

The replacements in the cation sublattice in superprotonic crystals

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A fundamental problem of modern condensed state physics is the relationship between structures and physical properties of the crystals. To elucidate the effect of isomorphic substitution on the kinetics of phase transitions, single crystals of $(K_{1-x}(NH_4)_x)mHn(SO_4)_{(m+n)/2} \cdot yH_2O$ solid solutions are grown in the $K_3H(SO_4)_2 - (NH_4)_3H(SO_4)_2 - H_2O$ system which end members are known to undergo superprotonic phase transitions with essentially different kinetics.

The use of $K_3H(SO_4)_2$ and $(NH_4)_3H(SO_4)_2$ solutions with a ratio of 9:1 led to a growth of crystals of the same structure type as $K_3H(SO_4)_2$: the single crystals were described by the chemical formula $(K_{1-x}(NH_4)_x)_3H(SO_4)_2$ [1]. Based on the refinement of the structural model, it was concluded that the $(K_{1-x}(NH_4)_x)_3H(SO_4)_2$ samples under study contain no less than 3% ammonium. This amount of ammonium turned out to be sufficient to significantly change the kinetics of structural phase transitions in comparison with $K_3H(SO_4)_2$ crystals, which is related to the formation of additional hydrogen bonds and the change in the anisotropy of the coordination environment of both cations and SO_4 tetrahedra.

The use of $K_3H(SO_4)_2$ and $(NH_4)_3H(SO_4)_2$ solutions with a ratio of 3:7 led to growth of single crystals of the same structure type as the high-temperature phase of $(NH_4)_3H(SO_4)_2$ [2]. The refinement of the structure with allowance for the replacement of potassium with ammonium and the analysis and comparison of the main crystallographic characteristics with the $K_3H(SO_4)_2$ crystal revealed that the $(K_{1-x}(NH_4)_x)_3H(SO_4)_2$ crystal under study contains about 57% ammonium. Studies of dielectric properties revealed that the grown samples have high protonic conductivity at the room temperature.

Solutions of $K_3H(SO_4)_2$ and $(NH_4)_3H(SO_4)_2$ with different ratio (K:NH₄) crystallize in different structure types. Using $K_3H(SO_4)_2$ and $(NH_4)_3H(SO_4)_2$ solutions with a K:NH₄ ratio close to 1:1, one can grow single crystals with a structure type differing from that of the initial compounds: the chemical formula of the grown single crystals is $(K_{1-x}(NH_4)_x)_9H_7(SO_4)_8 \cdot H_2O$ [3]. The structural study of the grown samples revealed that they contain no less than 4% ammonium. A comparison of the data on the $K_9H_7(SO_4)_8 \cdot H_2O$ and $(K_{1-x}(NH_4)_x)_9H_7(SO_4)_8 \cdot H_2O$ crystals [3] showed that the replacement of potassium with ammonium reduced the structural PT temperature by 8 K. At the same time, the formation of additional hydrogen bonds of NH₄ groups, which block the conductivity channels for K ions, led to a decrease in conductivity by 4 orders of magnitude, which indicates simultaneously the contribution of K ions to the conductivity of $(K,NH_4)_9H_7(SO_4)_8 \cdot H_2O$ compound.

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[1] E.V. Dmitricheva, et al. (2014) Crystallogr. Rep. 59(6), 878-884.

[2] E.V. Dmitricheva, et al. (2015) Crystallogr. Rep. 60(6), 814-820.

[3] E.V. Dmitricheva, et al. (2014) Solid State Ionics. 268, 68-75.

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