

# Unusual sequence of phase transitions in $(\text{NH}_4)_3\text{TiF}_7$ detected by optic and calorimetric studies



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## ABSTRACT

For the first time structural transformations were observed for one of the compounds belonging to the family of double salt fluorides  $\text{A}_3\text{MeF}_7 = \text{A}_2\text{MeF}_6 \cdot \text{AF}$ . Single crystals of  $(\text{NH}_4)_3\text{TiF}_7 = (\text{NH}_4)_2\text{TiF}_6 \cdot \text{NH}_4\text{F}$  were grown by evaporation of the aqueous solution. Polarizing optical observations, heat capacity and birefringence  $\Delta n = (n_o - n_e)$  measurements were performed in a wide temperature range 100–400 K. Two reversible, first order structural phase transitions were found to be followed by an unusual sequence of symmetry changes: cubic ( $G_3$ ) ( $T_{21} = 287.5 \text{ K}$ ;  $T_{21} = 291\text{--}310 \text{ K}$ )  $\leftrightarrow$   $P4/mnc$  ( $G_2$ ) ( $T_{11} = 358.5 \text{ K}$ ;  $T_{11} = 360 \text{ K}$ )  $\leftrightarrow$   $4/m$  ( $G_1$ ). The twin structures observed were described assuming the existence of cubic parent phase  $G_0$  with  $Pm\bar{3}m$  symmetry.

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## 1. Introduction

The family of crystals with elpasolite structure combines a great variety of anionic entities exhibiting different coordination. Compounds with octahedral polyhedron  $\text{MeX}_6$  ( $\text{Me} = \text{Ln}, \text{Al}, \text{Fe}, \text{Ti}, \text{Nb}, \text{Mo}, \text{W}, \text{etc.}$ ;  $\text{X} = \text{O}, \text{F}$  and  $\text{Cl}$ ) (sp.gr.  $Fm\bar{3}m, Z = 4$ ) were studied rather intensively [1]. Crystals with seven-coordinated anions and with the same symmetry are very interesting because of their specific physical properties associated with the possible phase transitions. This family contains ammonium fluoro-compounds such as  $(\text{NH}_4)_3\text{HfF}_7$ ,  $(\text{NH}_4)_3\text{ZrF}_7$  and others [2–5]. In the structures of these crystals fluorine atoms may form two types of polyhedra: either monocapped trigonal prism or pentagonal bipyramid. It should be noted that among the crystals with the general chemical formulation  $\text{A}_3\text{MeX}_7$  there is a class of compounds in which the seventh halogen does not belong to the  $\text{MeF}_n$  polyhedra and occupies a special crystallographic site. Crystal lattices of such materials contain two anionic species,  $\text{MeX}_6^{2-}$  and  $\text{X}^-$ , and a more correct chemical formulation should be written as a double salt  $\text{A}_2\text{MeX}_6 \cdot \text{AX}$ . Strong evidence for the

presence of two kinds of anions in the structure was obtained by IR spectra studies. It was found for  $(\text{NH}_4)_3\text{SiF}_7$  and  $(\text{NH}_4)_3\text{TiF}_7$  that the absorption band corresponding to the deformation vibrations of the ammonium ions is split into two components: at  $1400 \text{ cm}^{-1}$  and  $1467 \text{ cm}^{-1}$  for silicate and  $1410 \text{ cm}^{-1}$  and  $1465 \text{ cm}^{-1}$  for titanate, which are typical for hexafluorides  $(\text{NH}_4)_2\text{Si}(\text{Ti})\text{F}_6$  and ammonium fluoride  $(\text{NH}_4)\text{F}$  [11]. Depending on the sizes of the central atom and monovalent cation, the crystal symmetry of the  $\text{A}_2\text{MeF}_6 \cdot \text{AF}$  compounds is either tetragonal  $P4/mbm, Z = 2$ :  $\text{K}_3\text{SiF}_7$  [6],  $(\text{NH}_4)_3\text{SiF}_7$  [7],  $(\text{NH}_4)_3\text{GeF}_7$  [8], or cubic  $Pm\bar{3}m, Z = 1$ :  $(\text{NH}_4)_3\text{SnF}_7$  [9],  $(\text{NH}_4)_3\text{PbF}_7$  [10].

