

REPORT
on experiment HS-4571 performed at ESRF on BM1A

Title: Structural phase transitions and the nature of high protonic conductivity in $K_9H_7(SO_4)_8 \cdot H_2O$

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The purpose of the experiments at BM1A was to collect information on structural phase transitions and the nature of high conductivity in $K_9H_7(SO_4)_8 \cdot H_2O$ single crystals. $K_9H_7(SO_4)_8 \cdot H_2O$ is the first and the only known up to date representative of the line $M_9H_7(XO_4)_8$ in the crystal family $M_mH_n(XO_4)_{(m+n)/2}$ ($M = K, Rb, Cs, NH_4; X = S, Se, P, As$). The study of the temperature behavior of the dielectric permittivity and conductivity has shown a number of anomalies in the $K_9H_7(SO_4)_8 \cdot H_2O$ crystals [1]. It includes a superprotic phase transition at $T_{sp} \approx 398$ K accompanied by increasing of conductivity of two order of magnitude. The structural data obtained at ambient temperature [1] suggest that the occurrence of high conductivity in $K_9H_7(SO_4)_8 \cdot H_2O$ crystals with an increase in temperature correlates with a diffusion of the crystallization water.

Despite the progress in the study of $M_mH_n(XO_4)_{(m+n)/2}$ crystals, there are significant contradictions in the interpretation of the properties of superprotic phases. These contradictions are related both to the poor reproducibility of experimental data and to the absence of information about the crystal structure of the high-temperature phases of many compounds. The study of the atomic structure of $K_9H_7(SO_4)_8 \cdot H_2O$ crystals is of interest both for the characterization of this compound and for determining the general regularities and differences in the family of $M_mH_n(XO_4)_{(m+n)/2}$ crystals.

Using the beam time allocated, we have collected X-ray diffraction data for the $K_9H_7(SO_4)_8 \cdot H_2O$ single crystals in the temperature interval from 90 K to 450 K. The temperature dependences of the cell parameters a, b, c (Å) and the cell volume V (Å³) are shown in Figure 1.

At first, the measurements were carried out on heating up to 450 K. The results unambiguously revealed a structural phase transition accompanied by the change of symmetry from a monoclinic space group $P2_1/c$ to an orthorhombic space group $Pcan$ at a temperature of ~405 K. The high-temperature phase is enough stable up to 445 K. Sample quality worsens upon further heating and the formation of rings similarly to powder samples is observed in the diffraction images.

Also the appearance of some additional reflections was observed at temperatures higher than 405 K (Figure 2). Comparing the cell for these reflections with published data we found out that growth of $KHSO_4$ crystals takes place on a surface of the sample that was caused by a diffusion of the crystallization water from the bulk to the surface of the sample.

Then we carried out the measurements using the sample 2 of the same composition. The sample 2 was cooled down to 90 K and then heated up to 300 K (Figure 1). Diffraction data showed that ambient-temperature phase remains on cooling, and there are no phase transitions down to 90 K. Upon cooling the sample 2 diffuse scattering planes parallel $(0kl)$ were observed, their intensity increases on cooling (Figure 3). The reasons of this effect could be a freezing of the water molecules connected by H-bonds with SO_4 tetrahedra - they take certain positions upon cooling statistically and various structural clusters may be formed in their vicinity. This observation, being confirmed by more detailed analysis, could be rather unique case of structural disorder induced by cooling when entropy term does not favor a disorder.

Optical monitoring of the behavior of monocrystals upon heating, the diffraction data, including the temperature dependence of cell parameters, lead to interesting conclusions about a diffusion of crystallization water from crystals and its effect on the phase transition. In particular, before transition to the new phase we have observed a significant reduction of cell volume on $\approx 3,3\%$. Thus, the anomalies of conductivity observed in a range of temperatures of 360-390 K [1] correspond to an exit of

crystallization water from crystals. Therefore observed phase transition implies not only a change of crystal structure as it is normally expected but also it is accompanied by the changes in chemical composition for two phases. This information should be accounted for in the analysis of thermodynamics of this phase transition.

