Experimental report

21/05/2019

Proposal:	**5-11-429**	**Council:**	4/2018

Title: The new representative of solid acid conductors: the influence of thehydrogen subsystem on physical properties

Research area: Chemistry

This proposal is a new proposal

Main proposer:	**Irina MAKAROVA**
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Local contacts:	Estelle MOSSOU Laura CANADILLAS DELGADO

Samples: $Cs_6H(HSO_4)_3(H_2PO_4)_4$
$(K_{0.43}(NH_4)_{0.57})_3H(SO_4)_2$
$Cs_5H_3(SO_4)_4.H_2O$

Instrument	Requested days	Allocated days	From	To
D19	9	7	27/09/2018	04/10/2018

Abstract:

This project aims to study novel crystals of the family of $M_mH_n(AO_4)_{(m+n)/2}$ (М = K, Rb, Cs, NH_4; AO_4 = SO_4, SeO_4, HPO_4, $HAsO_4$), which are actively investigated to elucidate the influence of the hydrogen subsystem on the physicochemical properties of materials, stabilization of phases with high proton conductivity, and with a view to designing new functional materials, including for fuel cells. The current proposal aims to study of new $Cs_6H(HSO_4)_3(H_2PO_4)_4$ crystals. We expect to obtain precise structural data on an atomic structure of this compound at different temperatures, including information on hydrogen bonded network. Combined with our X-ray data, this information will allow us to establish a relationship between crystal structure and protonic conductivity, that is important both for the characterization of this compound and understanding of the common features in the $M_mH_n(AO_4)_{(m+n)/2}$ crystal family.

REPORT

on experiment 5-11-429 performed at ILL on instrument D19

Title: The new representative of solid acid conductors: the influence of the hydrogen subsystem on physical properties

Main proposer – Dr. Makarova Irina

This project aims to study novel crystals of the family of $M_mH_n(AO_4)_{(m+n)/2}$ (M = K, Rb, Cs, NH_4; AO_4 = SO_4, SeO_4, HPO_4, $HAsO_4$), which is actively investigated to elucidate the influence of the hydrogen subsystem on the physicochemical properties of materials, stabilization of phases with high proton conductivity, and with a view to designing new functional materials, including for fuel cells [1]. At the Shubnikov Institute of Crystallography the phase diagram of the CsH_2PO_4–$CsHSO_4$–H_2O ternary system was systematically studied for the first time, from which it became possible to synthesize and grow new compounds of mixed sulfate-phosphates of cesium in the form of large single crystals [2].

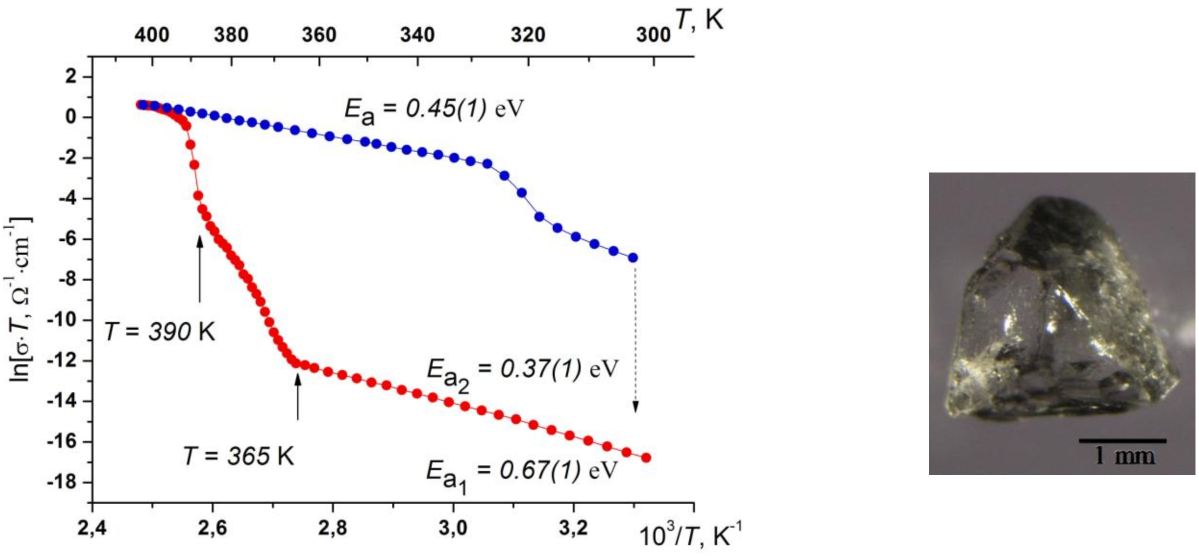
The purpose of the experiments at D19 is to study $Cs_6H(HSO_4)_3(H_2PO_4)_4$ single crystals - the new representative of the mixed system of CsH_2PO_4–$CsHSO_4$, and to collect information on the nature of high conductivity. As opposed to other hydrogen-containing compounds, the phase transitions in superprotonic crystals are accompanied by a hydrogen-bond network rearrangement, which results in a radical change of the physicochemical properties. These crystals are unique in the class of proton conductors, since the superprotonic conductivity is related to the structural features of these compounds rather than to the presence of doping additives. The use of neutron diffraction methods is associated with the need to obtain precise structural data on the atomic structure of hydrogen-containing compounds, including information about the hydrogen bonds.

