Phase transitions in as-grown $K_{0.2}Rb_{1.8}Cd_2(SO_4)_3$ langbeinite crystals: a birefringence study

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Abstract. Basing on temperature dependences of the light intensity transmitted through polarisation system and the birefringence of $K_{0.2}Rb_{1.8}Cd_2(SO_4)_3$ crystals, we have determined the phase transition temperature for this solid solution. A conclusion is drawn that the monoclinic and triclinic phases on the (x, T)-phase diagram for the mixed crystals $K_{2x}Rb_{2(1-x)}Cd_2(SO_4)_3$ should disappear at the triple points occurring at x < 0.1.

1. Introduction

A family of langbeinite crystals consists of more than thirty compounds with a general chemical formula $M_2^+ M_2^{++}(SO_4)_3$, where M_2^+ and M_2^{++} are respectively single-valent and bivalent metal cations [1]. These crystals are interesting from the viewpoint of sequence of their structural phase transitions. In order to classify the phase transitions in langbeinites, one can conventionally divide these crystals into three groups. The first one comprises such compounds as, e.g., $Tl_2Cd_2(SO_4)_3$ and $Rb_2Cd_2(SO_4)_3$, which undergo three phase transitions with the changes of point symmetry described according to the scheme 23 F 2 F 1 F 222 [2, 3]. However, not all of the phase transitions in this sequence can happen in some of the compounds belonging to this group. For example, $(NH_4)_2Cd_2(SO_4)_3$ crystals reveal only the 'upper' phase transition with the change of point symmetry 23 F 2 [4]. The crystals $K_2Cd_2(SO_4)_3$, $K_2Mn_2(SO_4)_3$, $K_2Co_2(SO_4)_3$ and some other belong to the second group which manifests a single phase transition with the symmetry change 23 F 222 [5–7]. Finally, the compounds belonging to the third group (e.g., $(NH_4)_2Mn_2(SO_4)_3$, $Tl_2Mn_2(SO_4)_3$ and $K_2Mg_2(SO_4)_3$) reveal no structural transformations at all in the overall temperature range where their crystalline phase is stable [8, 9].

The phase transitions into the phases with the symmetries 2 and 1 are improper ferroelectric-to-ferroelastic, while the transition into the phase 222 is proper ferroelastic [2, 3]. Notice that all the phase transitions in the pure compounds are of a first order. The phase diagram for the langbeinite crystals has been suggested in the work [10], basing on the analysis of their thermodynamic potential. It is interesting that a number of special points have been predicted on this phase diagram. In particular, these are triple points where the lines of phase transitions between the phases with the symmetries 23, 222, 2, 222, 2, 1 and 23, 2, 3 converge. Notice also that the trigonal phase with the symmetry 3 has never been observed in the langbeinite crystals.

The triple points have been detected experimentally on the pressure–temperature (p, T)-phase diagram of the langbeinite crystals $(NH_4)_2Cd_2(SO_4)_3$ $Tl_2Cd_2(SO_4)_3$ and $Rb_2Cd_2(SO_4)_3$ [8].

However, any attempts to identifying the symmetry of the phases induced by hydrostatic pressure represent a rather difficult experimental problem. As a result, the symmetries of the pressure-induced phases have not yet been determined. Besides, the triple point for the mixed crystals $[Tl_{1-x}(NH_4)_x]_2Cd_2(SO_4)_3$, where the lines of phase transitions between the phases 23, 2 and 1 converge has been detected at x = 0.05 [11]. Nonetheless, the theoretical phase diagram assumed in the work [10] does not predict such a triple point and so it has to be reconsidered. In our recent studies [12–15] we have not observed the triple points on the phase diagrams of the solid solutions undergoing the same sequence of phase transitions, e.g., for $Rb_{2x}Tl_{2(1-x)}Cd_2(SO_4)_3$ and $K_2Cd_{2x}Mn_{2(1-x)}(SO_4)_3$.

In the present work we have grown and studied experimentally the solid solution related to the initial pure compounds undergoing completely different phase transition sequences. These are 23 F 222 in $K_2Cd_2(SO_4)_3$ and 23 F 2 F 1 F 222 in $Rb_2Cd_2(SO_4)_3$. Our aim is the (x, *T*)-phase diagram of their solid solution.

2. Results and discussion

We have grown the $K_{2x}Rb_{2(1-x)}Cd_2(SO_4)_3$ solid solutions with the concentration x = 0.1 from an aqueous solution, using the chemical compounds K_2SO_4 (99.99%, Aldrich), Rb_2SO_4 (99.8%, Merck), and $3CdSO_4 \times 8H_2O$ (ultra-pure 13-4, Rreakhim). The growing process starts beginning from preparation of a relevant solution of stoichiometric powder of K_2SO_4 (0.39 g), Rb_2SO_4 (5.34 g) and $3CdSO_4 \times 8H_2O$ (11.42 g). After dissolving these compounds in bi-distilled water, we have filtered the solution and the crystals have been growing at 85°C during 2–3 weeks. As a result, we have obtained single crystals with the average lateral dimension of 11 mm and the weight of 4.15 g (see Fig. 1).

Fig. 1. As-grown single crystals of $K_{0.2}Rb_{1.8}Cd_2(SO_4)_3$.

