PFM studies of ferroelectric phase transition in superprotonic (K0.43(NH4)0.57)3H(SO4))2 crystals

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Abstract. The new superprotonic crystal (K0.43(NH4)0.57)3H(SO4))2 is investigated by the scanning probe microscopy and X-ray diffraction. It is shown by piezoresponse force microscopy (PFM) that the crystal is in paraelectric phase at room temperature. The ferroelectric phase transition in the crystal at the temperature decreasing from 296 to 282 K is revealed by PFM. The thin nanorelief is observed at the natural cleavage surface of the crystals by studying its topology with atomic force microscopy. The pits and hills of the nanorelief demonstrate the stable depth (height) of about 0.7 nm, which corresponds to 1/3 unit cell in c axis direction.

1. Introduction
A systematic study of the salt system of K3H(SO4)2–(NH4)3H(SO4)2–H2O solid solutions was performed for the first time at the Shubnikov Institute of Crystallography of the Russian Academy of Sciences [1]. It was found that using K3H(SO4)2 and (NH4)3H(SO4)2 solutions with different K:NH4 ratio led to the crystallization of compounds with different structure types.

The research of single crystals grown in the K3H(SO4)2–(NH4)3H(SO4)2–H2O system from solutions with a K:NH4 concentration ratio about 3:7 revealed that they had a composition (K0.43(NH4)0.57)3H(SO4))2 with trigonal symmetry at ambient conditions [2,3] such as the superprotonic phase of (NH4)3H(SO4)2 at high temperature. Studies of dielectric properties allowed revealing the high conductivity, being typical for known superprotonic compounds at high temperatures [3]. The conductivity σDC increased with increasing temperature from 10⁻⁹Ω⁻¹cm⁻¹ at 223 K to ~3×10⁻⁴Ω⁻¹cm⁻¹ at 353 K. For comparison, the (NH4)3H(SO4)2 crystals have the value σDC10⁻⁴Ω⁻¹cm⁻¹ at 425 K [4]. The values obtained for the activation energies U = 0.72 eV below 283 K and U = 0.52 eV above 283 K for (K0.43(NH4)0.57)3H(SO4)2 crystals correspond to the values U = 0.76 eV and U = 0.47 eV for the low- and high-temperature phases of (NH4)3H(SeO4)2 crystals, respectively [5]. Obtained results lead to the conclusion that the temperature 283 K corresponds to the structural transition of the crystals to the low-temperature phase probably with lower symmetry.

In this study, the temperature behavior of (K0.43(NH4)0.57)3H(SO4)2 crystal was investigated by piezoresponse force microscopy (PFM) below room temperature to detect the phase transitions. The topography of the fresh cleavage and polished surfaces of the crystals has been studied by atomic force microscopy (AFM).
2. Experimental

Single crystals of \((K_{0.43}(NH_4)_{0.57})_3H(SO_4)_2\) were grown by controlled reduction of solubility. Crystallization was carried out over the temperature range from 303 to 313 K. Solutions with a K:NH\(_4\) concentration ratio of \(-3:7\) yielded large single crystals with high optical quality and habitus as pseudo-hexagonal thin plates with the predominant face (001) (Fig. 1a).

The structure and composition of the crystalline samples were refined by X-ray structural analysis using an Xcalibur S diffractometer (Oxford Diffraction) with a CCD area detector at room temperature. The experimental diffraction data were processed using CrysAlis PRO [6]. Structure refinement was carried out using JANA2006 [7].

The crystals surface relief was investigated with scanning probe microscope NTEGRA Prima (NT-MDT Spectrum Instruments, Russia). All experiments were carried out under controlled conditions of the TRACKPORE ROOM-05 measuring complex (purity class 5 ISO (100), the accuracy of maintaining the air temperature in the range 298± 5 K is ±0.05 K, the relative air humidity is 35 ± 1%). Before study the samples were cleaved in air along the (010) plane perpendicular to the c axis. The fresh cleavage surface was studied in tapping mode of AFM. The \((K_{0.43}(NH_4)_{0.57})_3H(SO_4)_2\) crystal was investigated with two PFM methods using various ways of recording the piezoelectric response. The first one is traditional contact PFM method, the second one is a hybrid PFM [8]. PFM measurements were carried out with the same scanning probe microscope. The silicon cantilevers (NSG01 / Pt, NT-MDT Spectrum Instruments) coated with Pt were used. The alternating voltage \(V_{ac}\) was applied to the conductive cantilever with a frequency of 49 kHz and an amplitude of 8 V. The maximum interaction force between cantilever tip and surface was 160 nN.

