LATTICE DYNAMICS
AND PHASE TRANSITIONS

Phase Transitions in the Oxyfluoride $(NH_4)_3NbOF_6$

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Abstract—$(NH_4)_3NbOF_6$ single crystals were grown, polarization-optical studies were performed, and birefringence was measured over the temperature range 90–500 K. A sequence of first-order structural phase transitions was found at temperatures $T_{1\downarrow} = 259.7$ K and $T_{2\downarrow} = 257.7$ K with temperature hysteresis $\delta T_1 = 0.9$ K and $\delta T_2 = 1.9$ K. The transitions are accompanied by twinning and the following change in the crystal symmetry: cubic $\longleftrightarrow$ tetragonal $\longleftrightarrow$ monoclinic. Optical second harmonic generation is found to occur at room temperature, which indicates that the cubic phase is not centrosymmetric. It is assumed that the phase transitions are ferroelastic and ferroelectric in nature.

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1. INTRODUCTION

Contemporary technology for the production of metallic tantalum and niobium and their compounds is based on the processing of the fluorides of these elements [1]. The first stage of the production includes fluorination of the columbite–tantalite natural mineral $(Fe, Mn)(Ta, Nb)_2O_6$. The ammonium hydrofluoride NH_4HF_2 has been proposed to use as a fluorinating agent; the interaction with this compound at 200–350°C is accompanied by the formation of the corresponding ammonium fluorocomplexes [1]:

$$(M)(Ta,Nb)_2O_6 + 8NH_4HF_2 = NH_4MF_3 + (NH_4)_2TaF_7$$
$$+ (NH_4)_3NbOF_6 + 2NH_3 + 5H_2O.$$
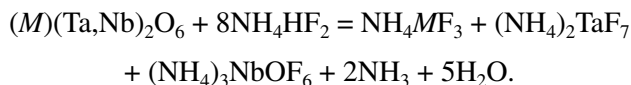
The niobium-oxyfluoride complex $(NH_4)_3NbOF_6$ has been known since 1866 and was described for the first time by Marignac [2]. It is deposited from a solution if there is a considerable excess of NH_4F [2, 3]. A more complicated synthesis of this compound in methanol is described in [4] (where the results of first x-ray studies of this compound are also presented). This compound was found to have an fcc unit cell with lattice parameter $a = 9.31$ Å and $Z = 4$. Later, Gorbunova et al. [5] made an attempt to determine the crystallographic structure of $(NH_4)_3NbOF_6$. Based on its isostructurality with $(NH_4)_3ZrF_7$ [6], the space group was assumed to be $Fm\bar{3}m$. It was noted in [5] that this symmetry implies that the $[NbOF_6]^{3-}$ complex anion is shaped like a pentagonal bipyramid. This variant is controversial because of too short F(O)–F(O) distances, which are

2.03 Å. The oxygen and fluorine atoms are statistically mixed between two positions due to complex disordering.

Among numerous oxyfluorides, there is a wide diversity of disordered compounds with an elpasolite-like structure whose anion sublattice is formed by fluorine–oxygen octahedra [7–9]. The high-temperature cubic phase of these materials belongs to space group $Fm\bar{3}m$ ($Z = 4$), which changes under structural transitions (both ferroelectric and ferroelastic) driven by the ordering in the anion octahedral sublattice. The fact that the $(NH_4)_3NbOF_6$ crystal is cubic at room temperature [4, 5] also suggests that the symmetry of the crystal can change under cooling.

In this work, polarization-optical studies were performed and the birefringence of an $(NH_4)_3NbOF_6$ crystal was measured over a wide temperature range (80–450 K) in order to search and study the phase transitions occurring in it. Birefringence was measured on $(100)_c$-cut plates using the Berec compensator method with an accuracy of $\cong 10^{-5}$. Twinning was studied for three crystallographic directions of the cubic lattice: $[001]_c$, $[110]_c$, and $[111]_c$.

