
LATTICE DYNAMICS
AND PHASE TRANSITIONS

Optical Studies of Phase Transitions in the $(\text{NH}_4)_3\text{VO}_2\text{F}_4$ Crystal

S. V. Mel'nikova and A. G. Kocharova

*Kirensky Institute of Physics, Siberian Branch, Russian Academy of Sciences,
Akademgorodok, Krasnoyarsk, 660036 Russia*

e-mail: msv@iph.krasn.ru

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Abstract— $(\text{NH}_4)_3\text{VO}_2\text{F}_4$ crystals were grown, and polarization-optical studies and measurements of birefringence were conducted on crystal plates of various cuts over a wide temperature range. Phase transitions were detected at temperatures $T_{1\uparrow} = 417$ K, $T_{3\uparrow} = 211$ K, and $T_{4\uparrow} = 205$ K (on heating) and at $T_{1\downarrow} = 413$ K, $T_{3\downarrow} = 210$ K, and $T_{4\downarrow} = 200$ K (on cooling). The transitions are accompanied by anomalies of the birefringence and by twinning. The sequence of changes in the phase symmetry is assumed to be as follows: cubic $Fm\bar{3}m \longleftrightarrow$ orthorhombic $Immm$ ($I222_1$) \longleftrightarrow monoclinic $112/m$ \longleftrightarrow triclinic $P\bar{1}$. Near temperatures $T_2 \approx 240$ – 250 K, an additional anomaly of the birefringence is observed, with the crystal retaining the orthorhombic symmetry.

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1. INTRODUCTION

Disordered compounds with a cryolite–elpasolite-like structure, whose anionic skeleton is formed by fluorine–oxygen octahedra, are representatives of the numerous family of oxyfluorides [1–4]. The high-temperature cubic phase of these compounds belongs to space group $O_h^5 - Fm\bar{3}m$ ($Z = 4$), which can be changed upon structural (ferroelectric) phase transitions (PTs) due to an ordering on the anionic octahedral sublattice. Despite the fact that there is a great body of relevant data and a wide spectrum of methods of study, the symmetry of distorted low-temperature crystal phases has not yet been established because of complex twinning, which lowers the cubic symmetry. Among ammonium compounds, there is likely the only crystal, namely, $(\text{NH}_4)_3\text{VO}_2\text{F}_4$, in which the PT from the cubic phase occurs at a high temperature. According to [5, 6], this transition occurs at a temperature of 418 ± 3 K. The high-temperature phase of the crystal has a cryolite-type structure with unit-cell parameters $a = 9.026$ Å and $Z = 4$ [7]. At room-temperature, the crystal is orthorhombic (space group $Immm$ or $I222_1$), with lattice parameters $a = 9.026$ Å, $b = 9.026$ Å, $c = 9.026$ Å, and $Z = 6$. Moreover, at temperatures of 210–220 K, an additional second-order PT was revealed [7]. At low temperatures, the crystal symmetry has not been established because of the appearance of differently oriented twins; however, the unit-cell parameters are given for the orthorhombic structure: $a = 9.161$ Å, $b = 18.71$ Å, $c = 6.202$ Å, and $Z = 6$.

The fact that the crystal is in a distorted phase at room temperature is favorable for studies. Samples can be prepared in a single-domain state (which is required for crystal-optical experiments) by growing from an aqueous solution near room temperature. In this work, we performed polarization-optical studies and measured the birefringence of the $(\text{NH}_4)_3\text{VO}_2\text{F}_4$ crystal over a wide temperature range (150–450 K) with the aim of searching for and studying PTs and determining the phase symmetries.

2. EXPERIMENTAL RESULTS

$(\text{NH}_4)_3\text{VO}_2\text{F}_4$ crystals were synthesized by mixing a hot aqueous solution of ammonium vanadate and hydrofluoric acid with addition of ammonia



The crystallization occurs during slow cooling of the solution to room temperature. The precipitate consists of small (~ 1 mm³) well-faceted orange octahedra and thin (~ 50 - μm -thick) plates. Growth single-crystal $(110)_c$ - and $(111)_c$ -cut plates were used to perform polarization-optical observations using an Axiolab polarizing microscope and to measure the birefringence by the Berek compensator method with an accuracy of ± 0.0001 .

