Ferroelastic Phase Transitions in (NH₄)₂TaF₇

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Abstract — The heat capacity, unit cell parameters, permittivity, optical properties, and thermal expansion of the (NH₄)₂TaF₇ compound with a seven-coordinated anion polyhedron have been measured. It has been found that the compound undergoes two successive phase transitions with the symmetry change: tetragonal \( T_1 = 174 \) K \( \rightarrow \) orthorhombic \( T_2 = 156 \) K \( \rightarrow \) tetragonal. The ferroelastic nature of structural transformations has been established, and their entropy and susceptibility to hydrostatic pressure have been determined.

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1. INTRODUCTION

There are many chemical compounds with the crystal structure containing four-, six-, or seven-coordinated fluorine polyhedra, among which the most commonly occurring are fluorides with the general chemical formulas \( A_{3}M_{2}F_{5}, A_{3}M_{2}F_{6}, A_{3}M_{2}F_{5}, \) and \( A_{2}M_{2}F_{6}, \) which have a perovskite-like crystal lattice [1–3]. The parent phases of these crystals are often have cubic or tetragonal symmetry, which can be lowered as a result of structural phase transitions associated, in particular, and, sometimes primarily, with rotations of the fluorine octahedra \( [M_{2}F_{5}] \), while remaining almost undistorted. The mechanism of the phase transitions can be governed either by the processes of ordering of the octahedra, which in the parent phase have several crystallographically and energetically equivalent orientations, or by insignificant displacements of the fluorine atoms due to rotations of the octahedra through small angles. As a rule, structural transformations of this type have a ferroelastic nature [1–3].

In addition to the compounds with six-coordinated polyhedra, which have been intensively studied for a long time, there are fluorides of the general formula \( A_{x}M_{2}F_{7} \) (\( x = 1, 2, 3 \)) with seven-coordinated anion polyhedra. By now, the number of known fluorides of this type is small and they have been studied rather superficially. The polyhedra \( [M_{2}F_{6}] \), as a rule, can be represented as either a monocapped trigonal prism or a pentagonal bipyramid [4, 5]. Their symmetry and the valence of the central atom determine the degree of disorder of the ligands and the symmetry of the crystal lattice as a whole. The \( A_{2}ZrF_{7} \) \( (A = K, \text{NH}_4) \) compounds have cubic symmetry (space group \( Fm-3m, Z = 4 \)) at room temperature [4, 5], whereas the symmetry of the \( A_{3}M_{2}F_{7} \) and \( A_{2}M_{2}F_{6} \) crystals also depends on the size of the cation \( A \). It is known that, in the series of \( ATaF_{7} \) \( (A = \text{Ca, Ba, Sr, Pb}) \) compounds, there can exist cubic and monoclinic structures [6], while the \( A_{2}TaF_{7} \) compounds can have a tetragonal \( (A = \text{Rb}) \) [7] or monoclinic \( (A = \text{K}) \) crystal lattice [4].

The available information on the stability of the parent phases of \( A_{x}M_{2}F_{7} \) fluorides to variations in the external parameters has been reduced in the main only to the data on structural transformations due to reversible phase transitions [4, 7, 8]. There are no data on the physical properties of these compounds, which are necessary to determine the nature and mechanism of the phase transitions, to construct models of the crystal structure, and to determine the degree of disorder of individual structural elements.

In this work, we grew crystals of a fluoride compound with seven-coordinated anion polyhedra, namely, \( (\text{NH}_4)_{2}TaF_{7} \), which was synthesized and described for the first time in 1866 [9]. We also investigated the heat capacity, unit cell parameters, permittivity, optical properties, and thermal expansion of this compound.
2. SYNTHESIS, IDENTIFICATION OF SAMPLES, AND PRELIMINARY INVESTIGATIONS

Single crystals of \((\text{NH}_4)_2\text{TaF}_7\) were synthesized by two methods. The first method consisted in sintering the initial hydrated tantalum oxide \((\text{Ta}_2\text{O}_5 \cdot n\text{H}_2\text{O})\) with the ammonium hydrodifluoride \((\text{NH}_4\text{HF}_2)\) at temperatures in the range from 150 to 200°C according to the reaction

\[
\text{Ta}_2\text{O}_5 + 7\text{NH}_4\text{HF}_2 = 2(\text{NH}_4)_2\text{TaF}_7 + 3\text{NH}_3 + 5\text{H}_2\text{O}.
\]

The cake thus obtained was subjected to leaching of water with addition of a small amount of concentrated \((40\%)\) HF (all concentrations are given in mass %). The solution was filtered off and slowly evaporated in air until transparent single crystals of \((\text{NH}_4)_2\text{TaF}_7\) precipitated.

