

PHASE TRANSITIONS

Influence of the Substitution of the Central *Me* Atom in Ammonium Oxyfluorides on Phase Transitions: IR Spectroscopy Study

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Abstract—Comparative investigations of infrared absorption spectra of ion–molecular crystals of the ammonium-containing oxyfluorides $(\text{NH}_4)_3\text{WO}_3\text{F}_3$ and $(\text{NH}_4)_3\text{MoO}_3\text{F}_3$ have been performed. It has been found that the parameters of the vibrational spectra exhibit anomalies in the ranges of internal vibrations of the MeO_3F_3 octahedral groups and ammonium ions near the phase transition temperatures. A comparative analysis of the IR spectra allows us to affirm that the studied phase transition in $(\text{NH}_4)_3\text{WO}_3\text{F}_3$ is primarily associated with the ordering of octahedral groups, whereas in $(\text{NH}_4)_3\text{MoO}_3\text{F}_3$, it is mainly due to the ordering of ammonium groups and the distortion of ammonium ions by the crystal environment.

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1. INTRODUCTION

Physical properties and mechanisms of phase transitions in cryolites $A_3\text{MeO}_3\text{F}_3$ and elpasolites $A_2A'\text{MeO}_3\text{F}_3$ depend both on the size of the central atom *Me* in the MeO_3F_3 octahedron and on symmetry of the octahedron itself; according to the fac- and mer-configurations of ligands, this symmetry can be trigonal C_{3v} or rhombic C_{2v} . Despite this fact, the symmetry of the crystal lattice of oxyfluorides at room temperature remains cubic ($Fm\bar{3}m$, $Z = 4$) due to static disorder of the F(O) atoms (Fig. 1) [1].

Substitution of the NH_4 ion for atomic cations at the octahedron center (4*b*) and in the interoctahedral cavity (8*c*) leads to possibility of additional structural disorder associated with orientational degrees of freedom of this ion. Moreover, the NH_4^+ tetrahedral ion in 4*b* site should be necessarily orientationally disordered.

Calorimetric investigations of ammonium oxyfluoride $(\text{NH}_4)_3\text{WO}_3\text{F}_3$ showed that this crystal undergoes a phase transition at 200 K; the transition is accompanied by a considerable entropy jump. The latter allows us to assume that this transition is associated with ordering processes of molecular ions of the lattice [2]. First Raman scattering investigations of the vibrational spectrum of this crystal confirmed the assumption of the lattice disorder in the cubic phase and its ordering below the transition point [3, 4].

For $(\text{NH}_4)_3\text{MoO}_3\text{F}_3$, the phase transition temperatures refined by the adiabatic calorimeter method were

$T_1 = 297.14$ K and $T_2 = 205.4$ K; it was established that the first-order transition occurs at T_1 [5].

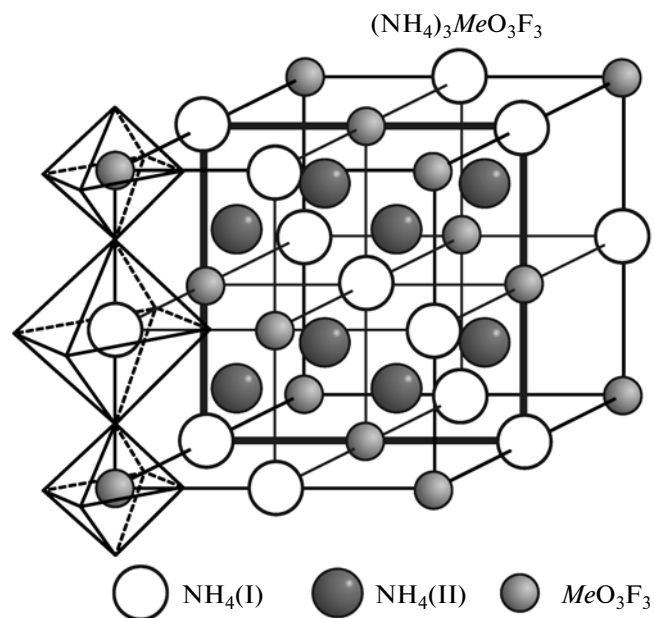


Fig. 1. Structure of the unit cell of the cubic phase of the $(\text{NH}_4)_3\text{MeO}_3\text{F}_3$ crystals. The ammonium cations are orientationally disordered and shown by spheres: a light sphere ($\text{NH}_4(\text{I})$) corresponds to the ammonium ion situated at the octahedron center (4*b*), and a dark sphere ($\text{NH}_4(\text{II})$) corresponds to the ammonium ion located in the interoctahedral cavity (8*c*). Positions of the oxygen and fluorine atoms in the MeO_3F_3 octahedra are also unknown.

