

OPTICAL PROPERTIES

Influence of Atmospheric Humidity on the Symmetry and Phase Transitions of Layered Potassium Oxyfluorides $K_2NbOF_5 \cdot H_2O$

S. V. Melnikova^{a,*} and N. M. Laptash^{b,**}

^a Kirensky Institute of Physics, Siberian Branch of the Russian Academy of Sciences,
Akademgorodok 50–38, Krasnoyarsk, 660036 Russia

* e-mail: msv@iph.krasn.ru

^b Institute of Chemistry, Far-Eastern Branch of the Russian Academy of Sciences,
pr. Stoletiya Vladivostoka 159, Vladivostok, 690022 Russia

** e-mail: laptash@ich.dvo.ru

Received November 22, 2012

Abstract—Crystals of $K_2NbOF_5 \cdot H_2O$ have been grown, polarization optical investigations have been performed, and the birefringence and rotation angle of the optical indicatrix have been measured in the temperature range 100–400 K. It has been found that, depending on the degree of atmospheric humidity, the layered $K_2NbOF_5 \cdot H_2O$ crystal at room temperature can be in three states, namely, *A*, *B*, and *C*, which differ in symmetry and properties of the crystal. The $K_2NbOF_5 \cdot H_2O$ crystal in the *A* state exists at a relative humidity $RH = 90\text{--}100\%$ and undergoes a first-order improper ferroelastic phase transition $P\bar{1} \leftrightarrow C2/m$, which is accompanied by strong anomalies of the optical characteristics, twinning, and shear strain x_6 at temperatures $T_2^\downarrow = 308$ K and $T_2^\uparrow = 313$ K. The most stable state of the $K_2NbOF_5 \cdot H_2O$ crystal is the *B* state ($RH = 20\text{--}90\%$), which retains the monoclinic symmetry $C2/m$ in the temperature range 100–370 K. In a dry atmosphere ($RH = 0\text{--}20\%$) or at $T_1 \approx 370$ K, the crystal becomes anhydrous (K_2NbOF_5) with the symmetry $P4/nmm$ (the *C* state). The difference between the crystals in the states *A* and *B* is explained by the presence or absence of water molecules in interlayer spaces.

DOI: 10.1134/S1063783413060243

1. INTRODUCTION

Considerable interest expressed by researchers in oxyfluoride compounds is explained by the possibility of producing new functional materials with acentric symmetry and wide range of transparency, because the structure of these compounds consists of cations *A* and isolated polar complexes $[BX_6]^{2-}$ [1]. A comparative analysis of compounds with the general formula A_2BX_6 (*A* = K, Rb, Cs, Na, NH_4 ; *B* = Nb, Mo, W; *X* = O (F)) has revealed that the structure of potassium crystals has a specific feature [1–8]. The anionic groups BX_6 in these compounds are isolated and located so as to form two types of interoctahedral polyhedra. The first type includes octahedral cavities formed by vertices of six adjacent complexes BX_6 . They are filled by one-half of all the potassium ions. The second type includes twelfold-coordinated polyhedra formed by faces of the BX_6 groups. They are only half-filled by the remaining potassium atoms. Free cavities can be filled by the water involved in the formation of crystal hydrates. With the loss of water, the general motif of the structure is retained, but the atomic coordinates

and unit cell parameters are changed, which leads to a change in the symmetry of the material. The anhydrous crystals K_2NbOF_5 , $K_2MoO_2F_4$, and $K_2WO_2F_4$ have the symmetry $P4/nmm$ (Nb: $a = 6.12$ Å, $c = 8.98$ Å, $Z = 4$) [2–4], whereas the grown crystal hydrates are monoclinic and have different space groups. According to [4–6], the crystal hydrates $K_2NbOF_5 \cdot H_2O$, $K_2MoO_2F_4 \cdot H_2O$, and $K_2WO_2F_4 \cdot H_2O$ have the symmetry $P2_1/c$ (Nb: $a = 6.241$ Å, $b = 6.197$ Å, $c = 17.935$ Å, $\beta = 95.03^\circ$, $Z = 4$), while the crystal hydrate $K_2MoOF_5 \cdot H_2O$ has the symmetry $C2/m$ [7].