The preliminary treatment of diffraction data and the refinement of the crystal structure at 300 K confirmed the structural model obtained using X-ray data [1]. The model of the crystal structure at 405 K was obtained with the use of the Charge Flipping method and JANA 2006 crystallographic packages [2]. Figures 4a and 4b show the atomic structure of crystals at 300 K ($K_9H_7(SO_4)_8 \cdot H_2O$) and at 405 K ($K_9H_7(SO_4)_8$ without H_2O).

The low-temperature phase of $K_9H_7(SO_4)_8 \cdot H_2O$ contains channels through which K ions could move; however these channels are blockiert by H_2O molecules (Figure 4a). An increase in temperature lead to breaking of the weak dynamically disordered hydrogen bonds bounding the crystallization water and the latter would diffuse out of the crystal, making channels free for the motion of K atoms (Figure 4b). Simultaneously new H-bonds network with possible additional positions are formed between SO_4 tetrahedra.

The obtained structural data suggests that physical properties of the $M_mH_n(XO_4)_{(m+n)/2}$ crystals may change according to different structural mechanisms. As it was discovered in $Rb_3H(SeO_4)_2$ [3], $K_3H(SO_4)_2$ [4], and other $M_3H(XO_4)_2$ crystals, high proton conductivity is related to the formation of a qualitatively new dynamically disordered network of hydrogen bonds in which both positions of the centers of hydrogen bonds and their orientations are disordered, that enables protons to move over vacant crystallographically equivalent positions.

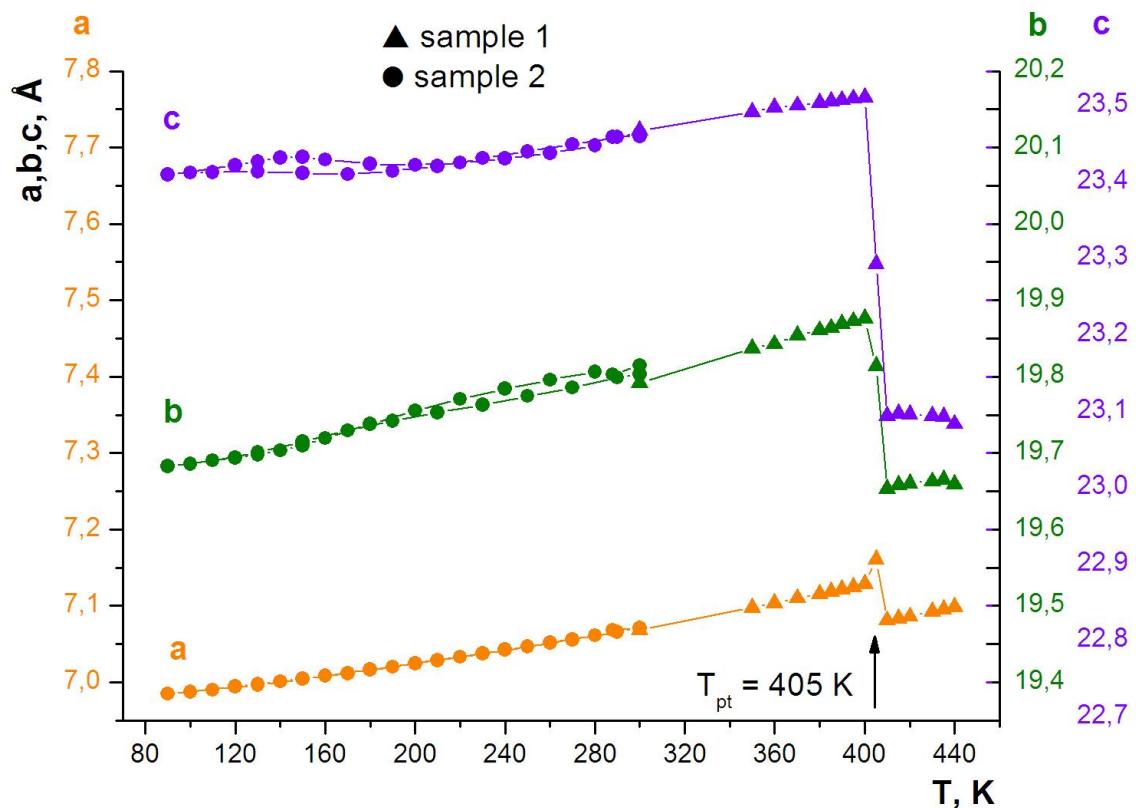
The emergence of high conductivity in $K_9H_7(SO_4)_8 \cdot H_2O$ crystals is related to the diffusion of crystallization water and motion of K ions, as well as to the transformation of the system of hydrogen bonds. It is possible to conclude that the backward water diffusion into the crystal structure with new H-bonds network will be hindered upon cooling. Hence, the stabilization of the high-temperature superionic phase and its supercooling to low temperatures are due to the formation of the new H-bonds network and slow backward water diffusion into the crystal.