In the second case, during heating, the initial hydrated tantalum oxide \(\text{Ta}_2\text{O}_5 \cdot n\text{H}_2\text{O}\) \((15\ g)\) interacted with concentrated \((40\%)\) HF \((45\ mL)\). A solution (20–25 mL) of concentrated ammonia \((25\%)\) was added to the filtered solution (the pH of the resulting solution was \(\sim 2\)). The formation of crystals of the studied complex occurred during a slow evaporation in air.

A careful chemical analysis for the fluorine content showed that the actual composition of the crystals corresponds to the formula \((\text{NH}_4)_2\text{TaO}_{0.3}\text{F}_{6.4}\). A similar partial isomorphic substitution of oxygen for fluorine was also observed in the related crystal \(\text{Rb}_2\text{TaF}_7\) [7]. However, because the content of the impurity does not exceed \(\sim 4\%\), in the future we will use the stoichiometric formula \((\text{NH}_4)_2\text{TaF}_7\).

The identification of the grown crystals and the determination of their structural parameters were performed on a D8-ADVANCE X-ray diffractometer \((\text{Cu}K\alpha\ radiation, \theta–2\theta\ scan mode)\). It was established that, at room temperature, the \((\text{NH}_4)_2\text{TaF}_7\) crystal has tetragonal symmetry \((\text{space group } \text{P}_4/\text{nmm}, Z = 2)\), as was previously found for the \(\text{Rb}_2\text{TaF}_7\) fluoride, whose structure was investigated in [7]. In the X-ray diffraction patterns of the ammonium compound, we did not reveal reflections indicating the presence of foreign phases in the sample. The replacement of the spherical cation \(\text{Rb}^+\) by the tetrahedral cation \(\text{NH}_4^+\) led to a slight change in the unit cell parameters:

\[
a = b = 5.8947(3) \, \text{Å} \quad \text{and} \quad c = 10.6856(5) \, \text{Å} \quad \text{for} \quad (\text{NH}_4)_2\text{TaF}_7; \quad \text{and} \quad a = b = 5.9118(3) \, \text{Å} \quad \text{and} \quad c = 10.617(1) \, \text{Å} \quad \text{for} \quad \text{Rb}_2\text{TaF}_7.
\]

The stability of the parent phase \((\text{NH}_4)_2\text{TaF}_7\) to variations in the temperature was investigated on a DSM-10M differential scanning microcalorimeter. The measurements were carried out in the temperature range from 110 to 350 K in the heating and cooling modes on a series of samples obtained from different crystallizations. The weight of the powder samples was \(\sim 0.10\ g\).

The preliminary calorimetric investigations revealed two anomalies in the heat capacity with maxima at the temperatures \(T_1 = 174.3 \pm 2.0\ K\) and \(T_2 = 154.5 \pm 1.0\ K\), which were observed during the heating at a rate \(dT/\Delta t = 8\ K\ \text{min}^{-1}\) and reproduced during the thermal cycling. The temperature dependence of the excess heat capacity of the \((\text{NH}_4)_2\text{TaF}_7\) compound is shown in Fig. 1a. The anomaly observed at the temperature \(T_2\) in the form of a sharp nearly symmetric peak with the maximum value \((\Delta C_p)_\text{max} \approx 70\ J\ (\text{mol K})^{-1}\) is characteristic of first-order phase transitions. This is also evidenced by the hysteresis of the phase transition temperature \(\Delta T_2 = 2.5\ K\), which was revealed during the cooling of the sample. The anomaly observed at the temperature \(T_1\) is significantly diffuse and amounts to only \((\Delta C_p)_\text{max}/(\Delta C_p)_\text{max} \sim 7\%\). A similar ratio between the enthalpies of the phase transformations was obtained by integrating the function \(\Delta C_p(T): \Delta H_1 \approx 25\ J\ \text{mol}^{-1}\) and \(\Delta H_2 \approx 280\ J\ \text{mol}^{-1}\). The small values of the thermal effects indicate slight distortions of the