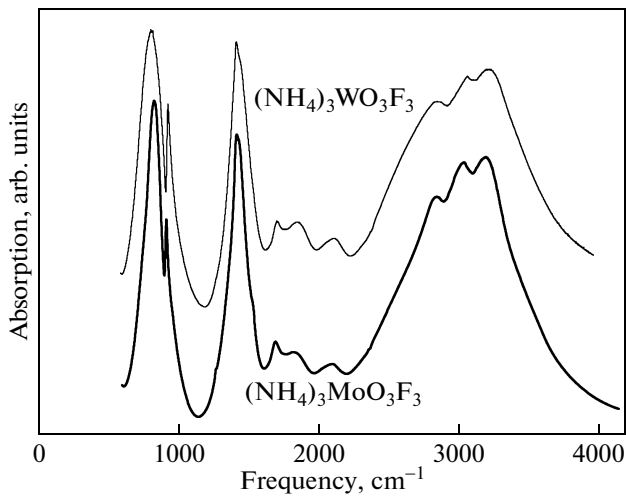
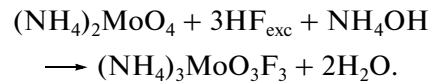


Fig. 2. Survey IR spectra of $(\text{NH}_4)_3\text{WO}_3\text{F}_3$ and $(\text{NH}_4)_3\text{MoO}_3\text{F}_3$ at room temperature.

In this work, we studied the influence of $\text{W} \rightarrow \text{Mo}$ substitution on the mechanisms of structural distortions and their manifestation in infrared (IR) absorption spectra.

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

Ammonium molybdate was the starting compound for synthesizing $(\text{NH}_4)_3\text{MoO}_3\text{F}_3$. A finely dispersed powder was obtained by the reaction



The procedure of the synthesis is described in [5].

Ammonium oxyfluoride $(\text{NH}_4)_3\text{WO}_3\text{F}_3$ was prepared from a hot solution of $(\text{NH}_4)_3\text{WO}_3\text{F}_4$ with excess NH_4F and subsequent gradual addition of the NH_4OH solution to $\text{pH} = 8$ until first portions of a white precipitate appeared. Fine transparent colorless octahedral crystals with the edge length of about $5 \mu\text{m}$ are formed by this rapid crystallization. After separation of a crystal precipitate from the mother liquor under slow evaporation in air, larger octahedra with the edge of about $40 \mu\text{m}$ crystallized [2].

The IR spectra were obtained for the KBr pellets containing 1% of the crystal powder under study using a Vertex 70 (Bruker) spectrometer in a range of $370\text{--}7500 \text{ cm}^{-1}$ with a resolution of 1 cm^{-1} . We used a Specac cryostat for investigations.

3. RESULTS AND DISCUSSION

3.1. General Structure of the Spectrum

Figure 2 shows the experimental IR spectra of $(\text{NH}_4)_3\text{WO}_3\text{F}_3$ and $(\text{NH}_4)_3\text{MoO}_3\text{F}_3$ at room temperature. No noticeable distinctions between these spectra are observed excluding the fact that the spectrum of molybdenum oxyfluoride in the range of internal vibrations of the fluorine–oxygen octahedra is insignificantly shifted to the low-frequency region. This is apparently associated with the distinction in the elec-

