PHASE TRANSITIONS, CRITICAL PHENOMENA, AND THE STRUCTURE AND DYNAMICS OF CRYSTAL LATTICES

Raman Spectroscopic Study of the Phase Transitions in the Cs₂NH₄WO₃F₃ Oxyfluoride

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Abstract—The Raman spectra of $Cs_2NH_4WO_3F_3$ elpasolite crystals are studied in the temperature range 93–373 K at pressures of up to 6.3 GPa. No indication of a phase transition is revealed from the Raman spectra as the temperature decreases to 93 K. An analysis of the Raman spectra measured under pressure demonstrates that the $Cs_2NH_4WO_3F_3$ elpasolite crystals undergo a phase transition at a pressure of 2.58 GPa. Judging from the behavior of the pressure dependences of the vibrational frequencies, the revealed phase transition is associated with the lowering of the symmetry of the WO_3F_3 octahedra.

1. INTRODUCTION

Perovskite-like crystals with a structure of the elpasolite (cryolite) $A_2B^{(1)}B^{(2)}X_6$ (where A and B are metal cations or more complex molecular ions and X is a halogen or oxygen anion) [1, 2] in the high-temperature phase have cubic symmetry (space group $Fm3m$, $Z = 4$). Upon partial substitution of oxygen ions for fluorine ions in oxyfluorides of the general formula $A_3MO_xF_{6-x}$ (A = NH₄, Cs, K, etc.; M = W, Ti, Mo, etc.), the initial cubic structure is retained and the fluorine and oxygen ions are randomly distributed over the crystal lattice [3].

As the temperature decreases, oxyfluorides of this family undergo sequences of phase transitions, which can be associated with the orientational ordering of the molecular ions [2, 4].

Calorimetric investigations performed for $Cs_2NH_4WO_3F_3$ crystals with a change in the temperature down to 80 K and at pressures up to 0.6 GPa did not reveal anomalies attributed to phase transitions, in contrast to other isomorphic crystals of the given family [4].

The purpose of this work was to search for phase transitions occurring at low temperatures (down to the boiling temperature of liquid nitrogen) under high hydrostatic pressures.

Unlike the simple perovskites ABX_3, in which all octahedra are equivalent, the elpasolites (also referred to as ordered perovskites) contain ionic groups of two types, namely, $B^{(1)}X_6$ and $B^{(2)}X_6$, which alternate along the three fourfold axes of the crystal. Therefore, the elpasolite cubic cell can be considered a perovskite cell with a double unit cell parameter.

2. EXPERIMENTAL TECHNIQUE

The Raman spectra of $Cs_2NH_4WO_3F_3$ elpasolite crystals at temperatures from 93 to 373 K were measured on a Bruker RFS100/S Fourier-transform Raman spectrometer in the frequency range 100–4000 cm⁻¹ in the backscattering geometry with a resolution of 1 cm⁻¹.

The experiments under high hydrostatic pressures (up to 6.3 GPa) at room temperature were performed on a setup equipped with diamond anvils (similar to that described in [5]). The diameter of the chamber containing the sample was equal to 0.25 mm, and the height of the chamber was 0.1 mm. The pressure was determined accurate to within 0.05 GPa from the shift of the ruby luminescence line. A ruby microcrystal was placed near an unoriented sample 50–70 μm in size. A carefully dehydrated mixture of ethanol and methanol taken in a ratio of 1 : 4 was used as a pressure-transmitting medium. The Raman spectra were excited by radiation from an Ar⁺ laser (514.5 nm, 500 mW) and recorded on a Dilor OMARS 89 multichannel Raman spectrometer. The small sizes of the samples and the strong diffuse scattering made it impossible to measure the Raman spectra in the low-frequency range. Moreover, the lines of the vibrational spectra of the diamond and alcohols contained in the hydrostatic medium overlapped the spectral range above 1200 cm⁻¹. For this reason, we could examine the Raman spectra only in the frequency range 160–1200 cm⁻¹.