The information about some preliminary results was done in the paper submitted to Crystallography Report and in the oral presentation on the XXVII European Crystallographic Meeting, Bergen, Norway, August, 2012. Refined results will be submitted to some other journals.

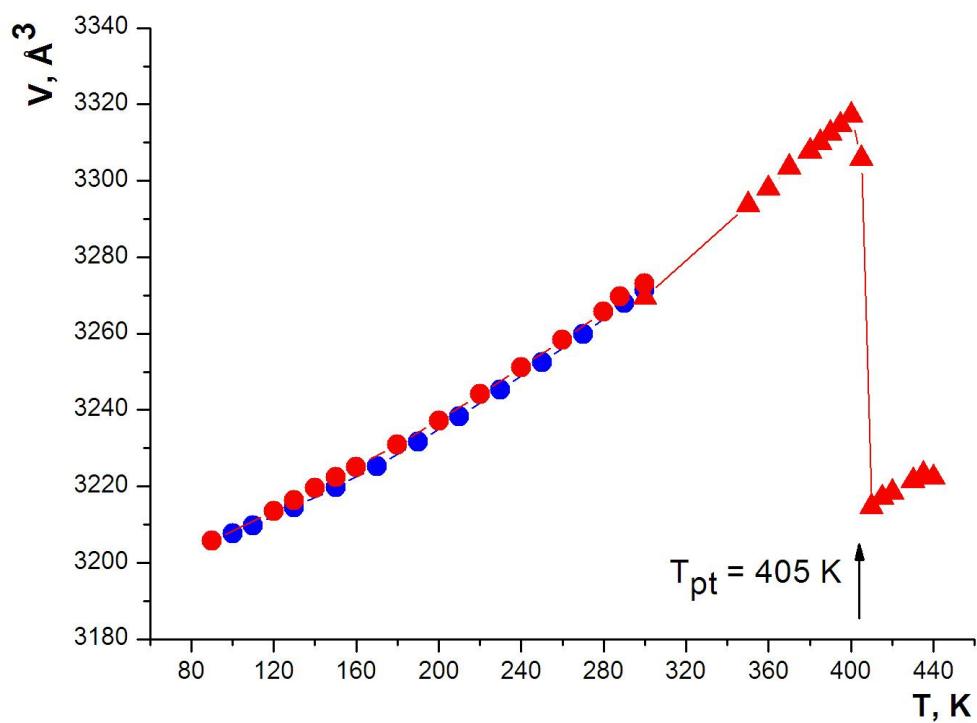
We wish to thank ESRF for the beam time allocation and our local contact for the qualified support on BM1A.

References:

- [1] I.P. Makarova, T.S. Chernaya, V.V. Grebenev, et al. Investigation of the structure and properties of $K_9H_7(SO_4)_8 \cdot H_2O$ single crystals. // Crystallography Reports. 2011. Vol. 56. No. 6.
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a



b

Fig. 1. $\text{K}_9\text{H}_7(\text{SO}_4)_8 \cdot \text{H}_2\text{O}$ crystals: the temperature dependences of cell parameters a , b , c (\AA) (a) and the cell volume V (\AA^3) (b).

