LATTICE DYNAMICS
AND PHASE TRANSITIONS

A Raman Scattering Study of the Phase Transition in the Ammonium Oxyfluoride $(NH_4)_3TiOF_5$

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Abstract—Raman spectra of a polycrystalline sample of the perovskite-like oxyfluoride $(NH_4)_3TiOF_5$ are measured in the frequency region 100–3600 cm^{-1} at temperatures ranging from 91 to 370 K under hydrostatic pressures of up to 9 GPa, which include the range of the phase transition from the orientationally disordered cubic phase to the low-symmetry phase. Anomalies in the spectral parameters due to the phase transition are revealed in the range of vibrations of $TiOF_5$ octahedral groups.

1. INTRODUCTION

Structural studies of oxyfluorides of the chemical formula $AA'MO_xF_{6-x}$ ($x = 1, 2, 3$) with the framework formed by fluorine–oxygen octahedra have revealed that, in the high-temperature phase, these compounds have cubic symmetry with space group $Fm\bar{3}m$, $Z = 4$. Upon replacement of the spherical cation by the tetrahedral ammonium ion $(NH_4)_3MO_xF_{6-x}$, the cubic structure remains stable; however, this results naturally in an additional disordering of the lattice because, in order for the ammonium tetrahedron residing in the octahedral environment (position 4b) to retain so high symmetry, it should have at least two equivalent positions. The local symmetry of the MO_xF_{6-x} octahedral ion can be tetragonal C_{4v} ($x = 1, 2$); orthorhombic C_{2v} ($x = 2, 3$), i.e., the *mer*-configuration; or rhombohedral C_{3v} ($x = 3$), i.e., the *fac*-configuration [1–3].

In the ammonium oxyfluoride $(NH_4)_3TiOF_5$ (the structure of its cubic phase [2] is shown in Fig. 1), the octahedral ion MO_xF_{6-x} has C_{4v} symmetry [4, 5]. The existence of a phase transition in $(NH_4)_3TiOF_5$ at 260 K was confirmed by differential scanning microcalorimetry and x-ray diffraction [2]. In our previous works [6, 7], we studied the ammonium oxyfluoride $(NH_4)_3WO_3F_3$, a structurally similar compound, and showed that the phase transition observed in this material is an order–disorder transition and that its main mechanism involves ordering of the fluorine–oxygen

octahedra. It remains unclear, however, whether the transition mechanism remains unchanged despite the fact that the quasi-octahedron in this compound has a different combination of fluorine and oxygen ligands. We report here on a Raman scattering study of the phase transitions in $(NH_4)_3TiOF_5$.