Recent investigations of the structure of the $K_2WO_2F_4 \cdot H_2O$ single crystal have demonstrated that, at room temperature, this compound has the symmetry group $C2/m$ ($a = 8.791$ (1) Å, $b = 8.792$ (1) Å, $c = 9.152$ (1) Å, $\beta = 98.675^\circ$, $Z = 4$) [8]. The water molecules are located in twelfold-coordinated polyhedra and held by hydrogen bonds with all the ligands. The chosen model of the structure with disordering of the crystal water in two positions around the twofold symmetry axis suggests the possibility of reducing the symmetry during cooling. Moreover, it was found [8] that,

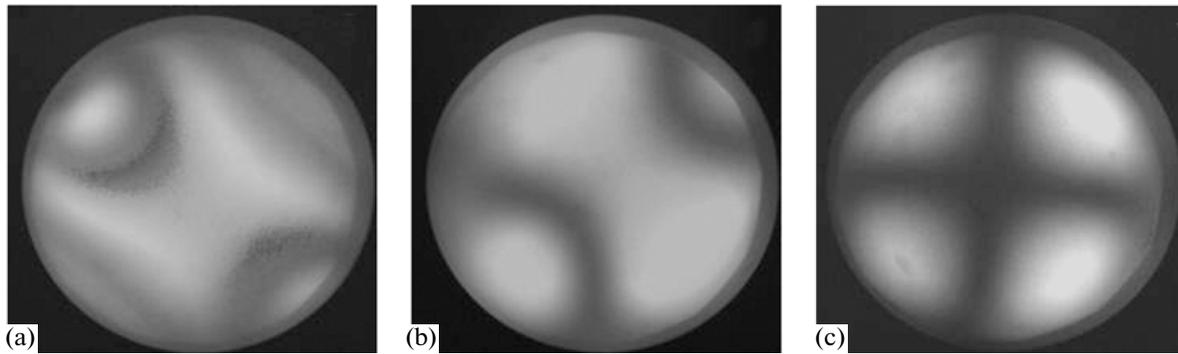


Fig. 1. Conoscopic patterns from the $(001)_T$ plates of the $K_2NbOF_5 \cdot H_2O$ crystal in the states A , B , and C .

depending on the degree of atmospheric humidity, the layered $K_2WO_2F_4 \cdot H_2O$ crystal can exist in two states (A and B) with different sequences of reversible and irreversible phase transitions. In samples of the A type, there is the following change in the symmetry of the phases: $P\bar{1} \leftrightarrow C2/m \rightarrow P4/nmm$. The second-order proper ferroelastic phase transition ($P\bar{1} \leftrightarrow C2/m$) is accompanied by the twinning and the appearance of the shear strain x_6 . In crystals of the B type, the reversible phase transition does not lead to a change in the crystal system: $m \leftrightarrow C2/m \rightarrow P4/nmm$. It was experimentally proved that the structure, symmetry, and lattice parameters of the $K_2WO_2F_4 \cdot H_2O$ crystal in the states A and B at room temperature are equal to each other, respectively [8]. The crystal water in $K_2WO_2F_4 \cdot H_2O$ disappears at $T_1 \approx 350\text{--}380$ K and then is easily recovered from the atmosphere during a day. It is assumed that the difference between the crystals in the states A and B is associated with the presence (A) or absence (B) of the water molecules (except for the crystal water) in interlayer spaces in the amount that does not exceed 0.1% of the total mass of the material.

In this work, we synthesized and grew the $K_2NbOF_5 \cdot H_2O$ single crystals, performed the polarization optical investigations, and measured the birefringence and extinction angle in the temperature range 100–400 K with the aim of searching for and studying phase transitions and determining the symmetry of the phases.