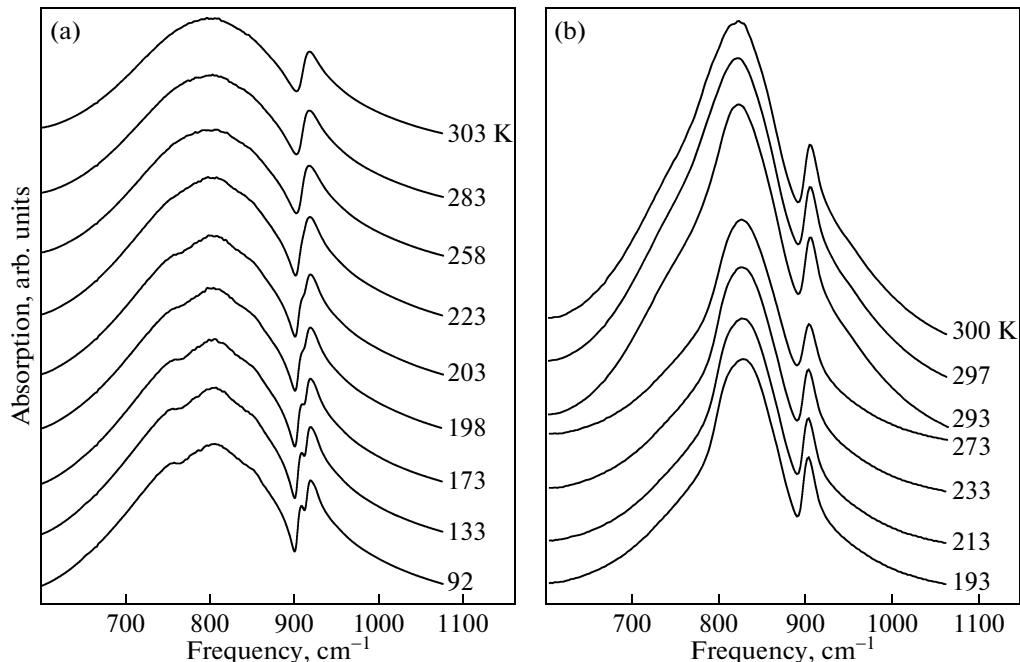


Fig. 3. Transformation of the IR spectral lines of (a) W-O in $\text{WO}_3\text{F}_3^{3-}$ anions and (b) Mo-O in $\text{MoO}_3\text{F}_3^{3-}$ anions upon phase transitions in $(\text{NH}_4)_3\text{WO}_3\text{F}_3$ and $(\text{NH}_4)_3\text{MoO}_3\text{F}_3$, respectively.

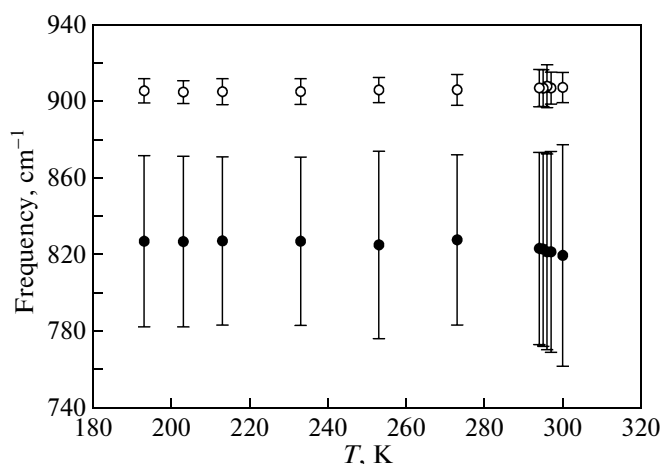


Fig. 4. Temperature dependences of frequencies of the lines at 600–1000 cm^{-1} for $(\text{NH}_4)_3\text{MoO}_3\text{F}_3$. Vertical segments show the half-widths of the lines.

tronic structure of these groups in crystals under study and agrees with the results of previous investigations of tungsten and molybdenum oxyhalogenides [6].

The range 600–1000 cm^{-1} contains the lines corresponding to the $\text{Me}-\text{O}$ stretching vibrations of the $\text{MeO}_3\text{F}_3^{3-}$ ions. To interpret the $\text{W}-\text{O}$ stretching vibrations of the $\text{WO}_3\text{F}_3^{3-}$ ions, their quantum-chemical simulations have been performed for two possible configurations with symmetries C_{3v} and C_{2v} . All calcu-

lations were performed with the GAMESS program package [7]. The results are presented in the table.