The polarized-light studies show that, at room temperature, the crystal does indeed possess orthorhombic symmetry. The $(110)_c$ plate demonstrates a good extinction and a conoscopic picture with the exit of the “acute bisectrix” of the angle between the optical axes

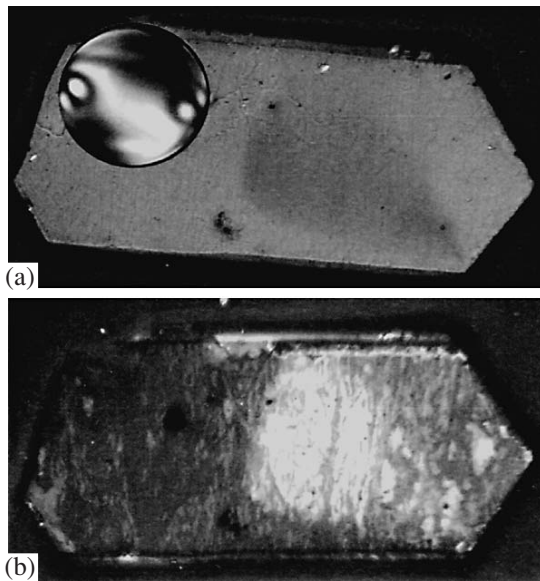


Fig. 1. Polarization-light study of a $(110)_c = (001)_{or}$ growth plate of the $(NH_4)_3VO_2F_4$ crystal: (a) plate shape and a conoscopic figure at room temperature, and (b) spotty pattern of extinction in the G_3 and G_4 phases.

and with the $(100)_c = (100)_{or}$ plane of the optical axes (Fig. 1a). The X-ray reflections from this plate correspond to $c = 6.264$ Å. Thus, the relations between the crystallographic directions of the cubic and orthorhombic phases of the $(NH_4)_3VO_2F_4$ crystal are as follows: $(100)_c = (100)_{or}$, $(110)_c = (001)_{or}$, and $(110)_c = (010)_{or}$.

During cooling of the $(110)_c = (001)_{or}$ plate, the extinction remains good only down to 210 K; below this temperature down to liquid-nitrogen temperature, the extinction of the crystal is not uniform. There are unclear spots with a running extinction, which is spread over 1° – 2° (Fig. 1b). On heating, the good extinction is recovered at 211 K. Above room temperature, the optical anisotropy is retained up to $T_{1\uparrow} = 417$ K and then a PT occurs to the isotropic state. During cooling, this PT is delayed and occurs at $T_{1\downarrow} = 413$ K. The crystal becomes anisotropic and is divided into twins.

The results of observations for the single-domain $(111)_c$ plates are different. Some samples (A) retain good extinction from 417 K to liquid-nitrogen temperature, while in other samples (B) the extinction radically deteriorates below 200 K. Bright diffuse color bands and a network of intersecting 120° and 60° boundaries appear (Fig. 2). During heating, the temperature range with such optical inhomogeneities is retained up to 205 K, and thereupon the extinction is recovered.

The measured birefringence in various samples is shown in Fig. 3. Curve 1 is measured on the $(110)_c$ plate

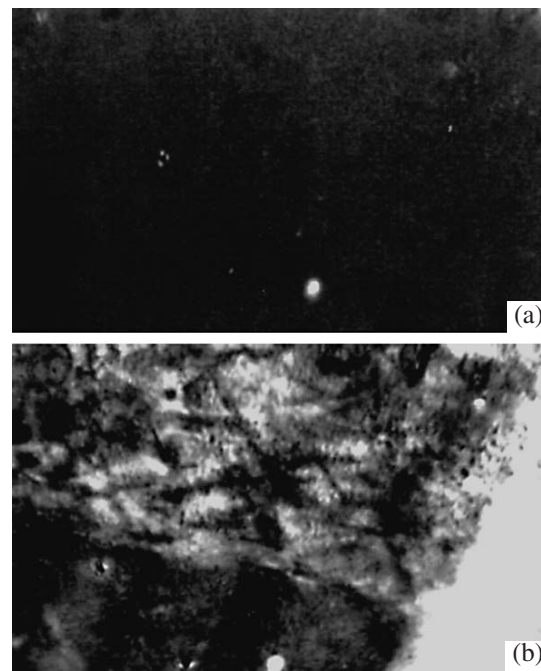


Fig. 2. Photomicrographs of a $(111)_c$ -cut plate (B) in various phases of the $(NH_4)_3VO_2F_4$ crystal: (a) good extinction in the G_1 , G_2 , and G_3 phases; and (b) twinning in the G_4 phase.