2. CRYSTAL GROWTH

Crystals of potassium oxofluoroniobate were synthesized by reaction of the initial niobium(V) oxide with a concentrated HF acid (40%) during the heating on a hotplate (for example, 20 g niobium oxide and 40–45 ml HF). Then, the solution was filtered off, and the potassium-containing reagent (chemically pure KCl, KHF₂, and KF) was introduced. The addition of these reagents in a stoichiometric ratio calculated for

the formation of K_2NbOF_5 did not lead to the desired result. According to the X-ray powder diffraction analysis, the abundant crystalline precipitate consisted of potassium oxofluoroniobates of the more complex composition: $K_5Nb_3O_3F_{14} \cdot H_2O$ or $K_3Nb_2OF_{11}$. An excess of KF was added to the obtained precipitate (for example, 20 g $K_5Nb_3O_3F_{14} \cdot H_2O$ was mixed with 5 g KF), which was dissolved in an aqueous solution of HF, filtered, and evaporated in air with the formation of lamellar crystals of the $K_2NbOF_5 \cdot nH_2O$ compound. Immediately after the growth, the crystals contained 1.9 H₂O (thermogravimetry data). With time, the water content changed and, at a relative humidity $RH = 40\text{--}50\%$, the composition corresponded exactly to the stoichiometric formula $K_2NbOF_5 \cdot H_2O$.

The crystals grow predominantly in the form of micaceous rectangular $(001)_T$ plates [2] with a perfect cleavage plane. The lateral faceting of these plates is performed on the $(110)_T$ and $(1\bar{1}0)_T$ planes. At the same time, the selected samples of the (010) cut are always polycrystalline intergrown twins with a misorientation of the optical indicatrix in the adjacent regions by the angle $2\varphi \approx 5^\circ$. This circumstance excluded the possibility of performing X-ray diffraction investigations of the synthesized material on a single crystal. In this work, we carried out the polarization optical investigations on the grown $(001)_T$ and (010) crystals and measured the rotation angle of the optical indicatrix and birefringence by the Berek compensator method with an accuracy of ± 0.0001 . The experiments were performed using an “Axioskop-40” microscope and a “Linkam LTS 350” temperature chamber in the range from 100 to 400 K.

3. EXPERIMENTAL RESULTS

The observations of $K_2NbOF_5 \cdot H_2O$ with the use of a light-polarizing microscope have revealed that, depending on the atmospheric humidity, this compound at room temperature can exist in three states (A , B , C) (Fig. 1) and transforms from one state into

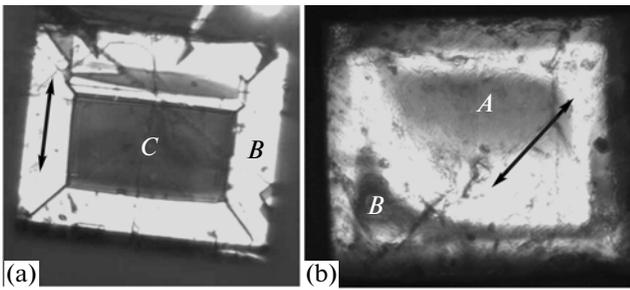


Fig. 2. Coexistence of the regions *A*, *B*, and *C* in the $\text{K}_2\text{NbOF}_5 \cdot \text{H}_2\text{O}$ samples at room temperature: (a) sample studied in the winter period (heating season, $\text{RH} \approx 20\%$) and (b) crystal in a humid atmosphere in the summer period ($\text{RH} \approx 90\%$). Arrows indicate the extinction positions.

another state with variations in the concentration of water vapors in the surrounding medium. One can observe the transition front moving from the edges toward the center (Figs. 2a, 2b). In the slowly running processes, the crystal plates remain transparent. These three states differ in the value of the optical anisotropy in the $(001)_T$ plates ($\Delta n_c \approx 0.01$ in the *A* state, $\Delta n_c = 0.02$ in the *B* state, and $\Delta n_c = 0$ in the *C* state) and in the arrangement of the axes of the optical indicatrix. At a relative atmospheric humidity of 90–100%, the crystal exists in the *A* state and is characterized by a strong birefringence Δn_c and a rotation of the optical indicatrix by the angle $\varphi_c = 43^\circ$ from the $[110]_T$ growth face. At a relative humidity $\text{RH} = 20\text{--}90\%$, the $\text{K}_2\text{NbOF}_5 \cdot \text{H}_2\text{O}$ crystal exists in the most stable form (the *B* state) with a weak birefringence Δn_c and a “direct” extinction of the (001) plate along the growth face ($\varphi_c = 0$). It is obvious that the *C* state is the K_2NbOF_5 tetragonal crystal [2]. The loss of the crystal water is possible even at room temperature with a humidity of less than 20%.