2. EXPERIMENT AND DISCUSSION OF THE RESULTS

2.1. Low-Temperature Measurements

The ammonium oxyfluoride $(NH_4)_3TiOF_5$ was prepared from a hot solution of $(NH_4)_2TiF_6$ with an NH_4F excess with the subsequent addition of a NH_4OH solution. This procedure resulted in the formation of small transparent colorless crystals in the form of octahedra. The synthesis technique is described in more detail in [2]. The x-ray diffraction analysis confirmed that the crystal has a cubic structure ($Fm\bar{3}m$; the unit cell parameter, 0.9113 nm). The x-ray diffraction patterns did not reveal any peaks that could be assigned to impurities of the initial components or to foreign phases.
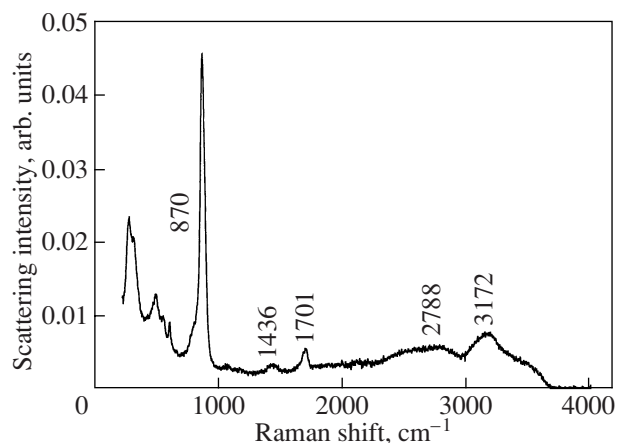
The Raman spectra were recorded in back scattering geometry in the frequency range 100–3500 cm^{-1} on an RFS100/S Fourier–Raman spectrometer (Bruker) with a resolution of 2 cm^{-1}. The spectra were excited with a Nd : YAG laser operating at a wavelength of 1.06 μm at a power of 1.3 W. Microcrystals of the material under
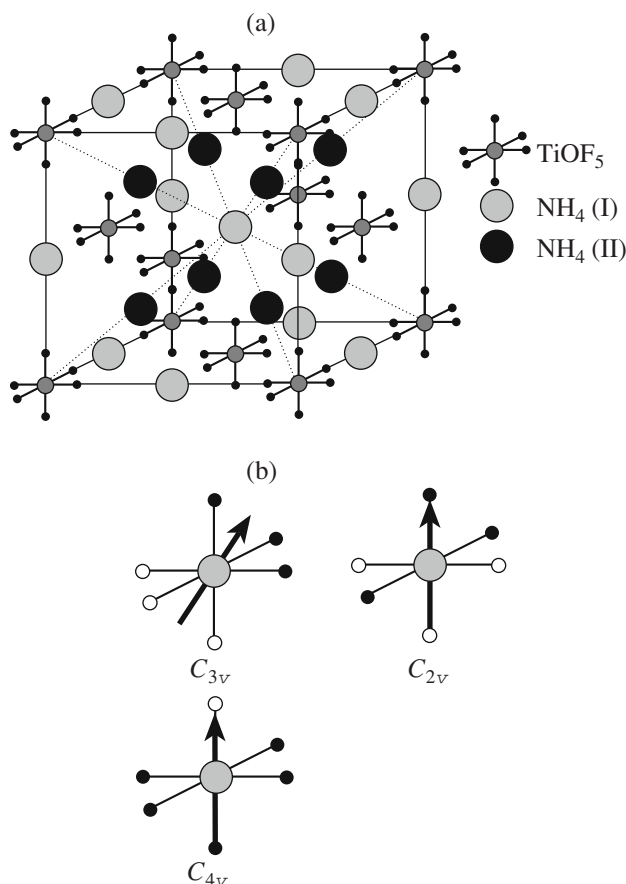
Fig. 1. (a) Structure of the unit cell of the cubic phase of the $(NH_4)_3TiOF_5$ crystal and (b) local symmetry of the MO_xF_{6-x} octahedral ion (arrows indicate the orientation of the dipole moments of the ions).

Fig. 2. Overall Raman spectrum of $(NH_4)_3TiOF_5$ at room temperature.

study were placed in a metallic container closed with a quartz glass. In studies of the behavior of the samples with variations in temperature, the container was placed in a Specac cryostat, which permitted spectral measurements in the range 83–523 K. The accuracy in the stabilization of the temperature was equal to ±0.4 K.