Based on its isomorphism with  $(\text{NH}_4)_2\text{SiF}_6 \cdot (\text{NH}_4)\text{F}$ , the crystal symmetry of  $(\text{NH}_4)_2\text{TiF}_6 \cdot (\text{NH}_4)\text{F}$  compound was first determined as  $P4/mbm$  ( $a = 8.33, c = 5.96 \text{ \AA}, Z = 2$ ) [11]. Additional reflections in the X-ray pattern were later found and another space group was suggested  $P4/mnc, a = 11.9492, c = 11.666 \text{ \AA}, Z = 4$  [12].

The substitution of the central atom in series of ammonium-based crystals  $(\text{NH}_4)_2\text{MeF}_6 \cdot (\text{NH}_4)\text{F}$  ( $\text{Me}: \text{Si}, \text{Ge}, \text{Ti}, \text{Sn}, \text{Pb}$ ) was accompanied by the unit cell size variation [6–12] which can be considered as a chemical pressure change, leading to symmetry modification. The dependence of the room temperature phases on the composition suggests possible structural transformations in fluorides  $(\text{NH}_4)_2\text{MeF}_6 \cdot (\text{NH}_4)\text{F}$  obtained by temperature change. To our knowledge, no work has been done for studying the room temperature structural stability of these compounds and revealing phase transitions, so far.

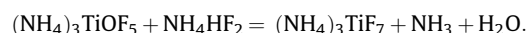
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This paper is devoted to the growth of single crystal of  $(\text{NH}_4)_2\text{TiF}_6 \cdot (\text{NH}_4)\text{F}$  double salt and preliminary research of the temperature range of its stability. To detect possible phase transitions, the temperature behavior of heat capacity as well as crystal-optical characteristics such as birefringence, extinction position, twinning were investigated. The calorimetric measurements were carried out using a differential scanning microcalorimeter DSM – 10 M (DSM). Optical studies were performed with a polarizing microscope “Axioskop-40” and a temperature chamber “Linkam LTS 350” in a temperature range of 90–400 K. Birefringence was measured by Berek’s compensator (“Leica”) with an accuracy of  $\pm 10^{-5}$ .

## 2. Crystal growth

The title compound (ammonium heptafluorotitanate,  $(\text{NH}_4)_3\text{TiF}_7 = (\text{NH}_4)_2\text{TiF}_6 \cdot \text{NH}_4\text{F}$ ) was synthesized from fluoride aqueous solutions.  $(\text{NH}_4)_2\text{TiF}_6$  of a reagent grade or synthetic  $(\text{NH}_4)_3\text{TiOF}_5$  [13] were used as starting materials, together with the reagent  $\text{NH}_4\text{F}$  or  $\text{NH}_4\text{HF}_2$ , respectively:



A large excess of fluoride agent ( $3\text{NH}_4\text{F}$  in the first case,  $2\text{NH}_4\text{HF}_2$  in the second one) is needed for the formation of single crystals of  $(\text{NH}_4)_3\text{TiF}_7$ . For example, 30–50 g of titanium salt and 15–25 g of fluoride reagent were dissolved with heating in 50–100 ml  $\text{H}_2\text{O}$  with the addition of a small amount of hydrofluoric acid to adjust the solution pH to 5–6. Slow evaporation of the solution in air gives hexagonal plates or trigonal prisms of  $(\text{NH}_4)_2\text{TiF}_6$  as the first type of precipitated crystals, in spite of large excess of  $\text{NH}_4^+$  and  $\text{F}^-$ . It is necessary to be careful not to miss the moment of isolation of tetragonal plates or tetragonal prisms of

$(\text{NH}_4)_3\text{TiF}_7$  before the co-precipitation of  $\text{NH}_4\text{HF}_2$  crystals. It should be noted that the real composition of the obtained crystals corresponds to  $(\text{NH}_4)_3\text{Ti}(\text{OH})_x\text{F}_{7-x}$  ( $x = 0.2\text{--}0.4$ ) in agreement with the fluorine content determined by pyrohydrolysis ( $54.5 \pm 0.8$  mass.%). But for simplicity, we will use the stoichiometric formula  $(\text{NH}_4)_3\text{TiF}_7$ .

## 3. Optical investigations

A habit of  $(\text{NH}_4)_3\text{TiF}_7$  single crystals corresponds to elongated rectangular prisms with extinctions along the growth faces. Small samples are single-domain and optically uniaxial, which is consistent with tetragonal symmetry [11,12]. Large crystals are characterized by twin boundaries equally spaced relative to the growth faces and by plane of twin boundary along (1 1 1) (Fig. 1a). Low uniaxial pressure, for instance induced by a needle, can easily move twin boundaries and rotate the fourfold axis to  $90^\circ$  (Fig. 1b).