The parameters of the spectral lines were determined by processing the experimental data with the PeakFit software package (SeaSolve Software Inc.) using the Voigt profile for the corresponding lines.
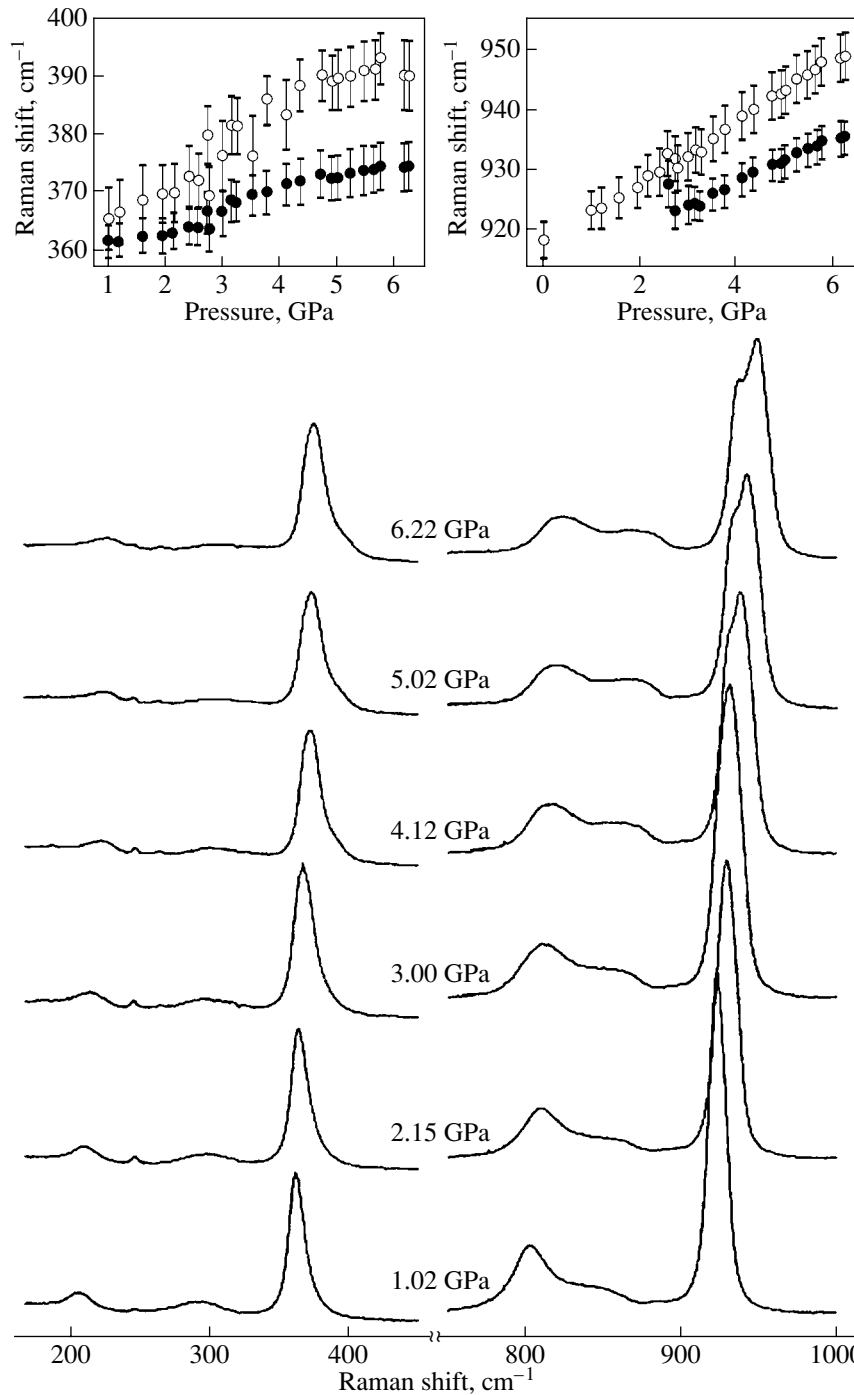
Evolution of the Raman spectra of the $Cs_2NH_4WO_3F_3$ crystal under pressure. The insets show the dependences of the parameters of the lines assigned to the bending and stretching vibrations of the $WO_3F_3^{3-}$ ions (the vertical segments indicate the half-widths of the lines).

3. RESULTS AND DISCUSSION

A decrease in the temperature did not lead to anomalous changes in the positions and widths of the spectral lines that could indicate a structural phase transition in the crystal under investigation.

The figure illustrates the evolution of the Raman spectra under pressure. The lines observed at frequencies below 500 cm⁻¹ correspond to the stretching vibrations of the W–F bonds and to the bending vibrations of the $WO_3F_3^{3-}$ ions. The most intense line revealed at a

frequency of 919 cm^{-1} in the experimental Raman spectrum at atmospheric pressure is attributed to the totally symmetric stretching vibrations of the W–O bonds. The complex line located in the frequency range from 750 to 870 cm^{-1} is assigned to other vibrations of the WO$_3$ ions. An increase on the pressure above 2.58 GPa leads to changes in the positions and widths of the spectral lines, which, as a rule, is associated with the occurrence of structural phase transitions. At pressures below 2.58 GPa, the Raman spectra in the range of stretching vibrations have a shape characteristic of the cubic phase of the crystal. An increase in the pressure results in the splitting of the spectral line at a frequency of 920 cm^{-1} (see inset to the figure). Since the corresponding vibration in the cubic phase is nondegenerate, the appearance of the second spectral line indicates an increase (probably, doubling) in the volume of the primitive cell of the structure and a lowering of the symmetry of the octahedron. The observed evolution of the Raman spectra of the Cs$_2$NH$_4$WO$_3$F$_3$ crystals, as compared to the spectra of other isomorphic oxyfluorides (such as (NH$_4$)$_3$WO$_3$F$_3$, etc.), allows us to make the inference that the phase transition is accompanied by a lowering of the symmetry. The fact that no indication of a phase transition was revealed with decreasing temperature can be explained by the very low temperature of this transformation.

4. CONCLUSIONS

Thus, we investigated the temperature dependences of the parameters of the lines in the Raman spectra of the Cs$_2$NH$_4$WO$_3$F$_3$ crystal. No spectral anomalies that could indicate a phase transition were revealed down to liquid-nitrogen temperatures. The effect of high hydrostatic pressures on the Raman spectra of the Cs$_2$NH$_4$WO$_3$F$_3$ crystal was studied for the first time. A phase transition from the cubic phase to the phase with a lower symmetry was found to occur at a pressure of 2.58 GPa. The analysis of the changes in the Raman spectra of the crystal demonstrated that the revealed phase transition is associated with the lowering of the symmetry of the WO$_3$F$_3$ octahedra. The occurrence of this transition suggests that the crystal most likely should undergo a phase transition at temperatures below 93 K.

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