2. EXPERIMENTAL

$(NH_4)_3NbOF_6$ single crystals were obtained through slow evaporation (in air) of niobium pentoxide in concentrated HF with a considerable excess (more than 200%) of concentrated (40%) NH_4F. After crystals formed, the growth solution was filtrated and then was
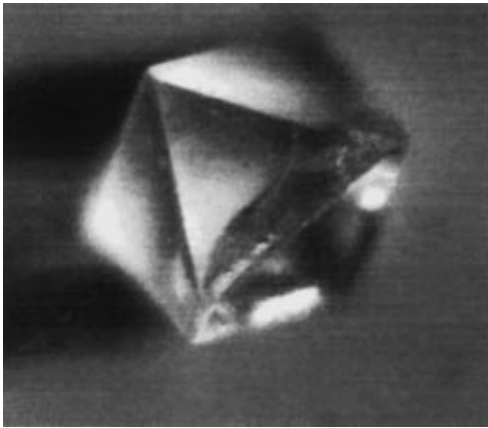
Fig. 1. Habit of $(NH_4)_3NbOF_6$ crystals.

used again to obtain higher quality bulk single crystals through subsequent crystallization of the complex. The grown single crystals were facetted transparent octahedra with pronounced $(111)_c$ faces (Fig. 1). This habit is typical of centrosymmetric crystals of the $m\bar{3}m$ crystal class.

The polarization-optical studies showed that the crystal is actually cubic at room temperature (phase G_1; Fig. 2a). However, under cooling to a temperature slightly below the ice melting point, the optical isotropy is distorted and polysynthetic twins form in the crystal. A phase transition occurs, and the crystal changes to another crystal system. In a $(100)_c$-cut plate (vertex of the octahedron) this transition occurs at a temperature $T_1 \approx 260$ K and is accompanied by the appearance of twin bands with boundaries along the $[110]_c$ direction

and definite extinction of the entire system along the $[100]_c$ direction (Fig. 2b). As the temperature decreases further to $T_2 \approx 258$ K, an additional change in the twinning pattern is observed. A new twin system with $[100]_c$ boundaries is superimposed on the previous system (Fig. 2c). The extinction in the sample remains the same (well-defined and distinct).

It has been found that a twinning pattern depends on the sample history and the rate of temperature change in the region of the transitions. Figure 3a shows the microphotographs of a $(100)_c$ cut of a crystal plate taken immediately after polishing under slow change in temperature (~1 K/h). Below 260 K (phase G_2), the sample is mostly in a single-domain state and its image becomes dark or bright as the microscopic stage is rotated. Below 258 K (phase G_3), the sample is divided into very small domains and exhibits distinct extinction. This sample looks absolutely different after a week (Fig. 3b). The photographs shown in Fig. 3b are likewise taken under slow variation in temperature. The crystal was not subjected to additional treatment. In the G_2 phase, the crystal looks optically isotropic, as is the case at room temperature, and below 258 K the sample splits into twins with unclear (twinkling) extinction near the $[100]_c$ direction.

Figure 4 shows the microphotographs of twinned patterns in different phases taken from the $(111)_c$ and $(110)_c$ cuts. In Fig. 4a, three types of twin boundaries rotated by 120° with respect to each other are seen in the G_2 phase. Extinction appears in different regions every 120°. The twin system becomes more complicated in the lower temperature phase.

The fact that the sample passes to a single-domain state under slow cooling near the transition temperature made it possible to measure the temperature depen-
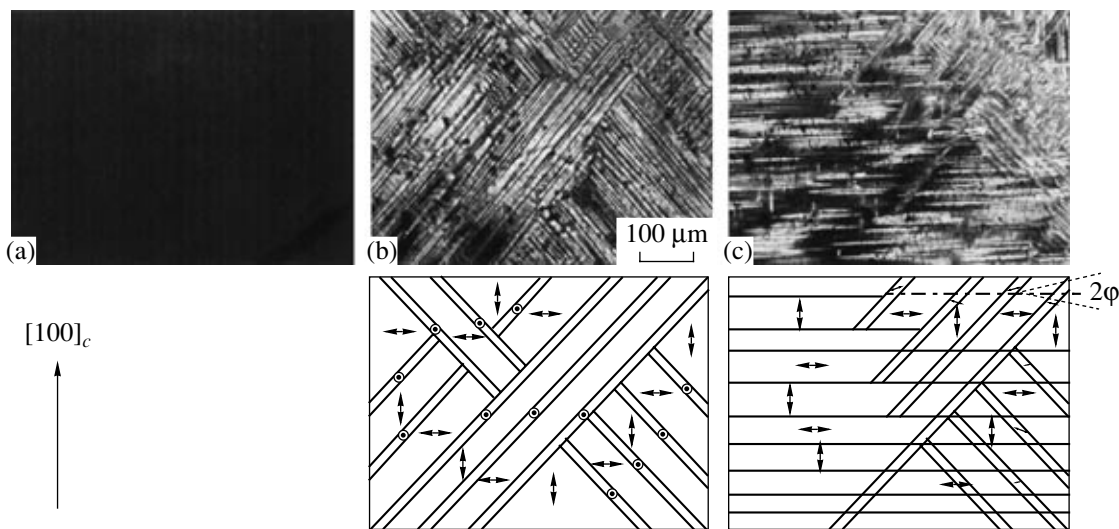

Fig. 2. Twinning observed with polarized light in $(100)_c$-cut plates of $(NH_4)_3NbOF_6$ crystal.