Figure 2 shows the experimental Raman spectrum of $(NH_4)_3TiOF_5$ at room temperature. The spectrum in the frequency range 750–1000 cm^{-1} contains an intense line, which can be assigned to the Ti–O stretching vibration of $TiOF_5$ ions. Significantly, this vibration is polar and it appears in the Raman spectrum of the non-polar cubic phase because of structural disorder. The lines of the Ti–F stretching and bending vibrations of this ion lie at lower frequencies. The spectrum in the ranges 2700–3500 and 1200–1600 cm^{-1} contains two lines of internal stretching modes and two lines of bending modes of the ammonium ion, respectively. The frequencies of these lines are close to those of the free NH_4^+ ion [8]. The aforementioned lines are noticeably broadened; however, their splitting is absent, which indicates a weak interaction of the ammonium ions with one another and with the crystalline environment.
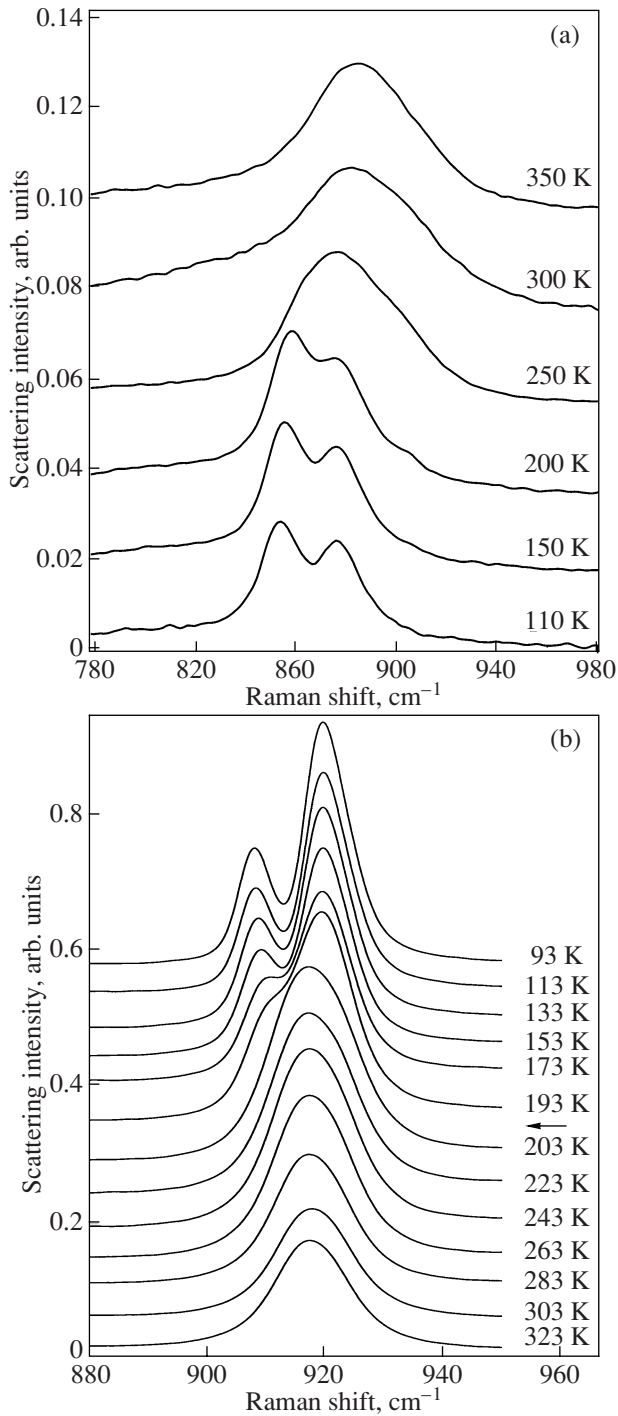
At room temperature, the line at 870 cm^{-1} is asymmetric because of the structural disorder. However, when observed under cooling, it clearly splits into two lines at the phase transition point (260 K). As the temperature decreases still more, the components of the doublet thus formed continue to move apart in frequency and become narrower (Fig. 3a). The narrowing of the Ti–O internal vibrations in $(NH_4)_3TiOF_5$ suggests that, below the phase transition temperature, the anions undergo orientational ordering. Similar changes were observed in $(NH_4)_3WO_3F_3$ [6, 7], where the strongest line at 917 cm^{-1}, which corresponds to the W–O stretching vibrations, also narrowed and split into two lines (Fig. 3b). The splitting of the nondegenerate Ti–O longitudinal vibration into a doublet can be associated only with the presence of a few quasi-octahedral ions in the primitive cell of the low-temperature phase of the crystal, i.e., with an increase (most probably, doubling) of its volume (Fig. 4).