Upon cooling, starting from room temperature,  $(\text{NH}_4)_3\text{TiF}_7$  exhibits a sharp phase transition at  $T_{21} = 287.5$  K into an optically isotropic phase (Fig. 2a and b). However, the sample does not become completely dark in low temperature phase, as is characteristic for cubic symmetry. Bright spots in the field of observation remain visible down to 80 K which is the lowest temperature for optical measurements. Refocusing the microscope into the sample showed that optical anisotropy results from a twin structure in the form of very narrow stripes along [1 1 0], which scatters the light (Fig. 2b). When approaching the transition at  $T_{21}$  on heating from low temperature, the twin regions change. The phase transition was detected by the appearance and moving of the room temperature phase front (Fig. 2c). Just before the phase transition front, the sample became single-domain and black. Upon heating, unlike cooling, the boundary between low temperature  $G_3$  and room temperature  $G_2$  phases moves very slowly over the crystal plate surface. Anisotropic phase  $G_2$  appears near 291 K and occupies half of the sample at 294 K. The moving process is finished at  $T \approx 310$  K. So the cubic – tetragonal

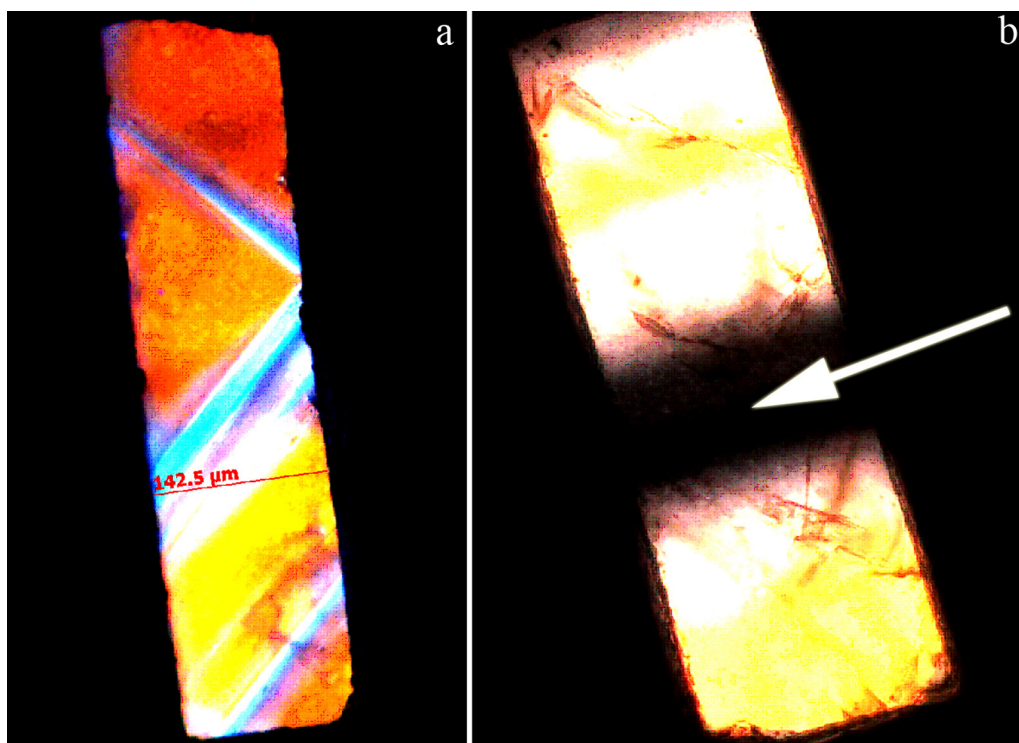
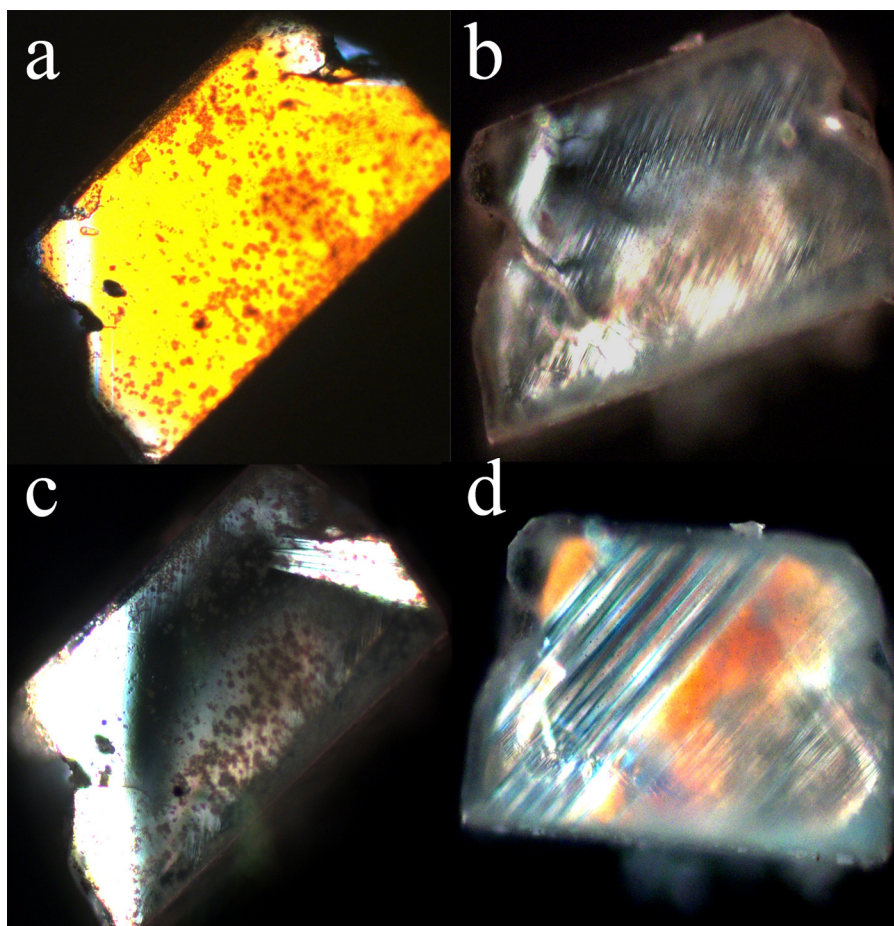