Despite the advance reached in the study of $M_mH_n(AO_4)_{(m+n)/2}$ 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. In the current situation, the establishment of the structural conditionality of anomalies in physical properties in $Cs_6H(HSO_4)_3(H_2PO_4)_4$ crystals is of obvious interest both for the characterization of this compound and understanding of the common features and differences in the family of $M_mH_n(AO_4)_{(m+n)/2}$ crystals.

Precision measurements of complex impedance showed that $Cs_6H(HSO_4)_3(H_2PO_4)_4$ single crystals transform to the superprotonic phase, and conductivity reaches $10^{-2}\ \Omega^{-1}\ cm^{-1}$ at a relatively low temperature of ~390 K (Fig. 1a). The crystals are in an optically isotropic phase at ambient conditions. At $T_{sp} \approx 380$ K the onset of structural phase transition was observed, and the growth of a new phase. At $T \approx 390$ K the transition to another high-temperature optically isotropic phase was observed in the samples. It should be mentioned that the weight loss of samples wasn't recorded at heating until the temperature reached. In comparison with other sulfate/phosphates of cesium, significantly different thermal behavior was registered in $Cs_6H(HSO_4)_3(H_2PO_4)_4$ crystals: high conductivity in the specimens is observed even after decreasing of temperature.

X-ray diffraction studies of $Cs_6H(HSO_4)_3(H_2PO_4)_4$ crystals revealed the structure type different from other superprotonic compounds: the space group $I\text{-}43d$ – the cubic phase already at ambient conditions [2].

Preliminary characterization of crystal samples was carried out using OrientExpress, an automatic Laue neutron-diffractometer (ILL). This procedure made it possible to check the absence of twinned components and to select single crystal samples with the required high quality for neutron-diffraction measurements (Fig. 1b).



