Characteristic Features of the Change of Domain Structure in Mixed \([(\text{NH}_4)_{1-x}\text{Rb}_x]_3\text{H(SO}_4]\text{_2}\) Crystals in the Vicinity of Superprotonic Phase Transition

L. F. Kirpichnikova*, M. Polomska**, A. Pietraszko***, V. S. Shakhmatov****, and B. Hilczer**

* Shubnikov Institute of Crystallography, Russian Academy of Sciences, Leninski pr. 59, Moscow, 119333 Russia  
** Institute of Molecular Physics, Polish Academy of Sciences, Poznan, 60-179 Poland  
*** Institute of Low Temperature and Structure Research, Polish Academy of Sciences, Wroclaw, 50-959 Poland  
**** Joint Institute for Nuclear Research, Moscow oblast, Dubna, 141980 Russia

Abstract—X-ray diffraction measurements of mixed \([(\text{NH}_4)_{1-x}\text{Rb}_x]_3\text{H(SO}_4]\text{_2}\) crystals of different compositions are performed. The characteristics of the change of the domain structure in the vicinity of the superprotonic–ferroelastic phase transition in crystals of different compositions are studied and compared with the variations of the crystal structure in the course of gradual substitution of ammonium by rubidium. This phase transition is theoretically described based on the phenomenological theory of a high-temperature phase transition. © 2005 Pleiades Publishing, Inc.

INTRODUCTION

Mixed \([(\text{NH}_4)_{1-x}\text{Rb}_x]_3\text{H(SO}_4]\text{_2}\) (TARHS) crystals belong to the family of protonic conductors described by the general formula \(M_x\text{H}(\text{XO}_4)_2\), where \(M = \text{NH}_4, \text{Rb}, \text{and Cs and } X = \text{S and Se}\) [1–5]. The structure of the high-temperature superprotonic \((\text{NH}_4)_3\text{H(SO}_4]\text{_2}\) (TAHS) phase is trigonal, sp. gr. \(R\bar{3}m\). The ferroelastic monoclinic phase (sp. gr. \(A2/\alpha\)) of this compound is formed below \(T_S = 413\) K [4, 6, 7]. Moreover, ammonium crystals at low temperature undergo four more phase transitions [4, 6]. TAHS crystals have three types of hydrogen bonds of which two link nitrogen atoms and oxygen atoms of sulfate tetrahedra. The third short symmetric hydrogen bond (2.54 Å) links two neighboring sulfate ions via the so-called apical proton [7]. It is important that \(\text{RbH(SO}_4]\text{_2}\) (TRHS) crystals undergo only one irreversible phase transition at \(T_S = 486\) K, whereas the phase formed below \(T_S\) is not ferroelastic. Below \(T_S\), the \(\text{RbH(SO}_4]\text{_2}\) crystals are monoclinic, sp. gr. \(C2/c\) [8], and, according to [5, 9], they are transformed into the superprotonic cubic phase at \(T_S\). The length of the apical hydrogen bond in rubidium-containing crystals is slightly shorter than in ammonium-containing ones [3, 5, 10]. The mixed \([(\text{NH}_4)_{1-x}\text{Rb}_x]_3\text{H(SO}_4]\text{_2}\) crystals exhibit superprotonic properties; the temperature of the superprotonic phase transition increases with the gradual substitution of rubidium by ammonium. The compounds with \(x > 0.5\) have two superprotonic phases [5, 9, 11].

Recently, we discovered an anomalous change of the ferroelastic domain structure in the vicinity of the superprotonic transition in the crystals of the \(M_x\text{H}(\text{XO}_4)_2\) family [12, 13]. The unusual change of the domain structure in the vicinity of the superprotonic transition is of special interest, because the establishment of the cause of such behavior is important for more clear understanding of the characteristics of the microscopic mechanism of the transition into the phase with high conductivity. Moreover, the mixed crystals in the \([(\text{NH}_4)_{1-x}\text{Rb}_x]_3\text{H(SO}_4]\text{_2}\) system attract attention because TAHS crystals below the point of the superprotonic phase transition show ferroelastic properties, whereas TRHS crystals do not possess such properties.

Thus, it is important to study the mixed \([(\text{NH}_4)_{1-x}\text{Rb}_x]_3\text{H(SO}_4]\text{_2}\) crystals in more detail. Below, we describe our further study of the ferroelastic domain structure of mixed TARHS crystals, the X-ray diffraction studies of the crystals of various compositions, and the theoretical consideration of the superprotonic–ferroelastic phase transition in one of the mixed crystals with a high rubidium content.

EXPERIMENTAL

The study of the temperature variations of the ferroelastic domain structure of mixed \([(\text{NH}_4)_{1-x}\text{Rb}_x]_3\text{H(SO}_4]\text{_2}\) crystals with \(x < 0.5\) showed that being cooled below \(T_S\) in a narrow (~2 K) temperature interval results in the appearance of a large num-
number of small lenslike domains (Figs. 1a and 1c). The domains are so small and distorted that it is difficult to establish how many orientational states can exist in this narrow temperature range. With further lowering of the temperature, large domains are also formed (Figs. 1b and 1d). We observed the domain walls of the $W$ and $W'$ type (Sapriel classification [15]) corresponding to the change of the symmetry from trigonal, $3m$, to monoclinic, $2/m$. In the superprotonic phase, the crystals are transparent and optically uniaxial. In the transition to the superprotonic phase, both TRHS crystals and also mixed crystals with $x > 0.9$ are disintegrated into small pieces. Below the first superprotonic phase transition, the crystals with high rubidium content also consist of very small domains, but no formation of large domains with further lowering of the temperature is observed. Below the temperatures ($\sim T_{S1} - 2$ K), small domains are transformed into defect regions; the sample loses its transparency and becomes turbid. As is seen from Fig. 2a, in the superprotonic phase, the polydomain (001) cut of a [(NH$_4$)$_{0.97}$Rb$_{0.03}$]$_2$H(SO$_4$)$_2$ crystal becomes transparent (Fig. 2b). With a further increase in the temperature, the second superprotonic phase is formed at $T_{S2}$, which is accompanied by the formation of brightly colored regions (Fig. 2c). The lowering of the temperature below $T_{S2}$ made the sample polycrystalline and nontransparent. However, not by heating the crystal up to $T_{S2}$, but by first heating it only up to the temperature of the first superprotonic state and then decreasing it, small domains are formed at the temperatures lower than $T_{S1}$. These domains are transformed into defect regions (Fig. 2d) at the temperature ($\sim T_{S1} - 2$ K). The X-ray diffraction studies showed that the first superprotonic phase of mixed crystals is trigonal and is described by the sp. gr. $R\bar{3}m$, whereas the second superprotonic phase consists of a crystal in the polycrystalline state. The superprotonic phase of TRHS