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Raman scattering study of ordering processes and phase transitions in $A_2BWO_3F_3$ oxyfluorides crystals

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Abstract. Raman spectra of perovskite-like $(NH_4)_3WO_3F_3$, $(NH_4)_2KWO_3F_3$ and $Cs_2(NH_4)WO_3F_3$ oxyfluorides are obtained in a wide temperature range including transition points. Transition anomalies are found and analyzed. Transformation in $(NH_4)_3WO_3F_3$ is shown to be bound with octahedron groups ordering and strong distortion of ammonium ions due to H-bond formation, that is accompanied by cell volume multiplication, hardening and formation of complex discrete low frequency lattice spectrum. Same cell doubling was found in $(NH_4)_2KWO_3F_3$, but without lattice ordering $Cs_2(NH_4)WO_3F_3$ lattice stays disordered down to 15 K.

1. Introduction

High temperature phases of $A_2BWO_3F_3$ ($A, B = K, Cs$) crystals belong to cubic syngony ($Fm\bar{3}m$ space group, $Z = 4$, see figure 1) [1]. Cubic elpasolite-like structure supposes orientation disorder of highly polar pseudo-octahedric $WO_3F_3^{3-}$ molecular anions. Replacing A^+ and/or B^+ cations with molecular groups (say, NH_4^+) one can assume them to be disordered as well. Ordering of these molecular ions under cooling should affect phonon spectra considerably and play a crucial role in phase transitions. Here we report results of Raman scattering investigation of such processes in $(NH_4)_3WO_3F_3$ (assigned below as A3), $(NH_4)_2KWO_3F_3$ (A2K) and $Cs_2(NH_4)WO_3F_3$ (C2A) oxyfluorides.

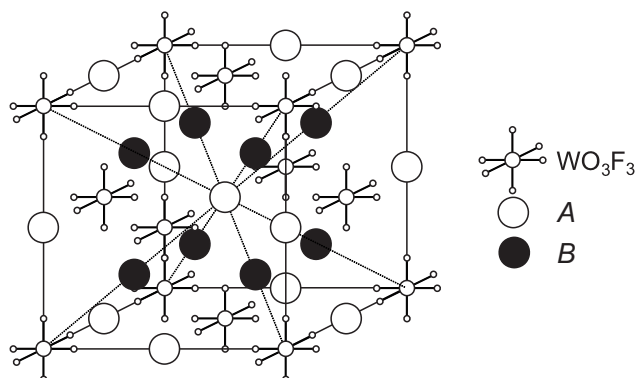


Figure 1. Structure of elpasolite-like $A_2BWO_3F_3$ crystal.

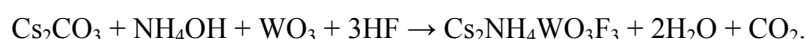
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2. Experimental

To obtain Raman spectra we used powders of small octahedral microcrystals 10 to 40 μm in size. Synthesis of A3 samples has been described in details earlier [2]. Powder X-ray analysis confirmed their single phase cubic structure with 0.9156 nm unit cell parameter.

A2K powders were obtained by spontaneous crystallization and by solid state reaction with further recrystallization. X-ray analysis [3] confirmed its composition in both cases, and ordered O_h positions of potassium cations. Replacement of ammonium for potassium decreased unit cell parameter considerably ($a_0 = 0,8958$ nm).

Powder of C2A was obtained by spontaneous crystallization from water solution according to:



Again, X-ray analysis confirmed elpasolite structure with $a_0 = 0,9292$ nm. It should be pointed out that in this case tetrahedral ammonium cations are placed into octahedral positions and should be disordered orientationally.

Raman back scattering spectra in 70–3600 cm^{-1} range were obtained with RFS 100/S Fourier Raman spectrometer (Bruker), with a Nd:YAG laser excitation (1.06 μm , 350 mW). Lower frequency (down to 15 cm^{-1}) spectra were obtained with TriVista 777 triple diffraction grating Raman spectrometer (Princeton Instruments, Inc.). Spectra were obtained within 15–500 K temperature range with ± 0.1 K stabilization during data acquisition.

3. Results and discussion

Figure 2 demonstrates sweep spectra of studied powders at room temperature. All spectra look very much alike. Most intense lines belong to 750–1000 cm^{-1} range and correspond to stretches of W–O bonds in $\text{WO}_3\text{F}_3^{3-}$ octahedrons. To interpret them we performed quantum chemistry simulations of two possible conformations of these ions: C_{3v} (*fac*-) and C_{2v} (*mer*-) [WO_3F_3] $^{3-}$ (details of simulations are presented elsewhere [4]). Position of the most intense line 917 cm^{-1} coincides practically with calculated value (915 cm^{-1}) for full symmetry W–O stretch of *fac*-conformer. Nearby weak complex band 775–850 cm^{-1} is close to calculated position (821 cm^{-1}) of twice-degenerated asymmetrical W–O vibration of the same conformer. Most intense calculated line of *mer*-conformer (810 cm^{-1}) should fall here as well, so we can conclude that in all studied crystals $\text{WO}_3\text{F}_3^{3-}$ groups exist in *fac*-conformation, with possible slight (virtual?) admixture of *mer*-conformers.