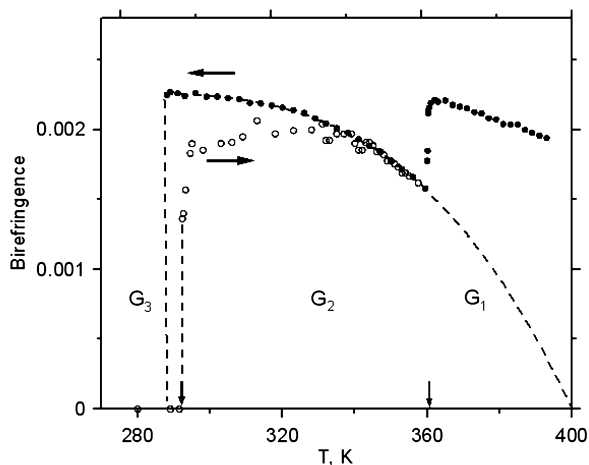
Fig. 1. The growth twins in the  $(\text{NH}_4)_3\text{TiF}_7$  crystal (a). Change of the fourfold axis location from horizontal to vertical under pressure induced by needle (b).



**Fig. 2.** Observation of phase transition at  $T_2$  in the (1 0 0) plane. Phase  $G_2$  at 310 K (a). Twin pattern in the cubic phase  $G_3$  (b). The phase front of transition at  $T_2$ . Twins are absent in the vicinity of the phase front (c). Twin pattern in tetragonal phase  $G_2$  at  $T = 310$  K (d).

transformation  $G_3 \rightarrow G_2$  occurs in a rather wide temperature range  $\Delta T \approx 20$  K. Further heating leads to the appearance of twins (Fig. 2d) which are similar to the growth twins (Fig. 1a).