In contrast to $(NH_4)_3WO_3F_3$, cooling of $(NH_4)_3TiOF_5$ does not induce any sharp changes in the region of ammonium vibrations (Fig. 5a) [6, 7]. For the $(NH_4)_3WO_3F_3$ compound in this range, we observe a substantial increase in the scattering intensity, the appearance of complex structured bands in place of single lines below the phase transition temperature, and an increase in the intensity under further cooling to 90 K (Fig. 5b). Such a structurization of the high-frequency part of the spectrum of this crystal originates from the formation of hydrogen bonds between ammonium protons and oxygen in the ordered anion sublattice.
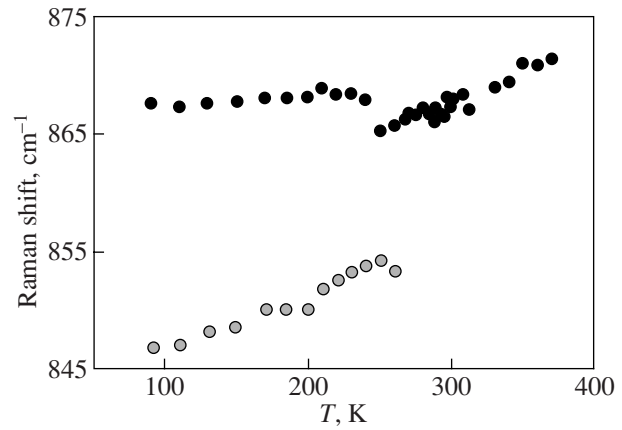
For $(NH_4)_3TiOF_5$ below the phase transition temperature, the lines of internal vibrations of ammonium ions remain broad and do not split. This transition does not apparently bring about ordering of ammonium ions and the formation of hydrogen bonds. This should possibly be attributed to the lower oxygen content in the structure of this compound.
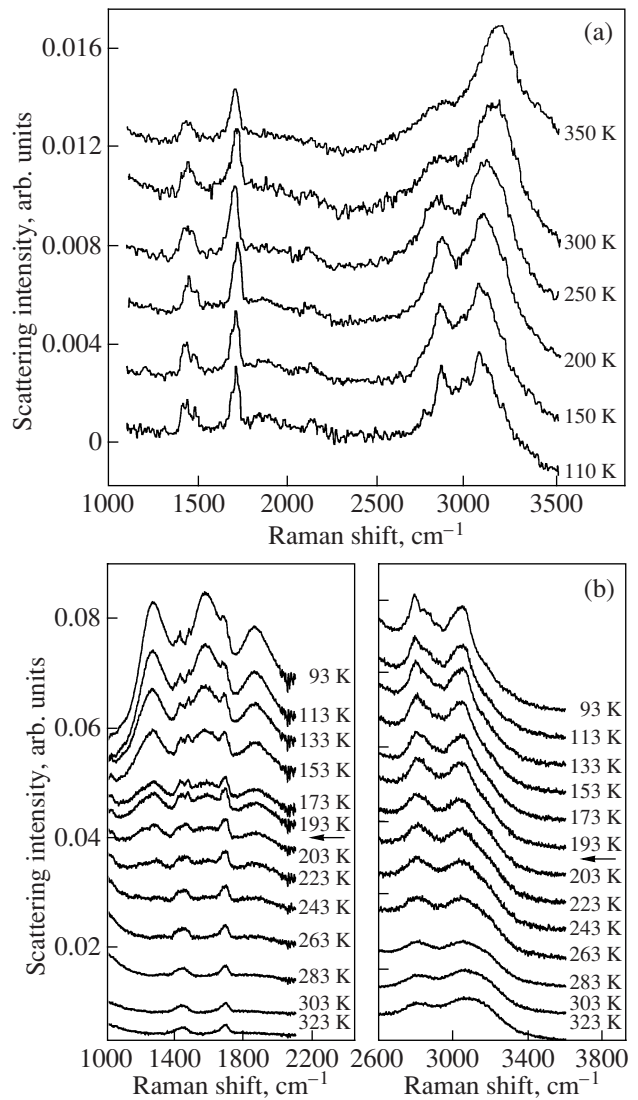
Fig. 4. Temperature dependence of the frequency of the line at 870 cm^{-1}.

Fig. 3. Evolution of (a) the line at 870 cm^{-1} during the phase transition in $(NH_4)_3TiOF_5$ and (b) the line at 917 cm^{-1} during the phase transition in $(NH_4)_3WO_3F_3$.

2.2. Measurements under Pressure

The experiments under high (up to 9 GPa) hydrostatic pressure at room temperature were performed on the setup with diamond anvils. The cell with the sample was 0.25 mm in diameter and 0.1 mm high. The pressure was determined to within 0.05 GPa from the shift