The complex profile at 600–890 cm^{-1} in the IR spectrum corresponds to the $\text{Me}-\text{O}$ polar vibrations, which are degenerate for the free ion of the fac-configuration. We can assume that the complex character of this band is associated with the splitting due to the crystal environment. The intensity ratio for these bands agrees with the calculated ratio for the fac-configuration. The lines at 902 cm^{-1} for $(\text{NH}_4)_3\text{MoO}_3\text{F}_3$ and at 920 cm^{-1} for $(\text{NH}_4)_3\text{WO}_3\text{F}_3$ are well noticeable in the IR spectra; they correspond to the computed frequency (918 cm^{-1}) of the totally symmetric $\text{Me}-\text{O}$ stretching vibration for the fac-configuration. Thus, the experimental results agree with those computed for the C_{3v} variant, and we can conclude that the $\text{MeO}_3\text{F}_3^{3-}$ ions in the crystals under study are preferentially located in the fac-configuration.

The ranges 2200–3800 and 1200–1600 cm^{-1} contain the lines corresponding to the internal stretching and bending modes of ammonium ions. The lines of internal vibrations are broadened in the spectra, and we observe the lines forbidden by symmetry of the free group: ν_1 (3040 cm^{-1}) and ν_2 (1680 cm^{-1}) [6]. Broadening can be associated with the fact that ammonium ions are located both in the 8c and 4b sites, and the NH_4^+ tetrahedral ion in the 4b site should be necessarily orientationally disordered. The appearance of forbidden lines can be associated both with the influence

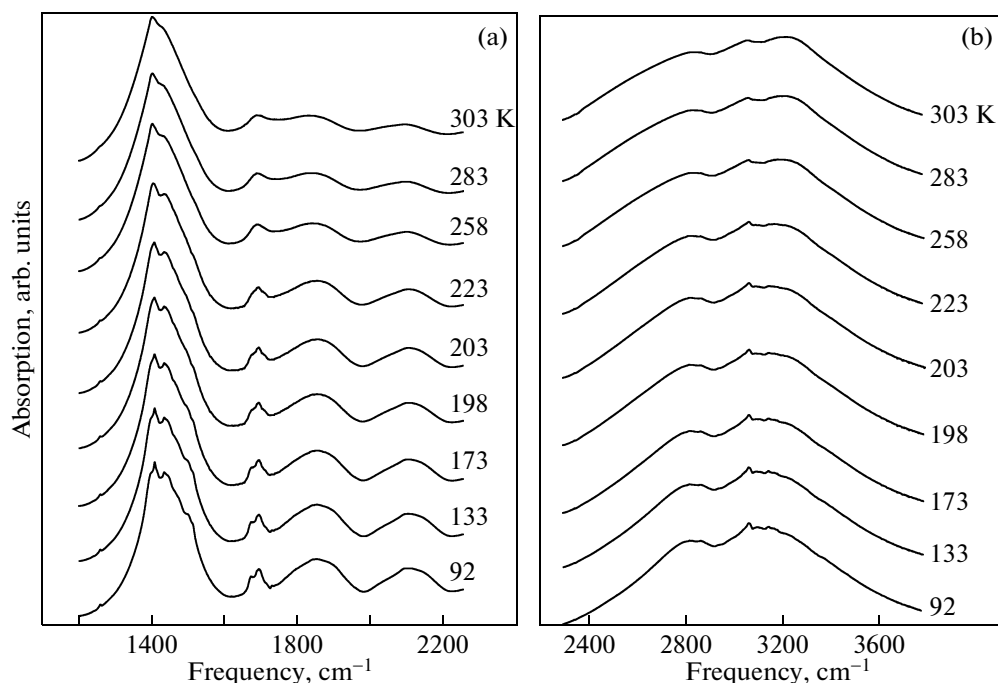


Fig. 5. Transformation of the spectra of (a) internal bending vibrations and (b) internal stretching vibrations of the ammonium ions during cooling of $(\text{NH}_4)_3\text{WO}_3\text{F}_3$.