Single-domain sample of the (1 0 0)-cut has at room temperature a rather small birefringence  $\Delta n = n_o - n_e = 0.00226$ . The  $\Delta n(T)$  temperature dependence of  $(\text{NH}_4)_3\text{TiF}_7$  is shown in Fig. 3. Upon cooling below  $T_{2\perp}$  birefringence abruptly drops to zero. Upon heating the anisotropic phase is gradually restored. Measurements of birefringence in the  $G_2$  phase are possible above 295 K, when



**Fig. 3.** Temperature dependence of the main birefringence of the crystal  $(\text{NH}_4)_3\text{TiF}_7$ . Dashed line shows extrapolation of the  $\Delta n(T)$  to zero.

more than half the sample area becomes tetragonal. The process of total recovery of the tetragonal symmetry continues until  $T \approx 330$  K, above that the dependence of  $\Delta n(T)_\perp$  on heating gradually coincides with the same at the cooling process  $\Delta n(T)_\perp$ .

Upon further heating, the main birefringence of crystal  $\Delta n = n_o - n_e$  decreases in a gradual manner. Extrapolating the  $\Delta n(T)$  data to high temperatures suggests the existence of the phase transition to the isotropic state near 400 K (dashed line in Fig. 3). However, birefringence abruptly increases at  $T_{1\perp} = 360$  K and a further increase of the sample temperature is followed by a gradual decrease of the optical anisotropy. This means that  $(\text{NH}_4)_3\text{TiF}_7$  undergoes another phase transition at  $T_1$  into  $G_1$  phase. Upon cooling, a jump of birefringence is observed at  $T_{1\perp} = 358.5$  K.

An unusual phenomenon is observed in repeating measurements of the birefringence of the same sample. Once the crystal was heated above 360 K, a reduction of the birefringence value was observed in the temperature regions  $T < T_1$  and  $T > T_1$ . Such a behavior of  $\Delta n$  can be explained by the formation of small domains observed in the sample upon repeated passages through first-order transition at  $T_1$ . At room temperature the stripe domains with the boundaries at  $45^\circ$  to  $[0 0 1]$ -direction occur in the planes (1 0 0) (Fig. 4a) which are similar to the growth twins (Fig. 1a). This structure is reduced on repeated heating and cooling cycles and not visible above  $T_1$  (Fig. 4b).

An optically isotropic section exists at room temperature in (0 0 1)-plane (Fig. 5a). Above 360 K twins appear with boundaries located along the  $[1 1 0]$ -direction (Fig. 5b). On cooling, twin boundaries disappear at about 359 K.

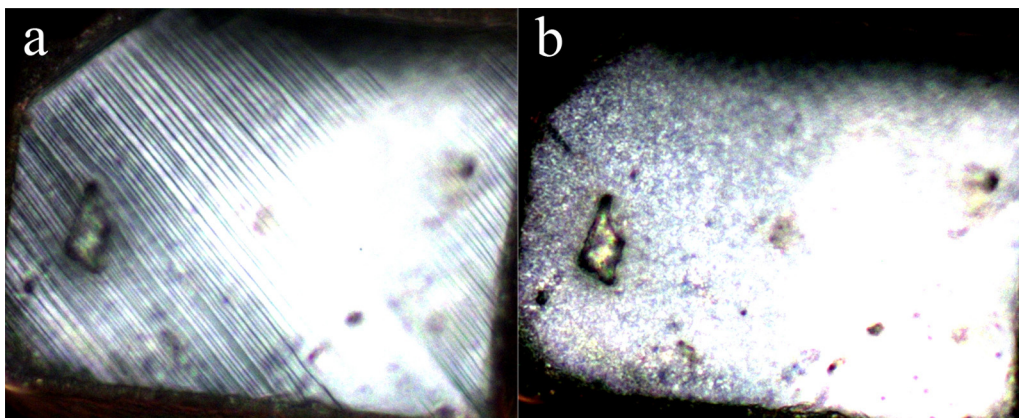


Fig. 4. The twin patterns formed in the (1 0 0) plate upon repeated cycling through a transition at  $T_1$ : stripe twins in  $G_2$  phase (a) and complicated picture in  $G_1$  phase (b).

It should be noted that slow decomposition of the  $(\text{NH}_4)_3\text{TiF}_7$  crystal was detected above 300 K, so the process of optical investigations was performed using oil under cover glasses.

#### 4. Calorimetric measurements

DSM measurements of  $(\text{NH}_4)_3\text{TiF}_7$  were carried out from temperature range of 110–380 K in heating and cooling modes on a series of the samples obtained from different crystallizations. The weight of the powder samples was  $\sim 0.10$  g. The rate of temperature change  $dT/d\tau$  ranged between 1 K/min and 32 K/min revealing the hysteretic phenomena. In the first stage, the heat flow through the sample and reference compound was recorded vs. temperature. Then, after elimination of background, the information on excess heat capacity  $\Delta C_p$  connected with the phase transitions was obtained.