with the exit of the acute bisectrix of the angle of the optical axes. On cooling, the birefringence (Δn_c) arises in a jumpwise manner at $T_{1\downarrow} = 413$ K, then increases

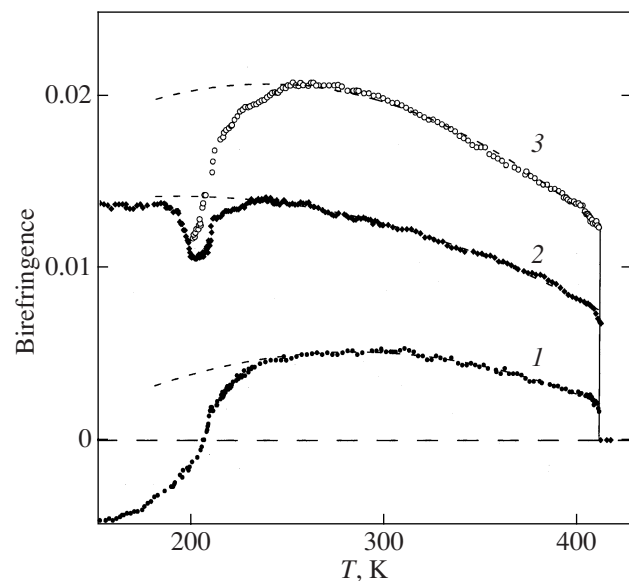


Fig. 3. Temperature dependence of the birefringence in $(NH_4)_3VO_2F_4$ growth plates measured on cooling: (1) $\Delta n_c(T)$ for a $(110)_c$ plate, (2) for sample A, and (3) for sample B.

gradually and, below ~ 240 K, starts to decrease and, reaching zero, changes sign. Curves 2 and 3 show the birefringence in the A and B plates, respectively. Note that Δn in plate B is significantly larger than that in the A plate. However, the temperature dependence of the birefringence at high temperatures is approximately the same for all the samples: there is a jump at a temperature $T_{1\downarrow} = 413$ K, a slow increase, and a bend in the $\Delta n(T)$ curve in the range ~ 240 – 250 K. On cooling at low temperatures, particularly in curve 2, two temperatures can be distinguished, 210 and 200 K, at which the $\Delta n(T)$ curves change their slopes. The measurement of birefringence in sample B is impossible at temperatures below 200 K because of the aforementioned optical inhomogeneities, which are pronounced at low temperatures. Figure 4 shows the temperature dependence of the birefringence in sample A on heating and on cooling. There are hysteresis phenomena in the temperature range 190–210 K.