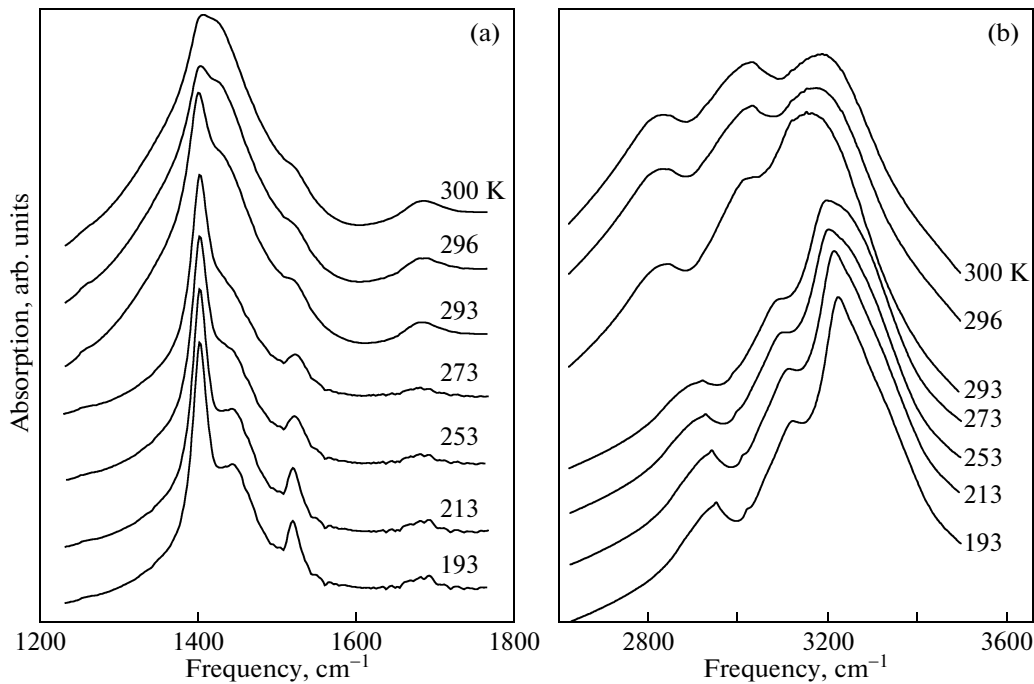


Fig. 6. The same as in Fig. 5 for $(\text{NH}_4)_3\text{MoO}_3\text{F}_3$.

of polar fluorine–oxygen octahedra and with the manifestation of strong anharmonicity of ammonium ions [6].

It should be noted that the region below 500 cm^{-1} corresponds to stretching vibrations of the *Me*–F bonds and bending modes of the $\text{MeO}_3\text{F}_3^{3-}$ ions.

3.2. Temperature Transformation of the Spectrum

The line corresponding to the nondegenerate vibration of the W–O bond (920 cm^{-1}) in the IR spectra of $(\text{NH}_4)_3\text{WO}_3\text{F}_3$ splits into the doublet below the phase transition point ($T = 200\text{ K}$); transformation of the IR spectrum is shown in Fig. 3a. The shape of a complex band at $600\text{--}890\text{ cm}^{-1}$ also varies; although we observe no separation of components, a complex structure of this band becomes visible. Similar variations of the spectrum are associated with the processes of orientations ordering of molecular ions during the phase transition. As we already mentioned above, both the ammonium ions and $\text{WO}_3\text{F}_3^{3-}$ ions should be orientationally disordered in the cubic phase. Splitting of the nondegenerate W–O vibration can be associated only with an increase in the volume of the primitive crystal cell by a factor of 2 as a minimum.

In contrast to tungstate, the anomalous behavior of spectral lines in the region of internal vibrations of the MoO_3F_3 octahedron occurs for molybdenum-containing compound neither at $T_1 = 297.14\text{ K}$ nor at $T_2 = 205.4\text{ K}$ as the temperature decreases (Fig. 3b).