The calorimetric investigations revealed two anomalies in the heat capacity behavior associated with the succession of phase transitions  $G_1 \rightarrow G_2 \rightarrow G_3$ . Maxima of the heat capacity peaks were located at the temperatures  $T_1 = 361 \pm 2.0$  K and  $T_2 = 293 \pm 1.0$  K, which were observed upon heating at  $dT/d\tau = 8$  K/min. Both anomalies were found to be reproducible during the thermal cycling. The temperature dependence of the excess heat capacity of  $(\text{NH}_4)_3\text{TiF}_7$  is shown in Fig. 6.

The enthalpy changes associated with the successive phase transitions were determined for a series of fresh samples by integration of the excess heat capacity temperature dependence  $\Delta H_i = \int \Delta C_p(T) dT$ . Both values were evaluated from the results obtained at a rate  $dT/d\tau = 8$  K/min and found rather different  $\Delta H_1 = 2100 \pm 200$  J/mol and  $\Delta H_2 = 5200 \pm 500$  J/mol.

We have also examined the dependence of the phase transition temperatures and their hysteresis  $\delta T_i$  upon the rate of thermal cycling (Fig. 7). Lowering  $dT/d\tau$  leads to the lowering of the thermal hysteresis and heat capacity anomalies. It was found that extrapolation to zero of the  $T_i(dT/d\tau)$  linear dependences gives following parameters:  $T_{11} = 360 \pm 1$  K,  $\delta T_1 \approx 5$  K;  $T_2 = 292.5 \pm 1$  K,  $\delta T_2 \approx 5$  K. These results mean that two strong first order transformations take place in  $(\text{NH}_4)_3\text{TiF}_7$ .

#### 5. Discussion

The polarizing optic and DSM studies, as well as measuring birefringence made it possible to establish the existence of two structural phase transitions between  $G_1$ ,  $G_2$  and  $G_3$  phases in  $(\text{NH}_4)_3\text{TiF}_7$  crystal. The symmetry of  $G_2$  was suggested as  $P4/mnc$  [12]. The phase  $G_1$  differs from  $G_2$  by the presence of the twin structure in slice (0 0 1) with the boundaries on (1 1 0). This fact shows that the group symmetry of  $G_1$  is lower than  $G_2$ . At the same

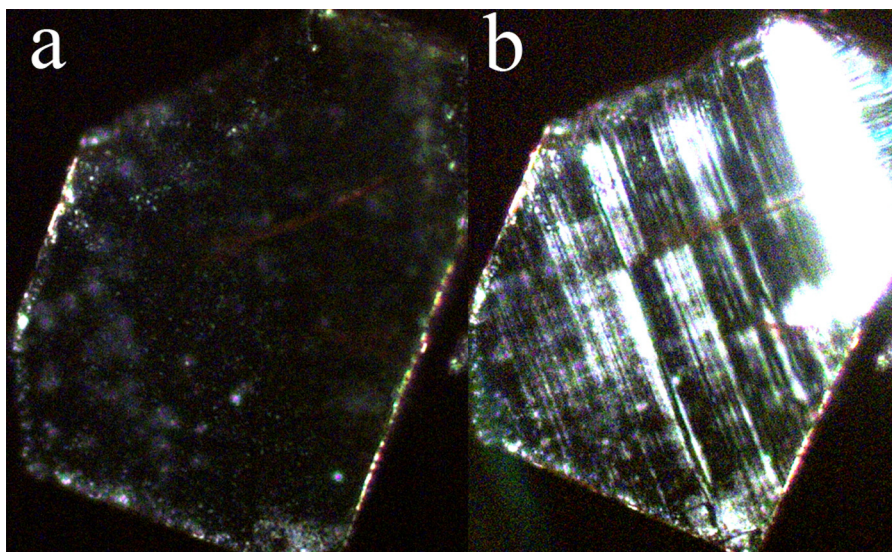


Fig. 5. The patterns observed by the microscope in (0 0 1) cut of the  $(\text{NH}_4)_3\text{TiF}_7$  crystal: the uniformity in  $G_2$  phase (a); twin walls in  $G_1$  phase (b).

