Poster Presentation

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New representatives of solid acid conductors: CsmHn((HSO4),(H2PO4))m+n

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Crystals - superprotonics are extensively studied with the goal of elucidating the influence of the hydrogen subsystem on the physicochemical properties and designing new functional materials. As opposed to other hydrogen-containing compounds, phase transitions in these crystals are accompanied by a hydrogen-bond network rearrangement, resulting in radical changes of their properties, in particular, in the appearance of proton conductivity about 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 rather than to the presence of doping additives. The occurrence of high superprotonic conductivity in the Me3H(XO4)2 (Me = K, Rb, Cs, NH4; X = S, Se, P, As) crystals is associated with the formation of a qualitatively new and dynamically disordered hydrogen-bond system [1]. In K9H7(SO4)8·H2O crystals, the only known representative of the Me9H7(XO4)8·xH2O family, the occurrence of high conductivity is associated with the outward diffusion of water molecules, the hydrogen-bond network rearrangement, and the formation of channels for the possible motion of K+ ions [2]. The hydrogen-bond rearrangement and the hindered back diffusion of water to the crystal bulk stabilize the high-temperature crystal structure and ensure its supercooling to low temperatures. The new crystals of Cs3(HSO4)2(H2PO4), Cs4(HSO4)3(H2PO4) and Cs6H(HSO4)3(H2PO4)4 were grown up in the CsHSO4–CsH2PO4-H2O system - enough big, with good optic quality [3]. The thermal and optical properties of crystals as well as their conductivity have been investigated in the temperature range 295 – 445 K. It was observed superprotonic phase transitions at 409, 411 and 365 K correspondingly. The distinction in the properties of Cs3(HSO4)2(H2PO4) and Cs4(HSO4)3(H2PO4) (sp. gr. C2/c at 295 K) is related to differences in nets of hydrogen bonds formed between different-occupied XO4 tetrahedra. Cs6H(HSO4)3(H2PO4)4 crystals (sp. gr. I-43d at 295 K) have the net of hydrogen bonds which is completely different. After cooling the high-temperature superprotonic phase preserves long enough without essential decrease in conductivity. This study was supported by the Russian Foundation for Basic Research (projects 13-03-12216 and 13-02-92693).

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