



Phase transitions in $(\text{NH}_4)_2\text{MoO}_2\text{F}_4$ crystal



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ABSTRACT

The mechanisms of temperature and high pressure phase transitions have been studied by Raman spectroscopy. Room temperature (295 K) experiments under high hydrostatic pressure up to 3.6 GPa for $(\text{NH}_4)_2\text{MoO}_2\text{F}_4$ have been carried out. Experimental data indicates a phase transition into a new high-pressure phase for $(\text{NH}_4)_2\text{MoO}_2\text{F}_4$ at 1.2 GPa. This phase transition is related to the ordering anion octahedron groups $[\text{MoO}_2\text{F}_4]^{2-}$ and is not associated with ammonium group. Raman spectra of small non-oriented crystals ranging from 10 to 350 K have been observed. The experiment shows anion groups $[\text{MoO}_2\text{F}_4]^{2-}$ and ammonium in high temperature phase are disordered. The phase transition at $T_1 = 269.8$ K is of the first-order, close to the tricritical point. The first temperature phase transition is related to the ordering anion octahedron groups $[\text{MoO}_2\text{F}_4]^{2-}$. Second phase transitions $T_2 = 180$ K are associated with the ordering of ammonium. The data presented within this study demonstrate that 2D correlation analysis combined with traditional Raman spectroscopy are powerful tool to study phase transitions in the crystals.

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1. Introduction

The phase transitions accompanied by the significant entropy changes and the sensitivity of the phase transitions to external pressure allow one to consider oxyfluorides as promising materials to achieve barocaloric effects. This offers new perspectives for using these compounds as active elements of solid-state coolers [1]. Besides barocaloric effect, oxyfluorides possess interesting structural, magnetic and optical effects [2–6]. The polarity of MeO_2F_4 complexes is attractive due to the possibility of obtaining new functional noncentrosymmetric materials with a wide transparency range [7,8].

At room temperature $(\text{NH}_4)_2\text{MoO}_2\text{F}_4$ crystals has orthorhombic symmetry (space group $Cmcm$, $Z = 4$). $(\text{NH}_4)_2\text{MoO}_2\text{F}_4$ has phase transitions at the temperatures $T_1 = 269.8$ K (space group $Pnma$) and $T_2 = 180$ K [9,10]. Phase transitions in crystals with six-coordinated anions containing F and O are usually associated with lattice instabilities related to rotation of the octahedron groups $[\text{MoO}_2\text{F}_4]^{2-}$ and ammonium group ordering process (Fig. 1).

The hydrostatic pressure and uniaxial stress along the b

direction induce fairly strong intensive and extensive barocaloric effects [11]. The external pressure is a fairly effective tool for changing the entropy of compounds that contain ordering ions or ionic groups. The method of Raman spectroscopy can be an additional powerful tool for studying phase transitions. This method allows one to estimate the role of molecular groups in the phase transition mechanism and character of phase transitions. In particular, temperature and baric phase transitions in other oxyfluorides [12,13] were studied by Raman spectroscopy.

The present paper describes the temperature and pressure dependent structural changes in $(\text{NH}_4)_2\text{MoO}_2\text{F}_4$ by using Raman spectroscopy to clarify the phase transition mechanisms.

2. Experimental

The single crystals of $(\text{NH}_4)_2\text{MoO}_2\text{F}_4$ were synthesized through $(\text{NH}_4)_3\text{MoO}_3\text{F}_3$ obtained from a mixture of ammonium molybdate aqueous solution with a concentrated solution of NH_4F . The resulting excess white precipitate of $(\text{NH}_4)_3\text{MoO}_3\text{F}_3$, which can contain an impurity of $(\text{NH}_4)_2\text{MoO}_3\text{F}_2$, was dissolved in an aqueous solution of HF. The transparent solution was then slowly evaporated in air, and well shaped single crystals of $(\text{NH}_4)_2\text{MoO}_2\text{F}_4$ in the form of prisms or thick plates were obtained [2].

Raman spectra were acquired using a Horiba Jobin Yvon T64000 spectrometer in backscattering geometry. The spectra were excited

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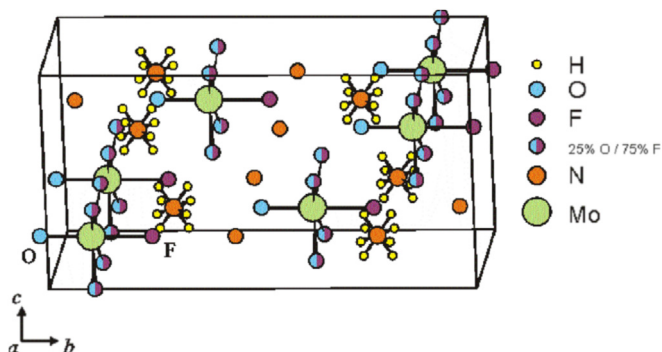


Fig. 1. Unit cell structure of $(\text{NH}_4)_2 \text{MoOF}_4$ in the orthorhombic phase.

using an Ar + laser (wavelength of 514 nm) with the power of 20 mW, corresponding to a laser power density of 60 W/cm^2 . Temperature measurements were taken by a closed-cycle helium cryostat ARS CS204-X1.SS. The temperature was controlled using a calibrated silicon diode LakeShore DT-6SD1.4L. The temperature stabilization accuracy was better than 0.2 K. The sample was placed in the indium gasket, with one side being opened and then mounted on the cold finger. During the experiments, the cryostat was pumped to a pressure of $1.0 \times 10^{-6} \text{ mBar}$.