The temperature investigations of the extinction positions of the $(001)_T$ plate in the *A* state have demonstrated that the φ_c angle depends on the temperature (Fig. 3, curve 2). In the temperature range from 100 to 300 K, the φ_c angle changes only slightly ($\varphi_c = 45^\circ\text{--}42^\circ$), but, with a further increase in the temperature, the φ_c angle sharply decreases to zero near $T_2^\uparrow = 313$ K. Because of the large changes in the angle $\varphi_c(T)$, during the measurement of the birefringence $\Delta n_c(T)$ we performed an additional orientation of the sample at each temperature point to match the coordinates of the optical indicatrix. The results obtained from the temperature measurements of the birefringence $\Delta n_c(T)$ of the crystal in the *A* state are presented in Fig. 3 (curve 1). The optical anisotropy at low temperatures $T \approx 100$ K reaches the maximum value $\Delta n_c \approx 0.016$. During the heating, the birefringence of the sample gradually decreases and, near $T \approx 312$ K,

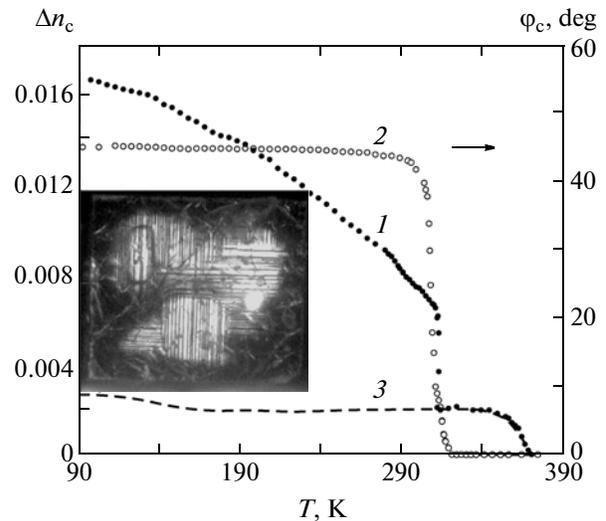


Fig. 3. Temperature dependences of (1) the birefringence $\Delta n_c(T)$ and (2) the rotation angle of the optical indicatrix $\varphi_c(T)$ for the $\text{K}_2\text{NbOF}_5 \cdot \text{H}_2\text{O}$ crystal in the *A* state. The inset shows the lamellar twin structure with boundaries along the $[110]_T$ direction, which is formed during cooling in the middle part of the sample. Curve 3 shows the behavior of the dependence $\Delta n_c(T)$ in the *B* state.

reaches the value $\Delta n_c \approx 0.006$; then at $T_2^\uparrow = 313$ K, it abruptly decreases to the value $\Delta n_c = 0.002$. With further heating, the birefringence Δn_c remains unchanged up to the temperature of 360 K; then, it gradually decreases, and at $T_1 \approx 370$ K, the optical anisotropy disappears: $\Delta n_c = 0$. The crystal becomes optically uniaxial.

If the sample is not heated above T_1 , then, during the cooling, the anomalies in the dependences $\Delta n_c(T)$ and $\varphi_c(T)$ are again observed, but they are shifted by $\delta T = 5$ K ($T_2^\downarrow = 308$ K). Moreover, at temperatures $T < T_2^\downarrow$, in the field of view of the light-polarizing microscope there appears a bright stripe twin pattern with boundaries along the $[110]_T$ direction (see inset in Fig. 3). This indicates a reduction of the crystal symmetry due to the ferroelastic phase transition. The optical indicatrices in the neighboring twins near 300 K are rotated through a very large angle $2\varphi_c \approx 86^\circ$. This pattern is frequently observed only in the middle part of the sample. At the edges of the plate, the “direct” extinction is retained along the $[110]_T$ direction. In repeated heating–cooling processes occurring through the temperature T_2 , the sample region with twins gradually narrows and can disappear completely.

