

**REPORT**  
**on experiment MA-2563 performed at ESRF on BM1A**

**Title: The nature of high protonic conductivity in  $\text{Cs}_6\text{H}(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)_4$  crystals**

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The purpose of the experiments at BM1A was to collect information on structural transitions and the nature of high conductivity in  $\text{Cs}_6\text{H}(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)_4$  single crystals.  $\text{Cs}_6\text{H}(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)_4$  is the new representative of the mixed system of  $\text{CsH}_2\text{PO}_4$ – $\text{CsHSO}_4$  in the crystal family  $M_m\text{H}_n(\text{XO}_4)_{(m+n)/2}$  ( $M = \text{K}, \text{Rb}, \text{Cs}, \text{NH}_4$ ;  $X = \text{S}, \text{Se}, \text{P}, \text{As}$ ). At the Shubnikov Institute of Crystallography, the phase diagram of the  $\text{CsH}_2\text{PO}_4$ – $\text{CsHSO}_4$ – $\text{H}_2\text{O}$  ternary system was systematically studied for the first time, based on which it became possible to synthesize and grow  $\text{Cs}_6\text{H}(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)_4$  single crystals [1]. Precision measurements of its complex impedance showed that the single crystal transforms to the superprotonic phase, and its conductivity reaches  $10^{-2} \Omega^{-1} \text{cm}^{-1}$  at a relatively low temperature of  $\sim 390 \text{ K}$  (Fig.1).

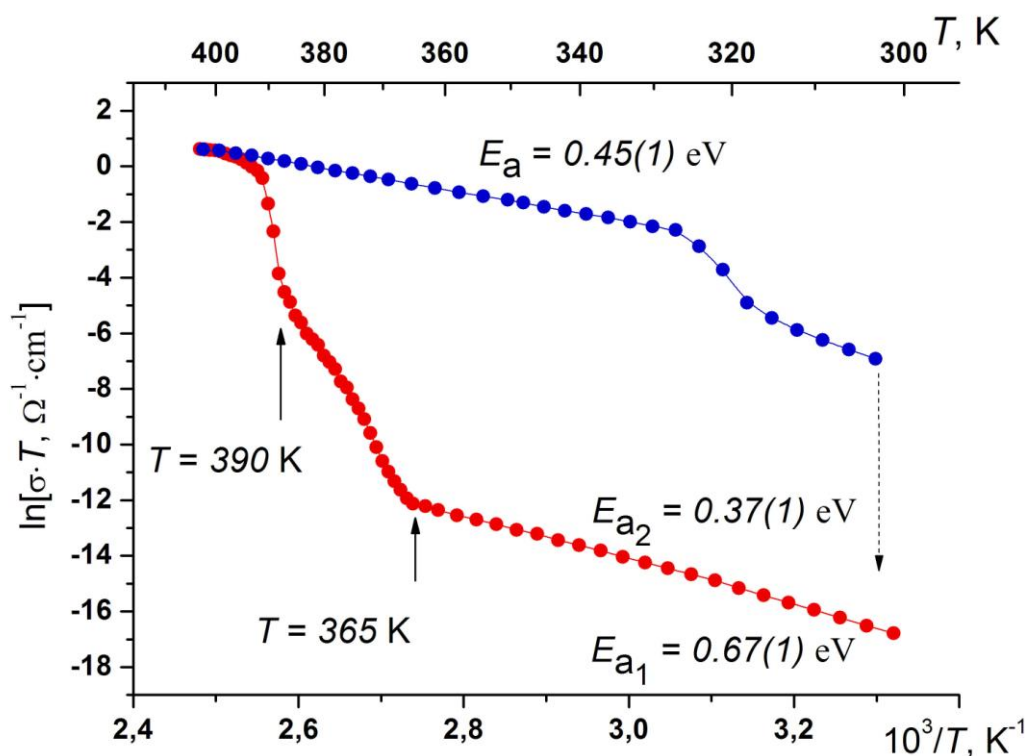


Fig. 1.  $\text{Cs}_6\text{H}(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)_4$  crystals: the temperature dependences of conductivity.

Despite the advance reached in the study of  $M_m\text{H}_n(\text{XO}_4)_{(m+n)/2}$  crystal family, there are significant disagreements in the interpretation of properties of superprotonic phases. This is also due to poor reproducibility of experimental data and the problems of collecting the data on high-temperature phases and, in some cases, the complete absence of information about the atomic structure of such phases [2]. From the point of view of practical application, the problem of the long-term stability of superprotonic phases must also be addressed. In the current situation, the establishment of the structural conditionality of anomalies in physical properties in  $\text{Cs}_6\text{H}(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)_4$  crystals is of obvious interest both for the characterization of this compound and understanding of the common features and differences in the family of  $M_m\text{H}_n(\text{XO}_4)_{(m+n)/2}$  crystals.