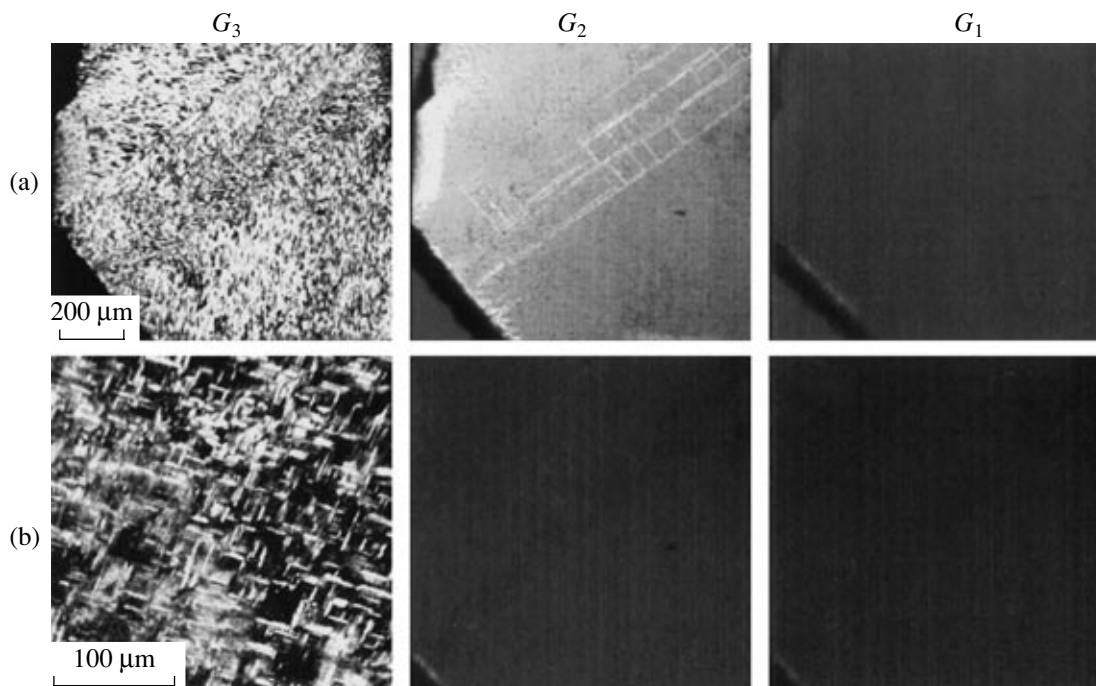G_3 G_2 G_1

Fig. 3. Twin patterns in $(100)_c$-cut plates observed under different experimental conditions: (a) a plate after treatment and (b) a week after the treatment. The photographs are taken under slow variation in temperature.

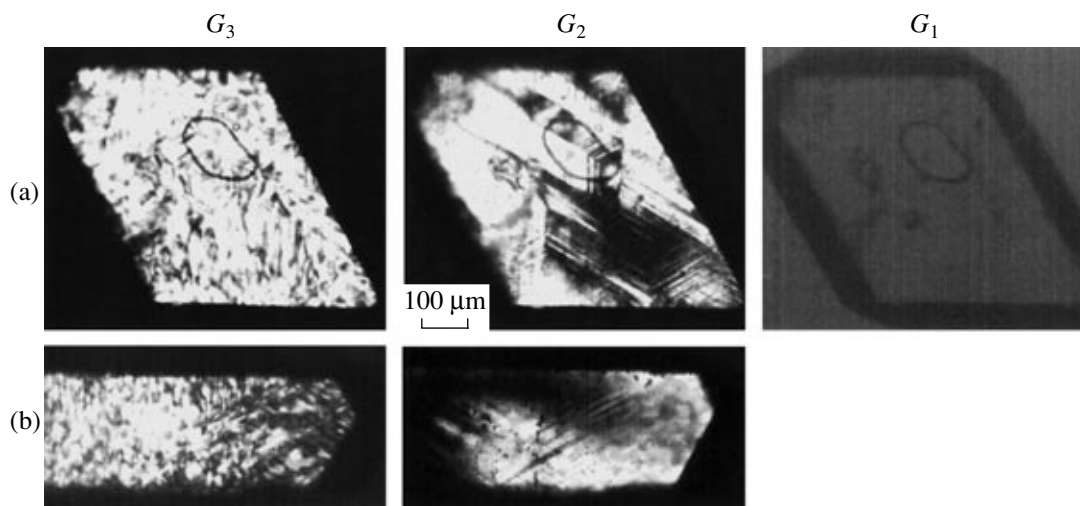G_3 G_2 G_1

Fig. 4. Twin patterns observed in grown plates: (a) the $(111)_c$ face (octahedron face) for different phases and (b) the $(110)_c$ face (octahedron edge) for different phases.

