

*The nature of high conductivity in solid acid proton conductors*

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Increasing energy consumption rates stimulate global interest in the study and development of alternative energy sources. One of the most rapidly developing fields associated with alternative energy sources is hydrogen energetics. To directly produce electrical energy, special devices, i.e., fuel cells providing direct chemical to electrical energy conversion were developed. Interest in superprotonic crystals  $MmHn(AO_4)_{m+n/2} \cdot \gamma H_2O$  ( $M = K, Rb, Cs, NH_4$ ;  $AO_4 = SO_4, SeO_4, HPO_4, HAsO_4$ ) is associated with the determination of the influence of the hydrogen subsystem on physicochemical properties and obtainment of materials for electrochemical devices. In contrast to other hydrogen-containing compounds, phase transitions in superprotonic crystals are accompanied by a radical change in properties, including the appearance of high proton conductivity at relatively low temperature ( $\sim 400$  K).

Structural data on these crystals are indicative of the existence of different mechanisms of changes in physical properties [1]: the formation of a dynamically disordered system of hydrogen bonds as in  $M_3H(XO_4)_2$ , crystallization water diffusion and formation of channels with partially occupied sites of atoms in  $(K, NH_4)_9H_7(SO_4)_8 \cdot H_2O$  [2], and the formation of a multiphase state. The transformation of bonds can stabilize the superprotonic phase and make it possible to supercool this phase practically to room temperature. Replacing ions with ammonium and the formation of additional hydrogen bonds can reduce conductivity in these crystals by four orders of magnitude or cause the occurrence of conduction already under ambient conditions.

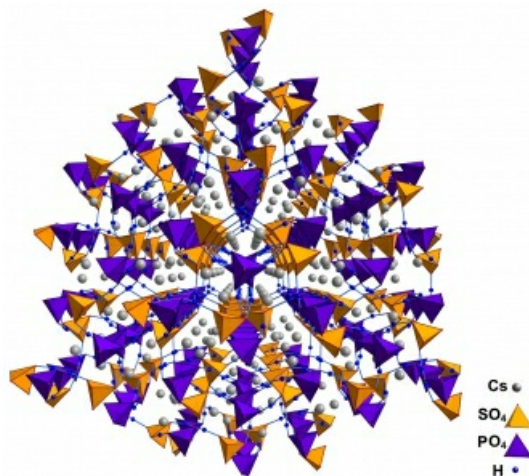
The kinetics of superprotonic phase transitions in  $Cs_3(HSO_4)_2(H_2PO_4)$ ,  $Cs_4(HSO_4)_3(H_2PO_4)$  and  $Cs_6H(HSO_4)_3(H_2PO_4)_4$  crystals [3] depends on their structure and composition significantly. The kinetics of the phase transitions of  $Cs_3(HSO_4)_2(H_2PO_4)$  and  $Cs_4(HSO_4)_3(H_2PO_4)$  change considerably owing to the statistical replacement of  $PO_4$  tetrahedra by the  $SO_4$  groups and decreasing the number of hydrogen bonds. The  $Cs_6H(HSO_4)_3(H_2PO_4)_4$  (Fig.) compound is chemically stable and exhibits reproducible properties.

This study was supported by the DST-RFBR collaboration (№13-02-92693, INT/RFBR/P-140) and by the Scholarship of the President of the Russian Federation (no. SP-1445.2016.1).

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**Keywords:** [crystal structure](#), [hydrogen bonds](#), [superprotonic phase transitions](#)