Using the beam time allocated, we have collected X-ray diffraction data for single crystals and powder samples of  $\text{Cs}_6\text{H}(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)_4$  in the temperature interval from 200 K to 410 K. The temperature dependences of the cell parameters are shown in Figure 2. Preliminary treatment of structural data unambiguously revealed structural phase transitions accompanied by the formation of multiphase compositions. The scheme of phase compositions is shown in Figure 3. It was established temperature range of the low-temperature phase (LT phase), the high-temperature phase (HT phase) as well as temperature range of multiphase states. The obtained scheme of phase compositions correlates with the temperature dependences of conductivity fully.

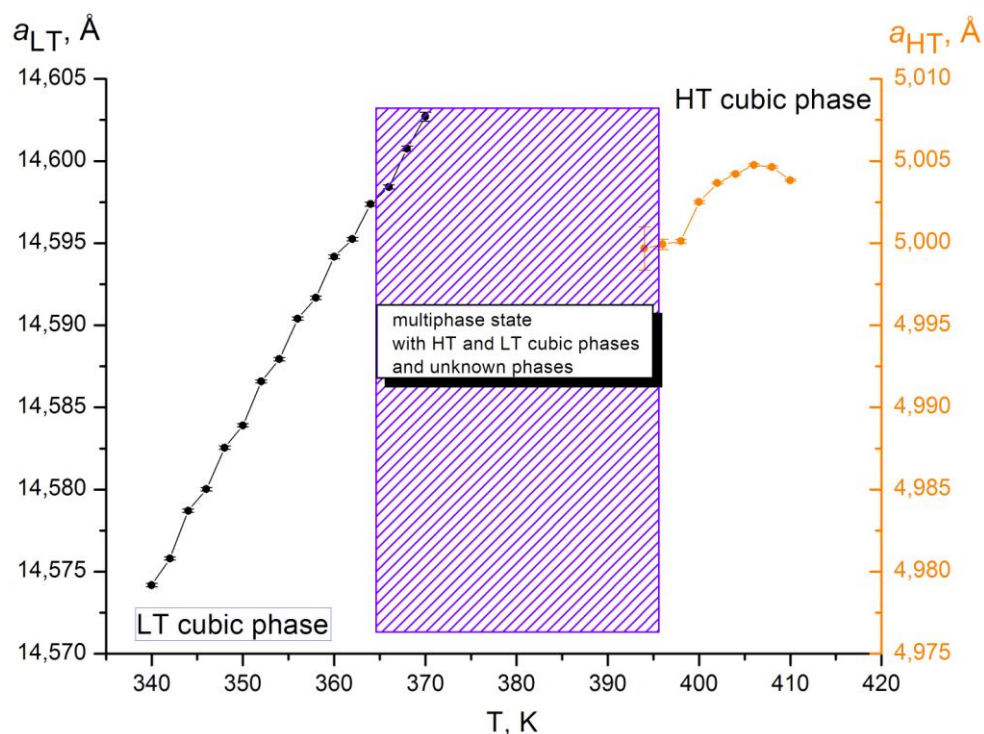


Fig. 2.  $\text{Cs}_6\text{H}(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)_4$  crystals: the temperature dependences of cell parameter  $a$  (Å).

