[MS28-P05] Solid acid proton conductors: the influence of hydrogen subsystems on physical properties.

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Interest in superprotonic crystals of $M_mH_n(XO_4)_{(m+n)/2}$ (M=K, Rb, Cs, NH_4; X=S, Se, P) is associated with the solution to fundamental problems of modern condensed matter physics: establishment of structural conditionality of anomalies of physical properties with the aim of designing new functional materials. Superprotonic crystals belong to a special class. As opposed to other hydrogen-containing compounds, phase transitions in these crystals are accompanied by a hydrogen-bond network rearrangement, resulting in a radical change in the physicochemical properties; in particular, these transitions give rise to proton conductivity of about 10^{-3} –10^{-1} Ω^{-1} cm^{-1}. These crystals are unique in the class of proton conductors, since the superprotonic conductivity is related to the structural features of these compounds, instead of consequence of impurity doping process. The occurrence of high superprotonic conductivity in the $M_3H(XO_4)_2$ crystals is associated with the formation of a qualitatively new and dynamically disordered hydrogen-bond system. This fact was found for the first time in the studies of structural phase transitions in the $Rb_3H(SeO_4)_2$ crystals [1] and was then confirmed for other $M_3H(XO_4)_2$ crystals, including $K_3H(SO_4)_2$ [2]. In $K_9H_7(SO_4)_8{\cdot}H_2O$ crystals, the only known representative of the $M_9H_7(XO_4)_8{\cdot}xH_2O$ family, the superprotonic phase transition at 405 K is associated with the diffusion of crystallization water, the hydrogen-bond network rearrangement, and the formation of channels for the possible motion of K atoms [3,4]. The hydrogen-bond rearrangement and the hindered back diffusion of water to the crystal stabilize the high-temperature phase and ensure its supercooling to low temperatures.

As a result of researches of the $CsHSO_4$ – CsH_2PO_4-H_2O system, the new crystals of $Cs_3(HSO_4)_2(H_2PO_4)$, $Cs_4(HSO_4)_3(H_2PO_4)$ and $Cs_6H(HSO_4)_3(H_2PO_4)_4$ [5] (enough big, with good optic quality) were grown up. The measurements of conductivity and optic researches of crystals showed superprotonic phase transitions at 409, 411 and 365 K correspondingly. The distinction in the properties of $Cs_3(HSO_4)_2(H_2PO_4)$ and $Cs_4(HSO_4)_3(H_2PO_4)$ (sp. gr. C2/c at 295 K) is related to differences in nets of hydrogen bonds formed between different-occupied XO_4 tetrahedra. $Cs_6H(HSO_4)_3(H_2PO_4)_4$ (sp. gr. I-43d at 295 K) has the net of hydrogen bonds that is completely different. After cooling crystals the high-temperature superprotonic phase preserve long enough without essential decrease in conductivity. These properties are especially attractive to practical applications. We are grateful to V.P. Dmitriev and D.Yu. Chernyshov (SNBL, ESRF, Grenoble) for help in conducting experiments with the use of synchrotron radiation and thank the ESRF for providing beam time on the BM1A beam-line. This study was supported by the Russian Foundation for Basic Research (project 11-02-01145) and the Physical Sciences Division of the Russian Academy of Sciences (Program for Basic Research "Physics of New Materials and Structures").

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