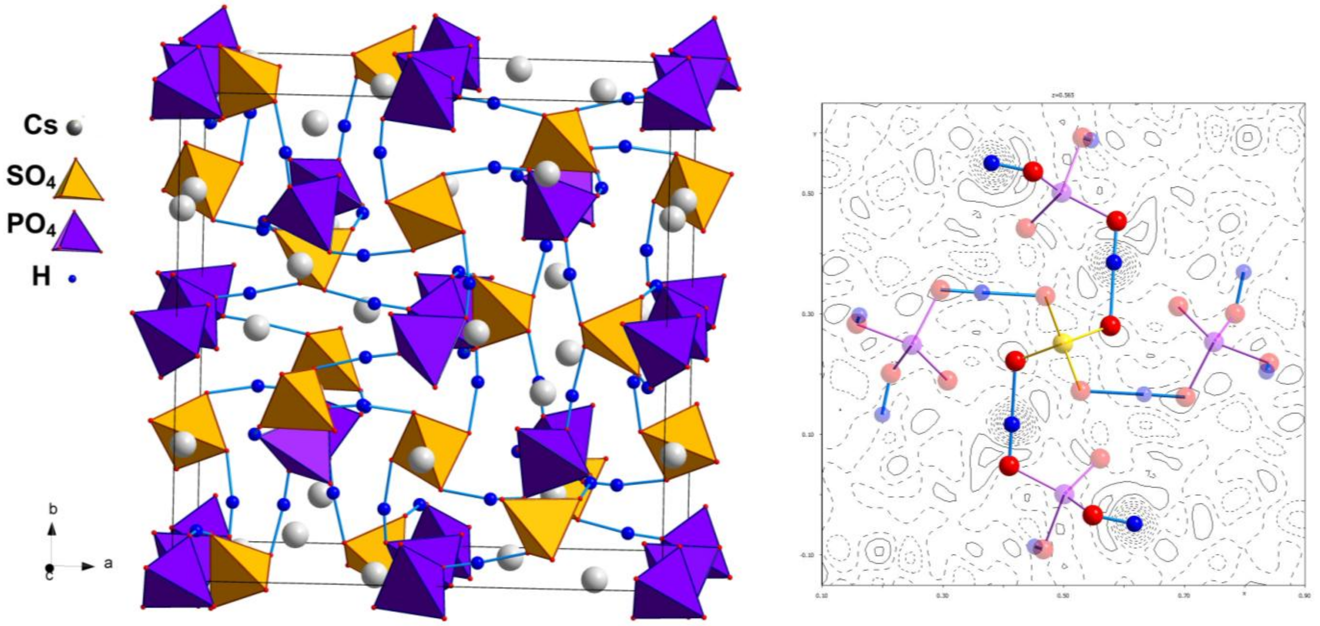
a b

Figure 1. $Cs_6H(HSO_4)_3(H_2PO_4)_4$ crystals: (a) the temperature dependences of conductivity; (b) one of the single crystal selected for experiments.

Two samples of $Cs_6H(HSO_4)_3(H_2PO_4)_4$ with H atoms and with H partly replaced by D atoms were used for experiments. The diffraction data were collected on the monochromatic four-circle diffractometer D19 (ILL). The wavelength used was 1.451366(36) Å, provided by a flat Cu(220) monochromator at $2\theta_M = 69.91°$ take-off angle. The samples were cooled up to 290 K, 200 K and 150 K at 2 K/min cooling rate. After these measurements the samples were warmed up to 360 K and 408 K at 2 K/min. To perform these measurements an Oxford Cryosystems 700 Series Cryostream (500 K- 80 K) has been used. The measurement strategy consisted on 5 omega (ω) scans with steps of 0.07° at different χ and φ positions [3]. The Multi-Detector Acquisition Data Software (MAD) from ILL was used for data collection. Unit cell determination was done by using PFIND and DIRAX programs, and processing of the raw data was applied using RETREAT and RAFD19 programs [4-6]. Absorption correction was applied using D19ABS program [7]. The refinement of the crystal structure was performed using JANA2006 crystallographic package [8].

To refine the crystal structure of $Cs_6H(HSO_4)_3(H_2PO_4)_4$ (samples with H and H/D) at different temperatures, the coordinates of the basic atoms from [2] were used as the initial data (without hydrogen atoms). Using neutron data the refined crystal parameters confirmed that the low-temperature phase is characterized by cubic symmetry with space group *I*-43*d*. Fig. 2a shows the atomic structure of $Cs_6H(HSO_4)_3(H_2PO_4)_4$ crystals (at 290 K). Special attention was paid to the localization of hydrogen atoms. Difference-Fourier maps calculated after refinement of the structural model with disregarded H atoms clearly indicated the positions of the hydrogen atoms (Fig. 2b, the map at 290 K for example). Obtained structural data allow concluding definitely about the system of hydrogen bonds in the compound under study. There is only one type of hydrogen bonds in the $Cs_6H(HSO_4)_3(H_2PO_4)_4$ (Fig. 2): the hydrogen bond connected SO_4 and PO_4 tetrahedra with a single-minimum potential. Each PO_4 tetrahedron is involved in three hydrogen bonds with O atoms as donors of these bonds, and each SO_4 tetrahedron is involved in four hydrogen bonds with O atoms as acceptors of these bonds. Such system is unique for superprotonic crystals and comparable with compounds of H_3PO_4 and H_2SO_4.

Diffraction data showed that ambient-temperature phase remains on cooling, and there are no phase transitions down to 150 K. Neutron diffraction data unambiguously revealed transition to high temperature phase, and the different behavior of the samples with H and with H/D at T > 380 K.



a b

Figure 2. $Cs_6H(HSO_4)_3(H_2PO_4)_4$ crystals: (a) the atomic structure at 290 K (SO_4 and PO_4 tetrahedra, and H-bonds are shown); (b) difference-Fourier maps (H atoms are disregarded, contour intervals are 0.5 fm/Å^3; atoms are shown, which are located near this cross section).

To elucidate the effect of isomorphic substitution on the kinetics of phase transitions, the diffraction data were collected for single crystals of $(K_{1-x}(NH_4)_x)_3H(SO_4)_2$ with x =0.57 at 300 and 250 K with the measurement strategy analogical to above. These crystals have particular interest because of the same structure type with the space group $R\bar{3}$ and high protonic conductivity at the room temperature according studies of dielectric properties as the high-temperature phase of $(NH_4)_3H(SO_4)_2$ [9]. Rise of conductivity can be related with the appearance of the threefold axis and the disordering of the O atoms involved in hydrogen bonds that lead to the formation of a dynamically disordered network of hydrogen bonds.

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

We are grateful to ILL for providing time on the instrument D19 and our local contacts Dr. Estelle Mossou and Dr. Laura Canadillas Delgado for the qualified support at carrying out our experiments.

References:

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