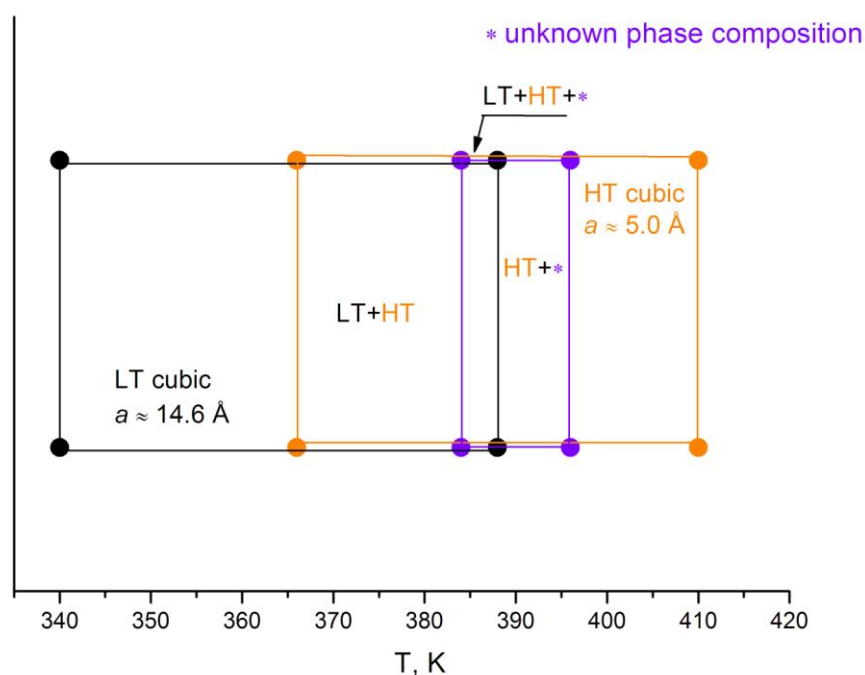


Fig. 3.  $\text{Cs}_6\text{H}(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)_4$  crystals: the scheme of the phase compositions in the temperature interval till 410 K.

The preliminary treatment of diffraction data for single-crystalline samples using *CrysAlis PRO* [3] and the refinement of the crystal structure revealed that the low-temperature phase is characterized by cubic symmetry with sp. gr. *I-43d*. The structure model was obtained by the charge-flipping method using *SUPERFLIP* [4] and *JANA2006* crystallographic packages [5]. Figure 4 shows the atomic structure of  $\text{Cs}_6\text{H}(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)_4$  crystals at ambient temperature.

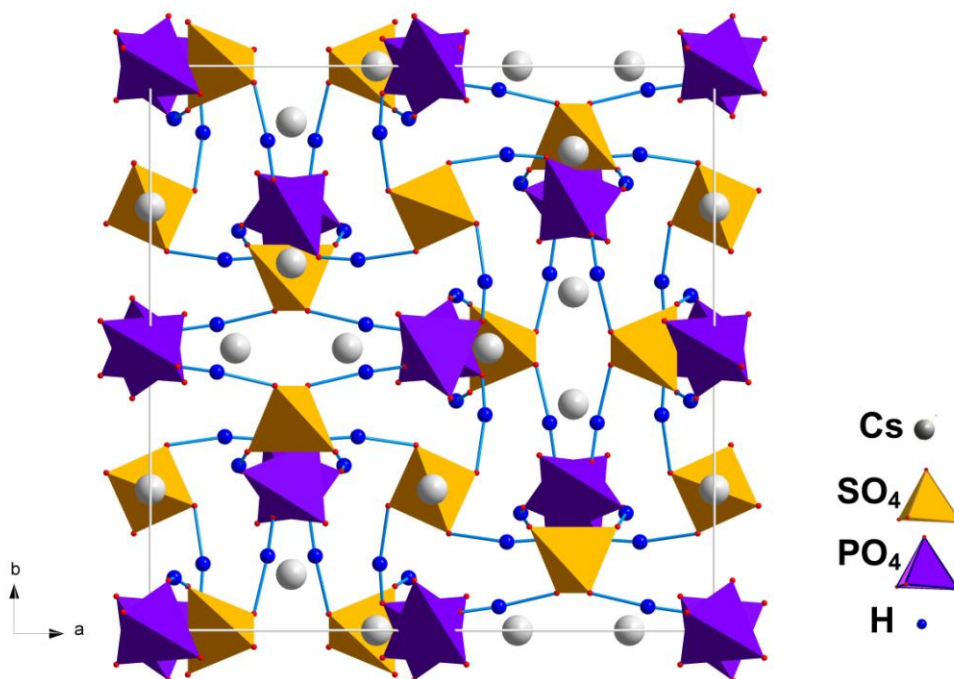


Fig. 4.  $\text{Cs}_6\text{H}(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)_4$  crystals: the atomic structure at ambient temperature.  $\text{SO}_4$  tetrahedra (yellow),  $\text{PO}_4$  tetrahedra (violet), and H-bonds (blue) are shown also.

On the basis of optical and SR data, we can suggest existence of a phase transition from the low-temperature cubic phase with the lattice parameter  $a \sim 14.6 \text{ \AA}$  to the high-temperature cubic phase with  $a \sim 5 \text{ \AA}$  at  $T \sim 365 \text{ K}$ . Taking into account the vicinity of the conductivity activation energy for  $\text{Cs}_6\text{H}(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)_4$  and  $\text{CsH}_2\text{PO}_4$  crystals [5] and similar lattice parameter of the  $\text{CsH}_2\text{PO}_4$  superprotonic cubic phase ( $a = 4.98 \text{ \AA}$ ), we can suggest that the high-temperature cubic phase of the  $\text{Cs}_6\text{H}(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)_4$  crystal has protonic conductivity and the structure of this phase is similar to that of  $\text{CsH}_2\text{PO}_4$ .

Diffraction data showed that ambient-temperature phase remains on cooling, and there are no phase transitions down to 200 K.

The information about obtained results is preparing for submission to journals.

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### **References:**

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