Figure 4 shows the temperature dependences of the frequencies of the lines in a range of $600\text{--}1000\text{ cm}^{-1}$ (vertical lines show the half-widths of corresponding modes). The absence of variations indicates that the phase transitions are not associated with ordering of the $\text{MoO}_3\text{F}_3^{3-}$ octahedra or change of their geometry.

The transformations of the spectra of internal bending and stretching vibrations of ammonium ions during cooling of $(\text{NH}_4)_3\text{WO}_3\text{F}_3$ are shown in Figs. 5a

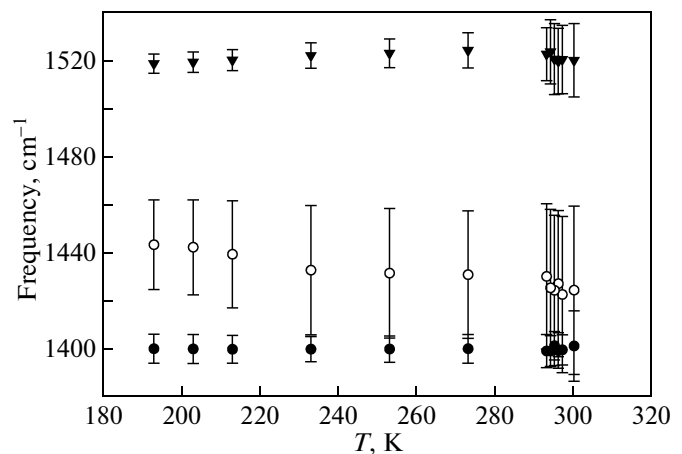


Fig. 7. Temperature dependence of the frequency of the F_2 mode of the NH_4^+ ions in $(\text{NH}_4)_3\text{MoO}_3\text{F}_3$. Vertical segments show a quarter-width of the lines at half-height.

Results of the quantum-chemical (ECP/SBKJC/B3LYP) calculation of the vibrational spectrum of the $\text{WO}_3\text{F}_3^{3-}$ ions

Vibrational symmetry	Frequency, cm^{-1}	Relative IR intensity
fac-configuration, C_{3v}		
A_1	915	2.5
E	821	10.4
A_1	415	5.5
E	342	0.4
A_1	336	0.2
E	334	1.2
A_1	274	0.2
E	252	1.3
E	175	0.2
A_2	—	0
mer-configuration, C_{2v}		
A_1	887	3.1
A_1	810	4.5
B_1	745	16.6
A_1	455	0.2
B_2	433	5.3
B_1	358	0
A_1	328	0.4
A_2	292	0.2
B_1	308	0
A_1	263	2.7
B_2	256	0.8
B_2	229	2.2
B_1	211	0
A_1	151	0.1
B_2	0.35	0

and 5b, respectively. Large widths of lines of their internal vibrations indicate that ammonium cations also remain orientationally disordered in the low-temperature phase. The disappearance of one of the lines in the region of stretching vibrations of the ammonium ions can be associated with the reduction of anharmonicity as the temperature decreases.

In contrast to tungstate, a decrease in temperature for molybdate leads to a noticeable decrease in the width of the spectral lines in the region of ammonium vibrations, which indicates ordering of these groups (Figs. 6a, 6b). Splitting of triply degenerate vibrations (bending mode F_2 [6]) associated with distortion of

ammonium ions by crystal environment (Fig. 7) is simultaneously observed.

4. CONCLUSIONS

Our comparative analysis of vibrational spectra of tungsten and molybdenum oxyfluorides allowed us to establish the following facts.

A comparison of the spectra of stretching vibrations of the $\text{WO}_3\text{F}_3^{3-}$ and $\text{MoO}_3\text{F}_3^{3-}$ anions with the results of the quantum-chemical calculations confirms that these cations are present in the structures of the crystals under study predominantly in the fac-configuration.

All molecular ions in the cubic phase of the crystals are orientationally disordered, which is confirmed by large widths of the corresponding lines.

It is established that the $\text{W} \rightarrow \text{Mo}$ substitution leads to the change of the mechanism of phase transitions. For the tungsten-containing compound, the phase transition is essentially associated with ordering of fluorine-oxygen ions, while for the molybdenum-containing compound, the ammonium cations are ordered.

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