dences of the birefringence of the $(NH_4)_3NbOF_6$ crystal. The results are shown in Figs. 5 and 6. Birefringence arises abruptly in the temperature range of two phase transitions and then decreases gradually (Fig. 5). Figure 6 shows the same dependences near the phase transitions. According to our measurements, optical anisotropy appears abruptly at $T_{1\downarrow} = 259.7$ K. The second phase transition (at $T_{2\downarrow} = 257.7$ K) is accompanied by an additional jump in birefringence and by anisotropy in the refraction indices typical of low-symmetry crystals (birefringence in neighbor twins has different values). Under heating, the phase transitions appear at higher temperatures, $T_{2\downarrow} = 259.6$ K and $T_{1\uparrow} = 260.6$ K. Therefore, the thermal hysteresis is $\delta T_1 = 0.9$ K and $\delta T_2 = 1.9$ K. Due to the difference in these values, the temperature range where the G_2 phase exists under

heating is twofold narrower than under cooling and its width is only one kelvin.

3. DISCUSSION

Our studies show that two ferroelastic phase transitions occur in the $(NH_4)_3NbOF_6$ crystal: at $T_{1\downarrow} = 259.7$ K and $T_{2\downarrow} = 257.7$ K. These transitions are accompanied by a jump in birefringence and temperature hysteresis typical of first-order phase transitions. The polarization-optical experiments show that the high-temperature phase is indeed cubic. According to Fig. 4a, after the first transition, the threefold axes disappear and a typical twinned structure forms in the $(\bar{1}11)_c$ plate. The symmetry of the G_2 phase can be judged from the data in Fig. 3. It is seen that the crystal is optically uniaxial in this phase and that the position of the optical axis in the single-domain state depends on the mechanical state of the sample. In Fig. 3a, the optical axis is in the plate plane, whereas in Fig. 3b the optical axis is tilted from this plane. This fact indicates that the G_2 phase is tetragonal, because only a fourfold axis can be along the [100] direction in a cubic crystal. This conclusion is confirmed by the measurements of birefringence in the G_2 phase. The birefringence value is the same in two neighbor extinct twins ("principal birefringence" of the uniaxial crystal), although the measuring conditions are different.

In the low-temperature phase G_3, there is either complete extinction along the $[100]_c$ direction (Fig. 3a) or extinction with a slight disorientation of the optical indicatrices in the neighbor twins around the previously existing fourfold axis (Fig. 3b). This indicates that the G_3 phase is monoclinic. In this case, the special direction in the monoclinic unit cell (the twofold axis or a normal to the plane) is along the previous fourfold axis and the optical indicatrix can be rotated around this direction. The twinning pattern of an $(NH_4)_3NbOF_6$ multidomain sample in different phases is shown in Fig. 2. Our studies also show that the unit cell of the G_3 (and, possibly, G_2) phase of the $(NH_4)_3NbOF_6$ crystal is oriented along the unit cell axes of the cubic phase. In this respect, the crystal studied differs significantly from pure fluoride elpasolites and cryolites [10, 11], in which low-temperature phases, the unit cell axes make an angle of 45° with the previous cubic cell axes.