The experiments were carried out under the conditions of high hydrostatic pressure at room temperature (295 K), using a diamond anvil cell with the sample chamber diameter of 0.25 mm and height of 0.2 mm. The pressure to the accuracy of 0.05 GPa was determined by the shift of the luminescence line ${}^2F_g \rightarrow {}^4A_{2g}$ of the Cr^{3+} ion of a ruby [15,16] microcrystal located near sample.

Pressure decompression brings crystal to the initial state. All the changes observed are reversible and can be reproduced with different samples taken from the same crystallization, within the experimental error (about 0.05 GPa).

3. Discussion

The full spectrum of the crystal $(\text{NH}_4)_2 \text{MoO}_2 \text{F}_4$ at 295 K and 10 K is presented in Fig. 2. A high degree of the ionic group disorder does not allow a full theoretical and group analysis. We divided the spectrum into the next parts: up to 200 cm^{-1} lattice vibrations; in the range from 200 to 700 cm^{-1} , stretching Mo–F vibrations and bending O(F)–Mo–O(F) vibrations of the $[\text{MoO}_2 \text{F}_4]^{2-}$ ions; in the range from 750 to 1100 cm^{-1} , stretching Mo–O vibrations of the $[\text{MoO}_2$

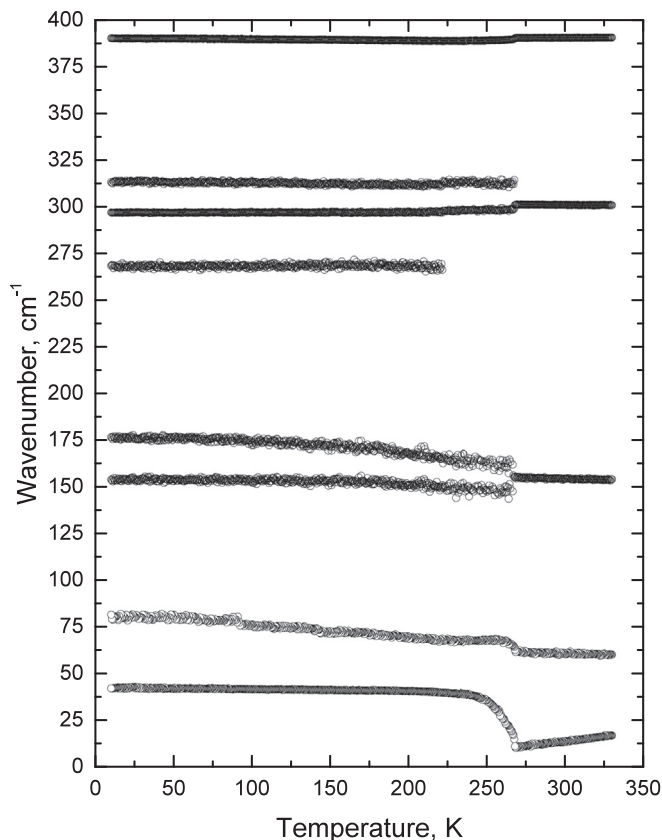


Fig. 3. Dependencies of the line positions on temperature in the range from 0 to 400 cm^{-1} .

$\text{F}_4]^{2-}$ ions; in the range from 1300 to 1800 cm^{-1} , ammonium bending vibrations; in the range from 2500 cm^{-1} to 3500 cm^{-1} , ammonium stretching vibrations are observed. The dependency of the line positions on temperature in the range from 0 to 400 cm^{-1} is presented in Fig. 3. New modes near 150 cm^{-1} and 300 cm^{-1} appear after the transition lower $T_1 = 270 \text{ K}$. In the range from 250 to 400 cm^{-1} , one can observe the stretching and bending vibrations of Mo–F as well as the bending vibrations of O–Mo–O. Up to the temperature $T_1 = 270 \text{ K}$, the positions of all the lines behave monotonically (Fig. 3). As additional information we included the

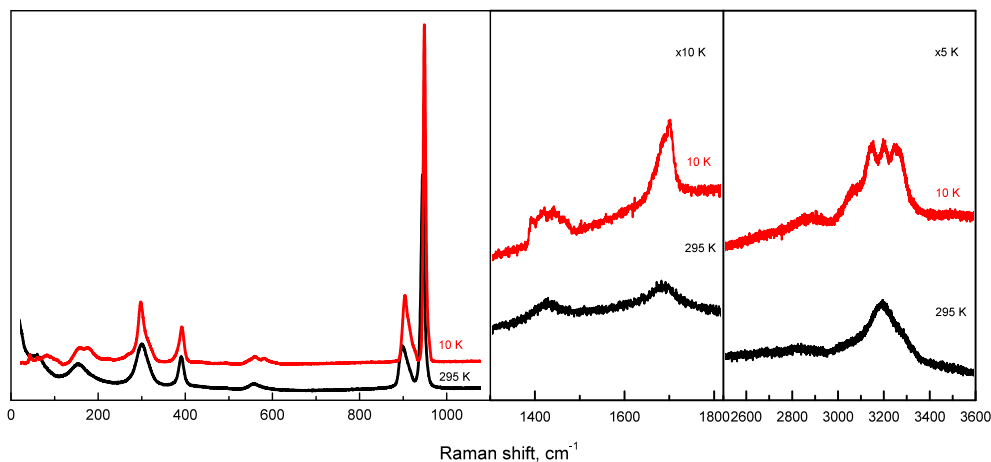


Fig. 2. Raman spectra of crystal $(\text{NH}_4)_2 \text{MoO}_2 \text{F}_4$ at 295 K and 10 K.

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