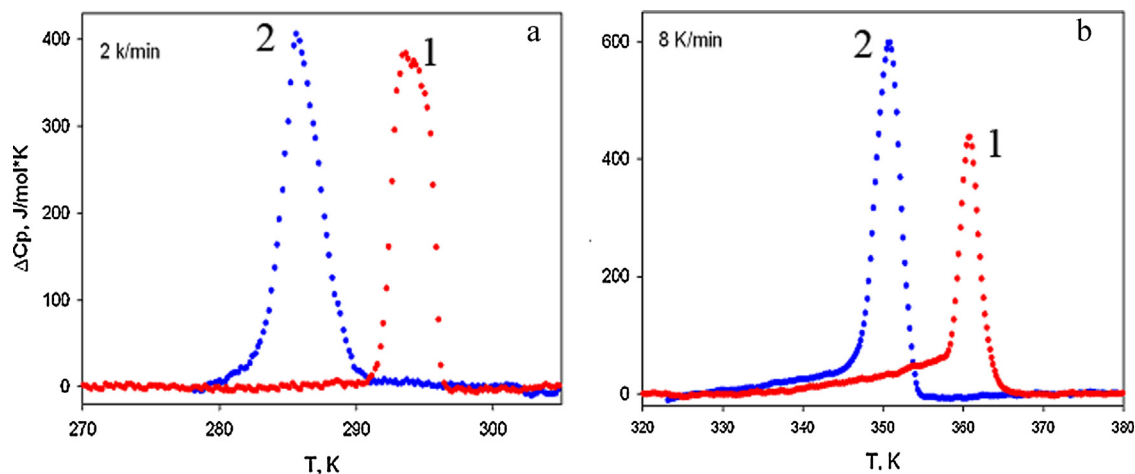


Fig. 6. Temperature dependence of the excess heat capacity on heating (1) and cooling (2) for phase transitions at  $T_2$  (a) and  $T_1$  (b).

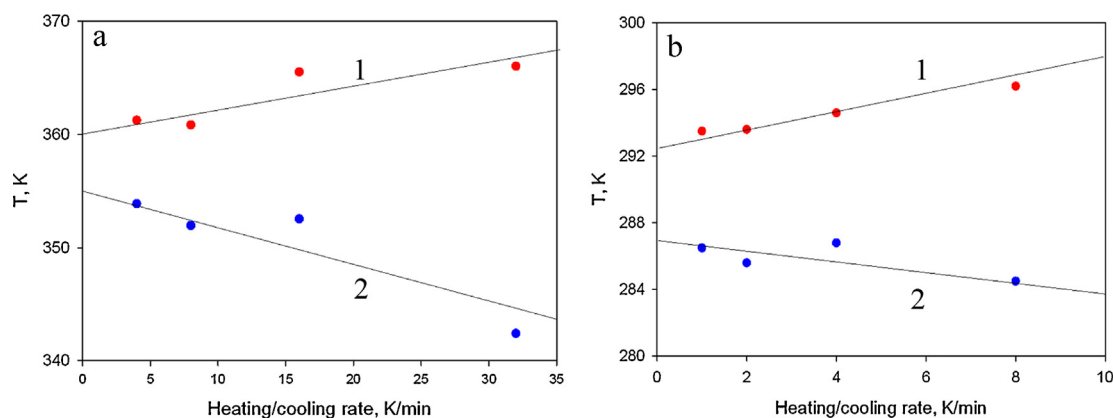


Fig. 7. Dependence of the phase transition temperatures on the  $dT/dt$  value on heating (1) and cooling (2) for transformations at  $T_2$  (a) and  $T_1$  (b).

time, observation of the optical axis coincided with the [0 1 1] direction in the twins makes evident the  $G_1$  phase tetragonal symmetry. Therefore, based on observations in polarized light, we assume the point symmetry of the  $G_1$  phase as  $4/m$ . The lack of the planes (1 1 0) in this symmetry group (compared to  $G_2$ ) is compensated by appropriate twinning (Fig. 5b).

According to the crystal-optic research performed in a quasi-static mode, the temperature of the phase transition between two tetragonal phases is:  $T_{11} = 358.5$  K,  $T_{11} = 360$  K with  $\delta T \approx 1.5$  K. The value  $T_1$  may vary insignificantly in different samples. Transition at  $T_1$  accompanied by a jump of the birefringence is reversible and not followed with any destruction of the sample.