In contrast to the crystal in the *A* state, the $(001)_T$ plate in the *B* state is characterized by a “direct” extinction ($\varphi_c = 0$) in the temperature range 90–370 K. In these samples, the birefringence is small and does not change in the temperature range 150–350 K

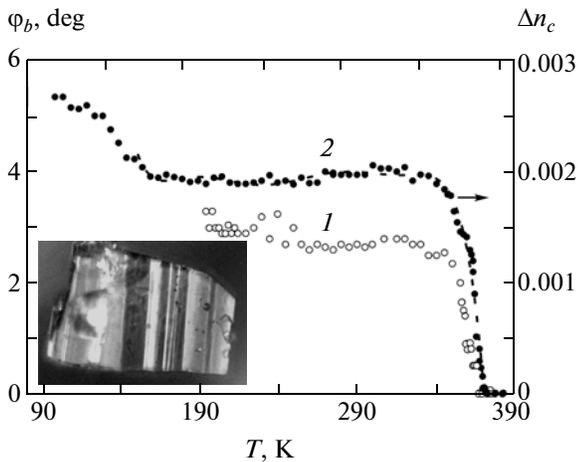


Fig. 4. (1) Temperature behavior of the misorientation angle in the twins $\varphi_b(T)$ and (2) temperature dependence of the birefringence Δn_c in the $(001)_T$ plates (the B state). The inset shows the twin pattern observed in the (010) cut of the $\text{K}_2\text{NbOF}_5 \cdot \text{H}_2\text{O}$ crystals in the states A and B .

(Fig. 4, curve 2). Below 150 K, the dependence $\Delta n_c(T)$ exhibits a small anomaly of unknown origin, whereas at the temperature $T_1 \approx 370$ K, the birefringence decreases to zero, and the crystal loses the crystal water and becomes tetragonal. For comparison of the optical anisotropies in the two states of the $\text{K}_2\text{NbOF}_5 \cdot \text{H}_2\text{O}$ crystal, the dependence $\Delta n_c(T)$ for the B phase is also shown in Fig. 3 (curve 3). It can be seen that, above $T_2^\uparrow = 313$ K, the temperature dependence of the birefringence in the $(001)_T$ plate is similar for the states A and B . The difference between the samples in the states A and B takes place only at temperatures below $T_2^\downarrow = 308$ K. The birefringence of the crystals in the A state drastically increases as a result of the phase transition at the temperature T_2^\downarrow (Fig. 3, curve 2), whereas the optical anisotropy of the sample in the B state changes only slightly (Fig. 3, curve 3).

The growth samples of the (010) cut in both the A and B states have a lamellar twin structure with the rotation of the indicatrices in the adjacent regions through a small angle $2\varphi_b \approx 5^\circ$ (see inset in Fig. 4). The temperature dependence of the extinction angle $\varphi_b(T)$ is shown in Fig. 4 (curve 1). The extinction angle has approximately the same value in the studied temperature range and vanishes at $T > T_1$.

4. DISCUSSION OF THE RESULTS

The above-described experimental results indicate that, at room temperature, the $\text{K}_2\text{NbOF}_5 \cdot \text{H}_2\text{O}$ crystal can have different symmetries in the states A , B , and C . The existence of a rotation of the optical indicatrix in two orthogonal planes $\varphi_c = 43^\circ$ and $\varphi_b \approx 2.5^\circ$ in the

$\text{K}_2\text{NbOF}_5 \cdot \text{H}_2\text{O}$ sample (the A state) with the maximum degree of atmospheric humidity proves that this crystal belongs to the triclinic symmetry class $P\bar{1}$.