We have studied the temperature dependence of the intensity of light (the wavelength of $\lambda = 632.8\ nm$) propagating through the system of crossed polarisers and a crystalline sample placed in between in an extinction orientation. The experiment has been performed at the room temperature. Despite of the fact that the crystals under study belong to the cubic crystallographic system at the room temperature (the point group of symmetry 23), a small remaining optical birefringence still exists It is known [15] that the residual birefringence in the paraelectric-paraelastic phase of the rubidium-cadmium langbeinite is of the order of $\sim 10^{-4}$. We have estimated the residual birefringence of our as-grown $K_{0.2}Rb_{1.8}Cd_2(SO_4)_3$ crystals, using a polarisation microscope. The light beam has propagated along the direction [111] in a 1.26 mm - thick sample.

We have found that the birefringence at the room temperature is of the order of 10^{-5}. As the temperature decreases and the crystals remain in their ferroelectric-ferroelastic and ferroelastic phases, the optical indicatrix should inevitably change its orientation. As a consequence, one

should observe some nonzero light transmission of the polarisation system. Hence, the temperature at which the intensity of the transmitted light becomes nonzero may be taken as an upper phase transition point T_1. The phase transition into the pure ferroelastic phase (T_3) is usually accompanied by drastic changes in the birefringence, which must be observable as a sharp light intensity change. Probably, the most difficult problem is identifying a point of the phase transition between the phases of the symmetries 2 and 1 (T_2). However, since the phase transformation in the pure $Rb_2Cd_2(SO_4)_3$ crystals is accompanied by a reconstruction of domain structure [16], it can manifest itself as a small anomaly observed in the temperature dependence of the light intensity.

Using a Senarmont technique, we have measured temperature dependence of the birefringence. Then the sample is placed into a closed-cycle cryostat CS202–X1.AL (Advanced Research Systems, Inc.) with a temperature regulation setup 9700 Scientific Instruments. The temperature has been changed using a heating run with the rate of $dT/dt = 1.0\,\mathrm{K/min}$. The temperature dependences of the light intensity passed through the analyser and the birefringence are shown in Fig. 2.
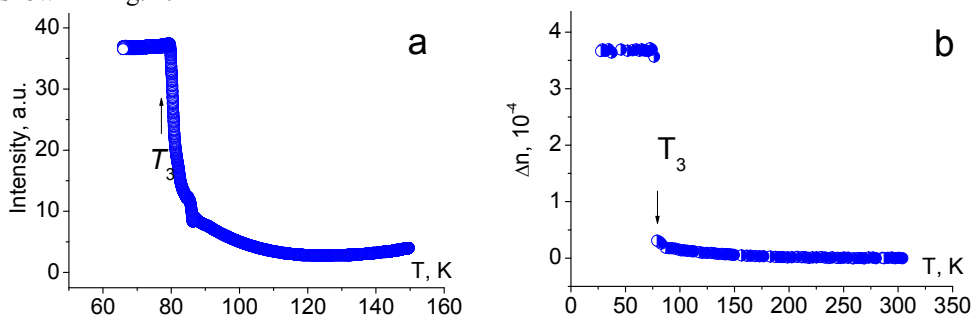

Fig. 2. Temperature dependence of the light intensity passed through polarisation system with the $K_{0.2}Rb_{1.8}Cd_2(SO_4)_3$ sample placed between crossed polarisers (a), and temperature dependence of the optical birefringence (b).

As seen from Fig. 2, only one phase transition is clearly observed in the solid solutions $K_{2x}Rb_{2(1-x)}Cd_2(SO_4)_3$ with x = 0.1. Obviously, this phase transition should be ferroelastic. It becomes obvious from the temperature dependence of the light intensity that this phase transformation is diffused. Under heating the ferroelastic phase begins to disappear at the temperature $T_3 \simeq 78$ K. A spike appearing at $T_2 = 86$ K on the temperature dependence of the light intensity (see Fig. 2a) corresponds to some movement of phase boundary across the laser beam. The cubic-to-monoclinic and monoclinic-to-triclinic phase transitions have not been detected in our experiments. Let us also remind that the pure $Rb_2Cd_2(SO_4)_3$ crystals reveal the relevant phase transitions at $T_1 = 129$ K, $T_2 = 103$ K i $T_3 = 68$ K [17], while in the pure $K_2Cd_2(SO_4)_3$ crystals a single structural (ferroelastic) phase transition is seen at 432 K.

In conclusion, the temperature regions of the monoclinic and triclinic phases narrow with increasing potassium concentration and then tend to zero at the concentrations lower than x ≈ 0.1. Hence, the triclinic and monoclinic phases should disappear at the triple points which occur under the potassium concentrations x < 0.1. This conclusion agrees with the fact that only one ferroelastic phase transition exists in the pure compound $K_2Cd_2(SO_4)_3$.

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Анотація. *На основі дослідження температурної залежності інтенсивності світла, що пройшло крізь поляризаційну систему і кристал $K_{0,2}Rb_{1,8}Cd_2(SO_4)_3$, та двозаломлення в роботі визначено температуру фазового переходу у цих твердих розчинах і показано, що моноклінна та триклінна фази повинні зникати з (x, T)-фазової діаграми кристалів $K_{2x}Rb_{2(1-x)}Cd_2(SO_4)_3$ у потрійних точках за умови x < 0,1.*