Fig. 5. Evolution of the spectra of internal bending and stretching vibrations of ammonium ions during cooling in (a) $(NH_4)_3TiOF_5$ and (b) $(NH_4)_3WO_3F_3$.
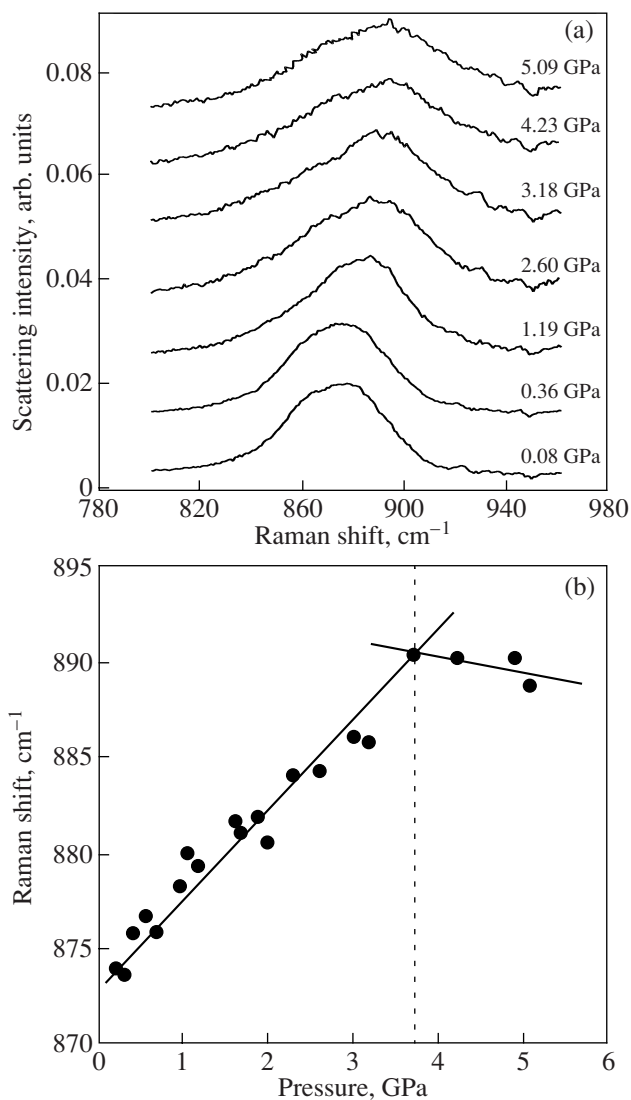
Fig. 6. (a) Evolution of the shape and (b) shift in the frequency of the line at 870 cm^{-1} under variations in the pressure.

in the luminescence band of ruby whose microcrystal was placed close to the sample. The pressure-transmitting medium was a thoroughly dehydrated mixture of ethyl and methyl alcohols. The Raman spectra were excited by the radiation of an Ar^{+} laser (514.5 nm, 500 mV) and recorded with an OMARS 89 multichannel Raman spectrometer (Dilor). Note that the strong diffuse light scattering from the chamber windows prevents obtaining Raman spectra at low frequencies, while the vibrational spectral lines of diamond and the alcohols overlap the region above 1200 cm^{-1}. Thus, it is only the strong line at 870 cm^{-1} that we succeeded to measure with a high accuracy.

The pressure-induced transformation of this line is illustrated in Fig. 6a. At low pressures, the frequency of the line increases linearly (Fig. 6b), while its width and intensity remain constant within the limits of experimental error. At pressures above ~3.8 GPa, the peak intensity of the line decreases noticeably and the

increase in the frequency practically stops (Fig. 6b), whereas its width increases markedly. All these changes can be a manifestation of a pressure-induced structural phase transition. At the same time, the line does not split, which suggests a difference in the low-temperature and high-pressure phases and the mechanisms of the corresponding phase transitions. The subsequent increases in the pressure (up to 8.46 GPa) did not initiate any substantial transient phenomena in the spectra.

3. CONCLUSIONS

Thus, we measured and analyzed, for the first time, the total Raman spectrum of the ammonium oxyfluoride $(NH_4)_3TiOF_5$ in the temperature range 93–323 K and identified the internal stretching and bending vibrations of ammonium ions and the vibrations of the Ti–O bonds of the anions.

The phase transition occurring in this compound at 260 K involves the doubling of the primitive cell and orientational ordering of the octahedra, as is the case in $(NH_4)_3WO_3F_3$, but, unlike this compound, it is not accompanied by the formation of hydrogen bonds.

The application of hydrostatic pressure initiates one more phase transition at ~3.8 GPa. No lattice ordering is observed in the high-pressure phase.

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