During heating of this sample above $T_2^\uparrow = 313$ K, the φ_c angle sharply decreases to zero, whereas the angle $\varphi_b \approx 2.5^\circ$ remains unchanged. The crystal becomes monoclinic.

The $\text{K}_2\text{NbOF}_5 \cdot \text{H}_2\text{O}$ crystal in the B state at room temperature belongs the monoclinic symmetry class, because we observe only $\varphi_b \approx 2.5^\circ$. In the $(001)_T$ plate, the axes of the optical indicatrix are arranged along the faceting $[110]_T$ and $[1\bar{1}0]_T$; therefore, for the samples of the B type, we chose the base-centered symmetry group $C2/m$ in contrast to the symmetry group $P2_1/c$ proposed in [5]. The investigations of the temperature dependences of the birefringence $\Delta n_c(T)$ and the angles $\varphi_c(T)$ and $\varphi_b(T)$ (Figs. 3, 4) showed that, at temperatures above T_2^\uparrow , the samples in the states A and B have the same optical characteristics and symmetry.

During the cooling, at $T_2^\downarrow = 308$ K the $\text{K}_2\text{NbOF}_5 \cdot \text{H}_2\text{O}$ crystals in the A state undergo a reversible first-order phase transition, which is accompanied by the twinning, the appearance of the shear strain x_6 , and the rotation of the optical indicatrix through the angle $\varphi_c \approx \pm 43^\circ$. This transition leads to a loss of elements of the symmetry group $C2/m$: the twofold symmetry axis and the mirror plane. There occurs a ferroelastic phase transition ($P\bar{1} \leftrightarrow C2/m$).

A similar situation was observed in the $\text{K}_2\text{WO}_2\text{F}_4 \cdot \text{H}_2\text{O}$ crystal [8], where in contrast to the $\text{K}_2\text{NbOF}_5 \cdot \text{H}_2\text{O}$ crystal, the change in the symmetry of the crystal in the A state occurs at lower temperatures: $T_2 \approx 270$ K.

The phase transition $P\bar{1} \leftrightarrow C2/m$ is referred to as the proper ferroelastic transition, because the anomalies of the optical constants below T_2 are described by the behavior of the strain component: $\delta n_c(T) \propto \varphi_c(T) \propto \eta(T) \propto x_6(T)$, where δn_c is the anomalous part of the birefringence, η is the transition parameter, and x_6 is the component of the shear strain.

Although the $\text{K}_2\text{NbOF}_5 \cdot \text{H}_2\text{O}$ crystal in the A state at T_2^\downarrow undergoes an identical change in the symmetry, we assume that, in this case, an “improper” ferroelastic transition takes place when there are no linear relationship between the transition parameter η and the strain component x_6 . This conclusion follows from several observations. First, there is no correlation between the temperature dependences of the deformation of the optical indicatrix $\delta n_c(T)$ and its rotation $\varphi_c(T)$ in the low-temperature range (Fig. 3, curves 1 and 2). Second, the phase transition at the temperature T_2 is a first-order transition, which is accompa-

nied by an abrupt change in the optical characteristics, the motion of the phase front over the sample, and the temperature hysteresis $\delta T = 5$ K.

The $\text{K}_2\text{NbOF}_5 \cdot \text{H}_2\text{O}$ samples in the *B* state does not undergo such a transition, and their monoclinic symmetry is retained down to the liquid-nitrogen temperature. The nature of the anomaly in the temperature of the birefringence $\Delta n_c(T)$ near 150 K has not been determined.

5. CONCLUSIONS

The performed investigations have demonstrated that, depending on the degree of atmospheric humidity, the $\text{K}_2\text{NbOF}_5 \cdot \text{H}_2\text{O}$ crystal at room temperature can exist in three states with different symmetries: $P\bar{1}$ in the *A* state, $C2/m$ in the *B* state, and $P4/nmm$ in the *C* state (anhydrous sample). The most stable state of the $\text{K}_2\text{NbOF}_5 \cdot \text{H}_2\text{O}$ crystal is the *B* state, because it exists at the normal humidity (RH = 20–90%). Based on the polarization optical observations, the symmetry of the $\text{K}_2\text{NbOF}_5 \cdot \text{H}_2\text{O}$ crystal in the *B* state was chosen to be $C2/m$, and not $P2_1/c$, which was proposed in [5].