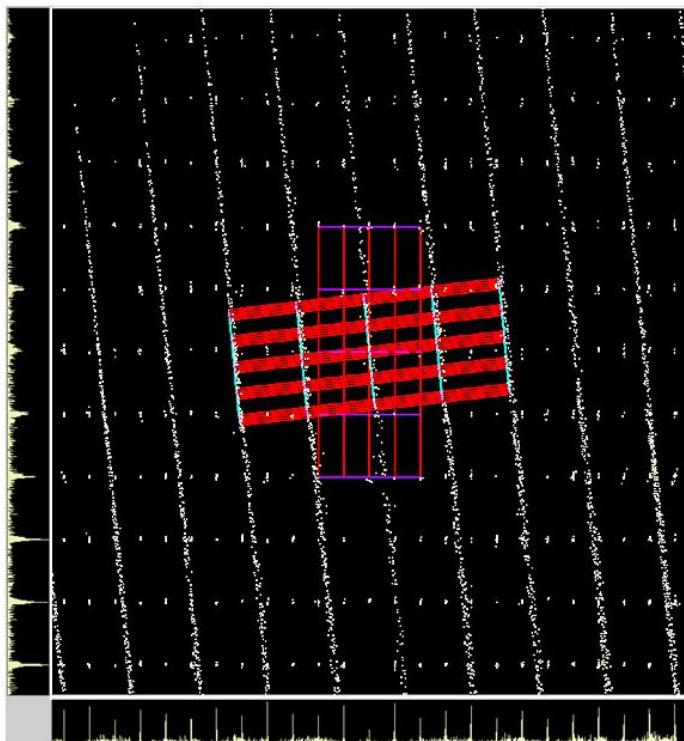


Fig. 2. The diffraction pattern at 430 K: there are reflections corresponding to the cells of $\text{K}_9\text{H}_7(\text{SO}_4)_8 \cdot \text{H}_2\text{O}$ and KHSO_4 crystals.

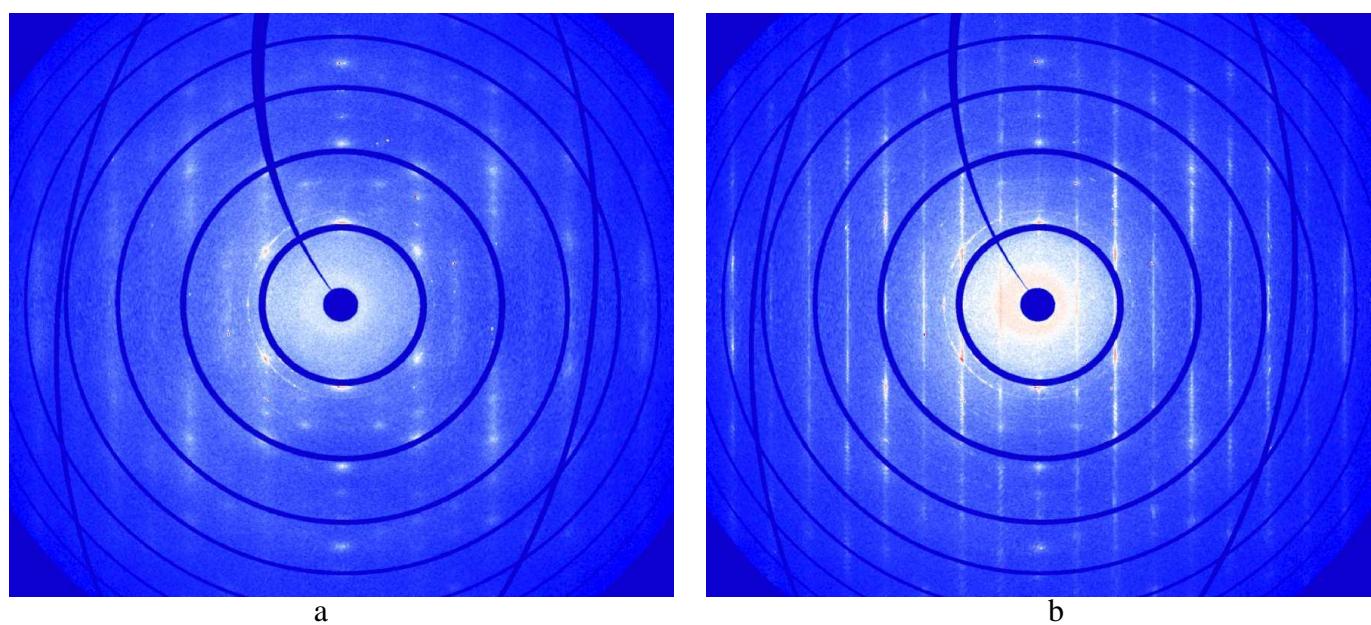


Fig. 3. The diffraction pattern at the plane $hk0.5$ at 288 K (a) and at 90 K: diffuse scattering planes parallel to $0kl$ are observed.