3. Results and discussion

X-ray study showed that the crystals had a trigonal symmetry, the space group \(R\bar{3}\), \(Z = 3\), \(a = b = 5.7768(3)\ Å, c = 22.0983(1)\ Å at \(T \approx 296\) K. The appearance of the threefold axis (and the trigonal symmetry) is due to the ratio K/N and the corresponding coordination of NH\(_4\) groups in the \((K_{0.43}(NH_4)_{0.57})_3H(SO_4)_2\) (Fig. 1b). This symmetry leads to the disordering of O atoms involved in hydrogen bonds, and, as a consequence, to the formation of a dynamically disordered network of hydrogen bonds and an increase in conductivity. Such an increase in symmetry and the formation of a dynamically disordered network of hydrogen bonds were observed in the high-temperature phases of isostructural superprotonic compounds at elevated temperatures.
Figure 2. AFM images of cleavage surface (001) of (K$_{0.43}$ (NH$_4$)$_{0.57}$)$_3$H(SO$_4$)$_2$ crystal. (a) Stepped microrelief of surface region (30×30 μm$^2$). (b) Nanorelief of one of the steps (5×5 μm$^2$).

Figure 3. AFM images of (K$_{0.43}$ (NH$_4$)$_{0.57}$)$_3$H(SO$_4$)$_2$ crystal as a function of temperature: (a) relief, contact AFM, (b), (c), (e) contact out-of-plane PFM (phase), (d) hybrid mode, hardness (arb. un).

The typical surface area of 30×30 μm$^2$ in size with stepped microrelief is shown in Figure 2a. The minimal steps height is 0.7 nm. The RMS parameter of roughness $R_q$ is 2 nm. The AFM image of smaller size (5×5 μm$^2$) is presented in Figure 2b. One can see the cleavage step with the islands and pits of height/depth about 0.7 nm and lateral sizes 50-150 nm and 20-100 nm, respectively. Such height/depth value is multiple to unit cell parameter and corresponds to 1/3 c.

As it ensues from the model of the atomic structure of (K$_{0.43}$ (NH$_4$)$_{0.57}$)$_3$H(SO$_4$)$_2$ crystal, along the c axis of the unit cell three layers of SO$_4$ tetrahedra connected by hydrogen bonds and K/NH$_4$ positions
among and between them are located. The nanorelief in the form of islands/pits observed on the surface, which height/depth is multiple $1/3 \ c$ axis of unit cell correlates with features of the layered structure of $(K_{0.43}(NH_4)_{0.57})\cdot H(SO_4)\cdot 2$ crystal. The analysis of the phase contrast AFM images showed that phase composition of the crystal cleavage surface was homogeneous.

The temperature changes (Fig. 3) were carried out with MP6LC thermostatic controller which allowed varying a temperature in the range from 243 to 393 K. The temperature changed three times from 296 ± 0.1 K to 278 ± 0.1 K and back. At room temperature PFM images demonstrated only homogeneous contrast. Decreasing temperature to 282 K allowed observing the appearance of dark contrast regions about 1 μm in size identified as ferroelectric domains. Increase temperature to 296K led to their disappearance. Therefore, the PFM investigations at decreasing temperature allowed observing the ferroelectric phase transition in $(K_{0.43}(NH_4)_{0.57})\cdot H(SO_4)\cdot 2$ crystal for the first time. It is shown that the phase transition is reversible. The obtained information supplements the structure and dielectric data [3].

4. Conclusion

In summary, we report the experimental measurements of the new superprotonic crystal $(K_{0.43}(NH_4)_{0.57})\cdot H(SO_4)\cdot 2$. Studies by AFM method gave the new information about morphology and piezoelectric response of natural cleavage surface and polished samples. At decreasing temperature, the PFM investigations allowed observing ferroelectric phase transition in $(K_{0.43}(NH_4)_{0.57})\cdot H(SO_4)\cdot 2$ crystals for the first time. The results of the PFM studies of the temperature change on the crystal surface correspond to the dielectric data for bulk samples, indicating modification of the conductivity at T~283 K, and the structural data, demonstrating changes of symmetry at superprotonic phase transitions in the crystals of the $(AO_4)_{(m+1/2)} $$\cdot$$ H_2O$ $(M = K, Rb, NH_4, AO_4 = SO_4, SeO_4)$ system.

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