3. DISCUSSION OF THE RESULTS

Our optical studies of $(\text{NH}_4)_3\text{VO}_2\text{F}_4$ have demonstrated that there are four characteristic temperatures for this crystal, namely, $T_1 = 413_{\downarrow}$ (417_{\uparrow}) K, $T_2 = 240$ – 250 K, $T_3 \approx 210_{\downarrow}$ (211_{\uparrow}) K, and $T_4 \approx 200_{\downarrow}$ (205_{\uparrow}) K. At these temperatures, an anomalous behavior of the birefringence is observed or (and) a twinning structure arises indicating a change in the crystal structure. From comparing the room-temperature birefringence of the single-domain growth plates studied, one can determine the orientation of samples A and B with respect to the axes of the orthorhombic unit cell. The normal to $(111)_c$ plate A makes an angle of 35° with the $[001]_{\text{or}}$ direction, while the normal to plate B is at an angle of 35° to $[010]_{\text{or}}$. Thus, in the optical studies, we have observed processes occurring along vector \mathbf{c} of the orthorhombic unit cell in sample A and processes occurring along vector \mathbf{b} in sample B. The good extinction observed in plate A over the entire temperature range agrees with the observations on the $(110)_c = (001)_{\text{or}}$ sample (Fig. 1). In this sample, the spotty pattern with unclear boundaries and “twinkling” extinction is due to intertwined small twins ($< 1 \mu\text{m}$ in size) that arise below 210 K as a result of loss of two symmetry planes. In plate A, this weak structure is indiscernible. At the same time, the good extinction observed in plate B down to 200 K indicates that, in the temperature range 210–200 K, the crystal exhibits the monoclinic symmetry with a singular direction along $[001]_{\text{or}}$. We believe that, over this temperature range, the crystal is most likely to have centrosymmetric group $112/m$, although polar groups 112 and $11m$ are also probable. The appearance of twins in plate B at temperatures below 200 K demonstrates that the crystal loses symmetry axes and planes and transforms into the triclinic phase. Of two space groups of the triclinic structure, space group $C_i^1 - P\bar{1}$ with inversion center is preferred.

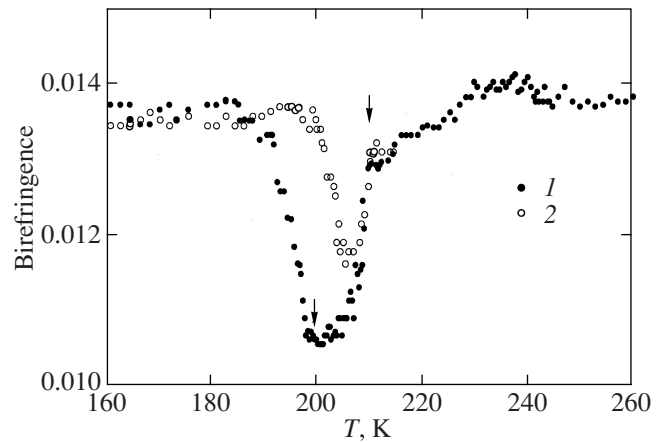


Fig. 4. Temperature dependence of the birefringence in sample A measured (1) on cooling and (2) on heating. The arrows show the transitions at $T_{3\downarrow}$ and $T_{4\downarrow}$.

Thus, the results obtained show the occurrence in the $(\text{NH}_4)_3\text{VO}_2\text{F}_4$ crystal of four PTs with the following sequence of phases: cubic $O_h^5 - Fm\bar{3}m$ (G_0) \longleftrightarrow orthorhombic $Immm$ ($I222_1$) (G_1) \longleftrightarrow orthorhombic (G_2) \longleftrightarrow monoclinic $112/m$ (G_3) \longleftrightarrow triclinic $C_i^1 - P\bar{1}$ (G_4). The $G_0 \longleftrightarrow G_1$ phase transition is a well-defined first-order PT; there are birefringence jumps, motion of the phase front, and thermal hysteresis $\delta T_1 \approx 4$ K. The $G_1 \longleftrightarrow G_2$ phase transition is of the second order; it is accompanied by a bend in the $\Delta n(T)$ curve with a smeared transition temperature, but the crystal system remains unchanged. The $G_2 \longleftrightarrow G_3$ and $G_3 \longleftrightarrow G_4$ transitions are not accompanied by birefringence jumps; however, these structural changes can be assigned to first-order transitions owing to the presence of thermal hysteresis: $\delta T_3 \approx 1$ K and $\delta T_4 \approx 5$ K.

4. CONCLUSIONS

Our studies have confirmed the occurrence of a phase transition (PT) to the cubic phase found earlier [6, 7]. Moreover, in the range 210–220 K, wherein a second-order PT was assumed, we have revealed a sequence of three PTs. The totality of experimental data obtained in this work strongly suggests the existence of a complex sequence of PTs: cubic (G_0) \longleftrightarrow orthorhombic (G_1) \longleftrightarrow orthorhombic (G_2) \longleftrightarrow monoclinic (G_3) \longleftrightarrow triclinic (G_4). These PTs occur in the $(\text{NH}_4)_3\text{VO}_2\text{F}_4$ crystal in the temperature range 420–200 K.

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