Additional domain structure with a twinning plane (1 1 1) is formed in the crystal after multiple cycling through the first-order transition  $T_1$ . This structure is clear in phase  $G_2$  (Fig. 4a) and smeared in  $G_1$  (Fig. 4b). The appearance of such twins in  $(\text{NH}_4)_3\text{TiF}_7$  can be explained by the assumption of the existence of the parent phase  $G_0$  with  $m\bar{3}m$  point symmetry. In this case, system of the twins in the  $G_1$  phase can be described by symmetry change  $m\bar{3}m \rightarrow 4/m$ , whereas in  $G_2$  the only visible twins are formed by losing the threefold axis at the phase transition  $m\bar{3}m \rightarrow 4/mmm$ .

Below  $T_{21} = 287.5$  K there is a strong first order transition to the cubic phase. In addition to some cracking of the crystal plate there is the movable twin structure with the walls along (1 1 0). This transition is also reversible. Upon heating, the tetragonal symmetry is slowly restored in the temperature range  $T_2 = 291$ –310 K.

The temperatures  $T_1$  and  $T_2$  determined in calorimetric and optical studies agree well with each other. Mismatch of the  $\delta T_1$

values can be explained by dynamic character of thermal anomalies measurements.

As it is seen in Figs. 3 and 6, there is a good agreement between the behavior of excess heat capacity and birefringence. In accordance with the first order transformation characterized by a strong  $\Delta n$  jump, the heat capacity peak at  $T_2$  is almost symmetrical. On the other hand, smooth increase of  $\Delta C_p$  between  $T_2$  and  $T_1$  coincides with a gradual decrease of birefringence in the same temperature range.

The entropy changes at the phase transitions  $\Delta S_i$  have been determined by integration of the area under the  $\Delta C_p/T(T)$  curves. Both phase transitions followed by significant values:  $\Delta S_1 = \int (\Delta C_p(T)/T) dT = 6 \pm 0.6$  J/mol K and  $\Delta S_2 = \int (\Delta C_p(T)/T) dT = 18.3 \pm 2$  J/mol K. As one can see, transformation at  $T_2$  is characterized by rather large entropy change and can be considered as connected with significant distortion of the structure. The reversible cracking of crystals observed in polarizing-optic measurements allow us to suppose that phase transition at  $T_2$  is reconstructive.

## 6. Conclusions

For the first time structural phase transitions were observed in one of the crystals belonging to the family of double salt compounds  $A_3\text{MeF}_7 = A_2\text{MeF}_6 \cdot \text{AF}$ .

Optic and calorimetric studies have shown that  $(\text{NH}_4)_3\text{TiF}_7$  undergoes two reversible first order structural transformations. Analysis of the polarizing-optic investigation results in conjunction with the X-ray data [12] has allowed us to suggest the

following unusual sequence of the symmetry change observed on heating: cubic ( $G_3$ ) ( $T_2 = 291$  K)  $\leftrightarrow$   $P4/mnc$  ( $G_2$ ) ( $T_1 = 360$  K)  $\leftrightarrow$   $4/m$  ( $G_1$ ).

Complex twinning of the tetragonal phases appearing after cycling  $(\text{NH}_4)_3\text{TiF}_7$  through the first-order transition at  $T_1$  can only be explained assuming the existence of high temperature cubic parent phase with  $m\bar{3}m$  symmetry. Such a supposition is supported by the results of X-ray studies on some double salt crystals  $A_3\text{MeX}_7$  at room temperature. The symmetry of  $(\text{NH}_4)_3\text{SnF}_7$  [9] and  $(\text{NH}_4)_3\text{PbF}_7$  [10] was characterized as a cubic one with the  $Pm\bar{3}m$  ( $Z = 1$ ) space group. It is possible that this space group is the parent one of all phases observed in  $(\text{NH}_4)_3\text{TiF}_7$  including  $G_3$  low-temperature cubic phase. Twins found in  $G_3$  show that its symmetry is lower than  $m\bar{3}m$ .

Both phase transitions found in  $(\text{NH}_4)_3\text{TiF}_7$  have noticeable features of the first order transformations: jumping change of birefringence at  $T_i$ , large values of both thermal hysteresis and entropy change. This suggests that both transitions are associated with significant structural changes, especially at  $T_2$ .

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