The $\text{K}_2\text{NbOF}_5 \cdot \text{H}_2\text{O}$ crystal in the *A* state undergoes a sequence of reversible and irreversible phase transitions in the temperature range from 100 to 600 K. The change in the symmetry $P\bar{1} \leftrightarrow C2/m$ occurs upon the first-order phase transition at temperatures $T_2^\downarrow = 308$ K and $T_2^\uparrow = 313$ K. This transition is an improper ferroelastic phase transition, which is accompanied by the appearance of the shear strain x_6 . In the *B* state, no change in the symmetry has been revealed. The irreversible transition between the monoclinic and tetragonal phases of the crystals in the states *A* and *B* is observed at the temperature $T_1 \approx 370$ K and accompanied by the loss of the crystal water. The structural water is easily recovered from the atmosphere during a day.

The difference between the crystals in the states *A* and *B* was explained in detail [8] by the possible presence of water molecules held by hydrogen bonds in interlayer spaces of the samples in the *A* state. This assumption is confirmed by experiments on the observation of twinning upon repeated passages through the temperature T_2 (see inset in Fig. 3). After the holding at relatively high temperatures in the range from 320 to 340 K, the region of the sample with ferroelastic twins in the *A* state gradually narrows due to the loss of “interlayer” water at the edges, whereas the region of the sample in the *B* state increases.

According to [8], the most stable state of the $\text{K}_2\text{WO}_2\text{F}_4 \cdot \text{H}_2\text{O}$ crystal is the *A* state, even though the mass of the “interlayer” water is relatively small and does not exceed 0.1% of the total mass of the substance. It was assumed that the freezing of this water at the temperature $T_2 \approx 270$ K leads to an ordering of

crystal water molecules in one of the two positions and to a reduction of the symmetry due to the ferroelastic transition $P\bar{1} \leftrightarrow C2/m$. In [8], it was shown that the crystal water is also retained in the lattice by hydrogen bonds between the water molecules and all the ligands. These bonds are sufficiently strong in the $\text{K}_2\text{WO}_2\text{F}_4 \cdot \text{H}_2\text{O}$ crystal; therefore, the crystal hydrate exists at RH = 0–100% and at temperatures below $T_1 \approx 380$ K.

In the $\text{K}_2\text{NbOF}_5 \cdot \text{H}_2\text{O}$ crystal, the *A* state is unstable and exists only at a maximum relative humidity of the atmosphere (90–100%). The ordering of H_2O molecules due to the phase transition occurs at a higher temperature $T_2^\downarrow = 308$ K than in the tungsten compound. Moreover, the region of the existence of the crystal hydrate itself is limited by the degree of humidity RH = 20–100%. The dehydration can proceed even at room temperature in a sufficiently dry atmosphere. This suggests that hydrogen bonds holding both the crystal water molecules and the “interlayer” water molecules in $\text{K}_2\text{NbOF}_5 \cdot \text{H}_2\text{O}$ are considerably weaker than those in $\text{K}_2\text{WO}_2\text{F}_4 \cdot \text{H}_2\text{O}$.

Thus, the layered $\text{K}_2\text{NbOF}_5 \cdot \text{H}_2\text{O}$ crystal studied in this work, like the $\text{K}_2\text{WO}_2\text{F}_4 \cdot \text{H}_2\text{O}$ crystal, is very sensitive to variations in the concentration of water vapors in air. The water molecules penetrate into interlayer spaces and change the properties of the material without changing the crystal structure. The presence of such “interlayer” water in the crystal is characteristic of some minerals with a layered structure (montmorillonite, mica).

ACKNOWLEDGMENTS

This study was supported by the Council on Grants from the President of the Russian Federation (grant no. NSh-4828.2012.2).

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Translated by O. Borovik-Romanova