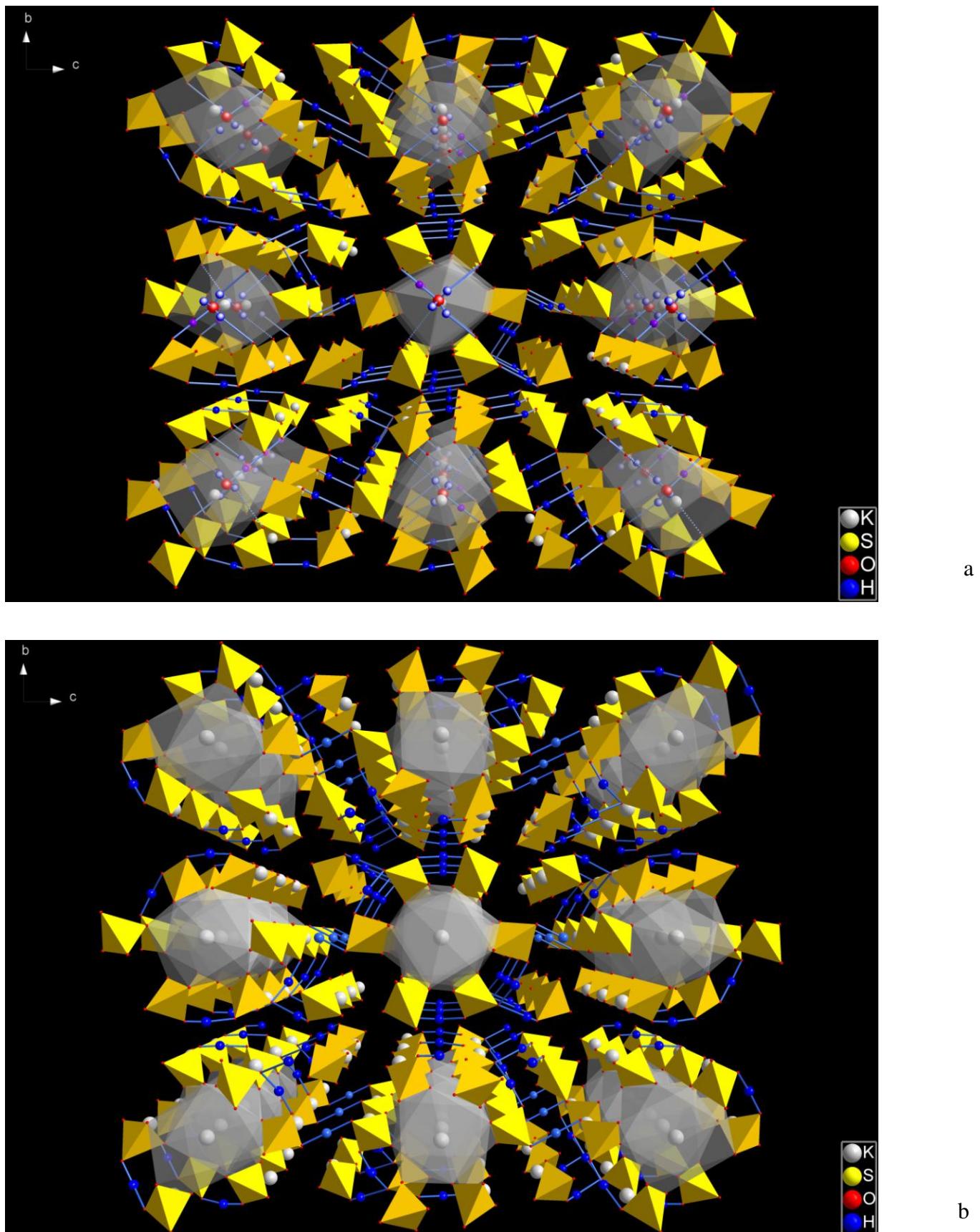


Fig. 4. $\text{K}_9\text{H}_7(\text{SO}_4)_8 \cdot \text{H}_2\text{O}$ crystals: (a) the atomic structure at ambient temperature and (b) at 405 K, without H_2O . Coordination polyhedra of K9 atoms (K5, K6 at 405 K accordingly, grey), SO_4 tetrahedra (yellow) and H-bonds (blue) are shown also.