All the above experiments performed with polarized light, as well as the octahedral habit of the crystal and the x-ray data from [4, 5], are in good agreement with each other and show that the high-temperature phase of the $(NH_4)_3NbOF_6$ crystal belongs to the centrosymmetric crystal class $Fm\bar{3}m$, as is the case for cryolites and elpasolites [10, 11]. However, our experiment on optical second harmonic generation suddenly gave a positive result. When a powder sample of the $(NH_4)_3NbOF_6$ crystal was irradiated by infrared laser light at room temperature, we observed intense generation of green
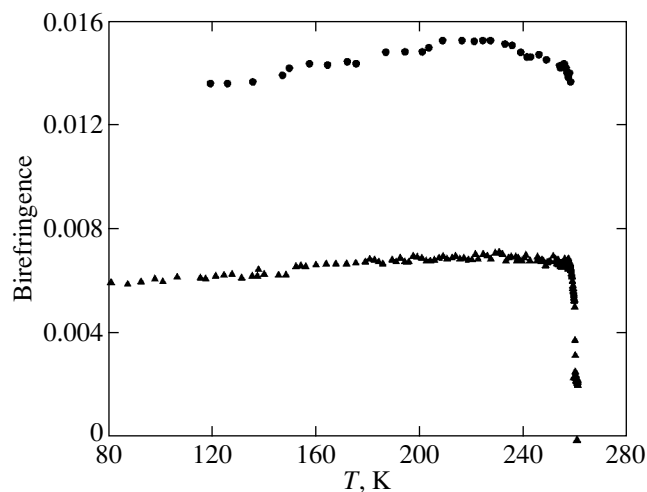

Fig. 5. Temperature dependence of birefringence in an $(NH_4)_3NbOF_6$ crystal measured for a (100)-cut plate.

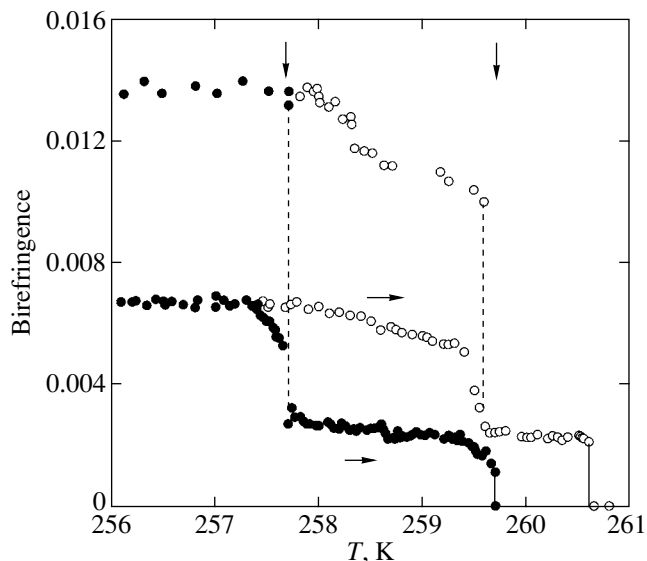**Fig. 6.** Thermal hysteresis of birefringence in an $(NH_4)_3NbOF_6$ crystal measured over the temperature range of phase transitions.

light. This fact indicates unambiguously that the crystal belongs to cubic noncentrosymmetric crystal class $F\bar{4}3m$ or $F23$, for which a crystal is shaped like a tetrahedron rather than an octahedron (Fig. 1). In this case, if the initial phase belongs to group $F23$, then it is impossible to explain the existence of the phase belonging to a tetragonal group (even over a narrow temperature range), because this group is not a subgroup of cubic group $F23$. These contradictions make it impossible to draw an unambiguous conclusion concerning the crystal symmetry at room temperature. It seems rea-

sonable to assume that, at room temperature, the crystal is not in the initial phase but rather in an intermediate phase. As for the initial (G_0) phase, it is a high-temperature praphase having the highest cubic symmetry $Fm\bar{3}m$. In this case, a crystal grown in the form of an octahedron, should be twinned in the G_1 phase, which has to manifest itself in the x-ray structural experiments. The existence of the tetragonal phase even with $F23$ symmetry at room temperature is also explicable. In this case, one more transition should occur between the two cubic phases above room temperature. However, we failed to reveal this transition using the optical methods. Moreover, the crystal decomposes even at ≈ 500 K [3].

4. CONCLUSIONS

Our experiments on $(NH_4)_3NbOF_6$ crystals have revealed monoclinic $\longleftrightarrow$ tetragonal $\longleftrightarrow$ cubic ($F\bar{4}3m$ or $F23$) phase transitions. The shape of the crystals shows that the transition to the cubic $Fm\bar{3}m$ phase is possible at high temperatures. The optical second harmonic generation at room temperature and the geometry of the unit cell in the low-temperature phases show that, in contrast to the pure fluoride compounds [10, 11] other mechanisms of phase transitions are possible in $(NH_4)_3NbOF_6$. The structural changes in the distorted phases can bring about to the appearance of not only new components of spontaneous strain (ferroelastic phase) but also to spontaneous polarization (ferroelectric phase).

To obtain more reliable information about the crystal structure at room temperature, the number of phase transitions, their thermodynamic characteristics, and structural changes under the phase transitions, we are performing x-ray studies and heat-capacity measurements over a wide temperature range.

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