in phase II at 378.9 K, recorded as the 2D-detector image on D9 and shown as the ω-scan profile.

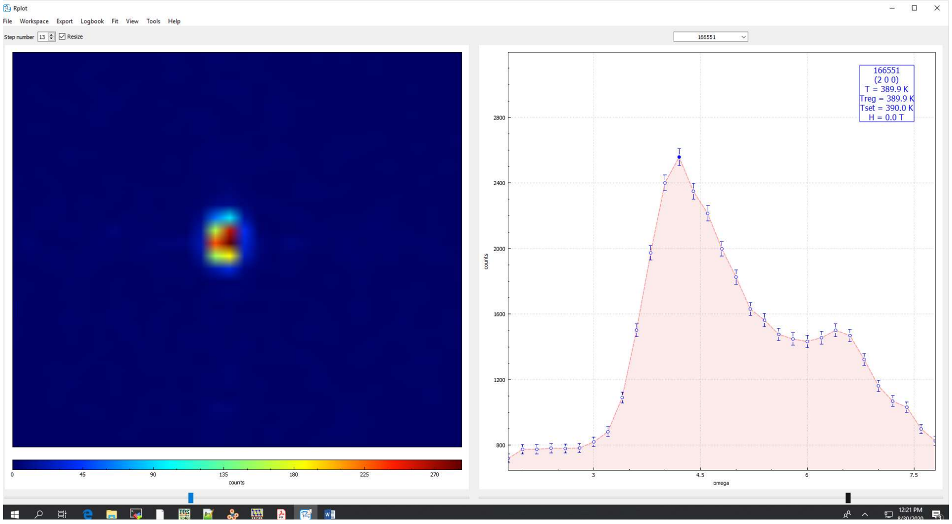


Fig. 4. Reflection 200 of dabcoHReO$_4$ in phase I at 390 K, recorded as the 2D-detector image on D9 and shown as the ω-scan profile.

Nonetheless, the data collection was carried out and the data reduction and structural analyses were performed. However, the precision of these structural determinations was too low for unequivocally determining the space-group symmetry of dabcoHReO$_4$ phase II.

The observed worsening of the crystal quality, and as a consequence the worsening of the diffraction pattern in phase II, can be explained by the strong strain associated with the phase transition between dabcoHReO_4 phases III and II. At this 1st-order transition the lattice parameter *a* shortens by 3.2%, *b* extends by 5%, and the monoclinic angle *β* changes from about 91 to 90^{O} [1]. This strain is so large, that the transition front passing through the sample crushes the single crystal, especially in the regions of structural defects, which are usually present in the macroscopic samples. It is worth pointing out that we were able to collect good X-ray data (on much smaller crystals) in phase II, but due to the very high absorption of X-rays by the sample containing the heavy Re atoms, it is difficult to resolve the controversy concerning the crystal symmetry of dabcoHReO_4 phases II and I [2,3]. Nonetheless, further experiments are being planned for determining the symmetry of dabcoHReO_4 in these phases, which is essential for fully understanding the mechanism of the ferroelectric-paraelectric phase transition in this compound.

References

[1] M. Szafrański, A. Katrusiak, G. J. McIntyre, Ferroelectric order of parallel bistable hydrogen bonds. *Phys. Rev. Lett.* **89** (2002) 215507 1–4.

[2] H.-L. Cai, W. Zhang, D.-W. Fu, Y. Zhang, and R. G. Xiong, Comment on *Ferroelectric order of parallel bistable hydrogen bonds*. *Phys. Rev. Lett.* 109, 169601 (2012).

[3] M. Szafrański, A. Katrusiak, Reply to Comment on *Ferroelectric order of parallel bistable hydrogen bonds*. *Phys. Rev. Lett.* **109** (2012) 169601-1–2.