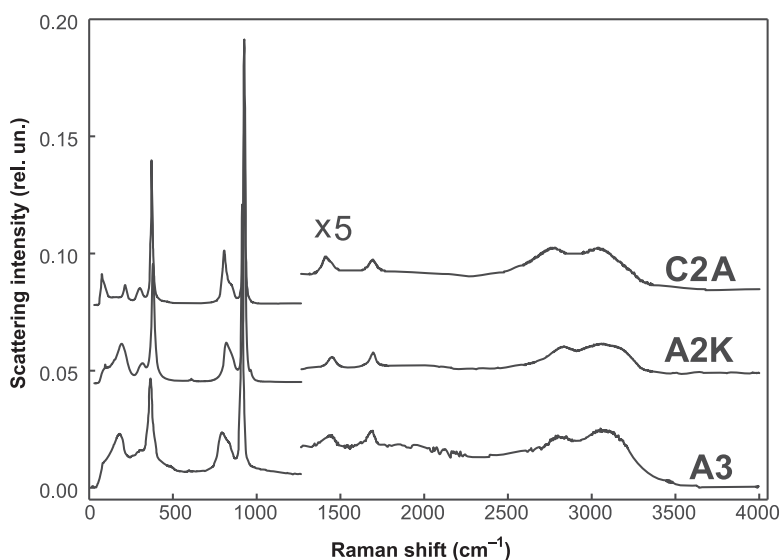


Figure 2. Sweep spectra of studied samples at room temperature.

Ranges of 2700–3500 cm^{-1} and 1200–1600 cm^{-1} include two lines each, that correspond to stretching and bending internal modes of ammonium ions. These modes are rather wide but not split, while their positions (2770 cm^{-1} and 3092 cm^{-1} for stretches, 1489 cm^{-1} and 1697 cm^{-1} for bending

modes) are quite close to those of the free ion (3040 cm^{-1} , 3145 cm^{-1} , 1400 cm^{-1} , 1680 cm^{-1} according to data [5]). This small line shift and absence of line splitting (conformational or factor-group) confirm slight distortion of ammonium ions by crystal neighborhood and by their interaction.

Region of $200\text{--}500\text{ cm}^{-1}$ corresponds to bending and W–F stretching modes. Their positions and intensity distribution agree well with calculated results [4] for C_{3v} conformer.

Below 100 cm^{-1} , the wide wing of central peak starts to grow in all samples, without any fine structures. That agrees well with strong orientational disorder in all crystals at room temperature.

Under cooling most intense line in A3 spectrum (917 cm^{-1}) splits into doublet of two narrow lines at the phase transition point (200 K). Figure 3 demonstrates temperature dependences of positions and widths of resulting doublet components: damping anomaly is seen clearly. Complex band at $775\text{--}850\text{ cm}^{-1}$ transforms as well – with smaller widths its three components become clearly visible 1–2 K below the transition point, and everyone of them splits into doublet under further cooling, making a group of six overlapping contours. Such sharp decrease of line widths may be attributed to orientational ordering of $\text{WO}_3\text{F}_3^{3-}$ anions.

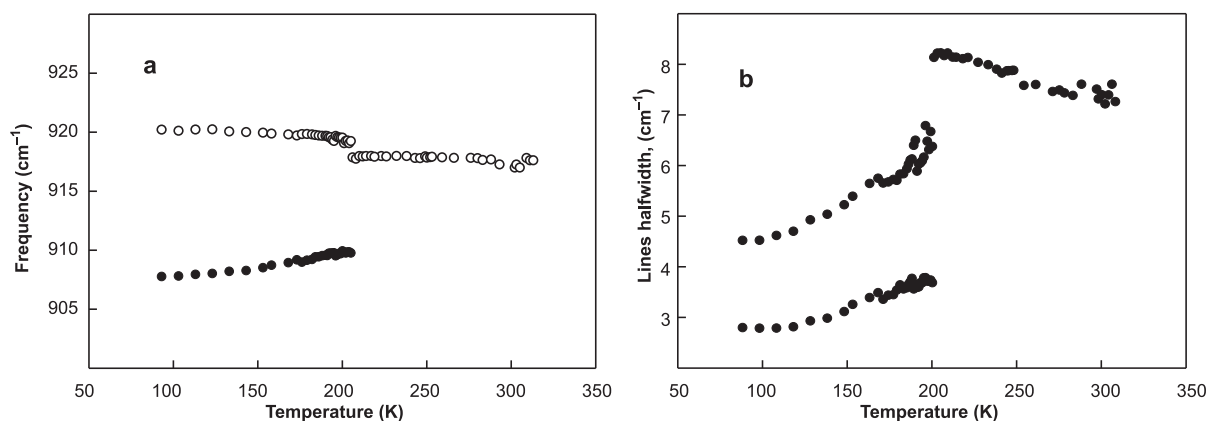


Figure 3. Parameters (a – frequencies, b – widths) of W–O line in A3 crystal as functions of temperature.

Sharp anomalies are observed with ammonium lines as well. Their intensities grow considerably, forming intense complex bands instead of separate lines. Lines here stay wide, but this strong modification of the spectrum reveals considerable deformation of ammonium ions and their strong interaction with neighbouring $\text{WO}_3\text{F}_3^{3-}$ anions. Probably ordering of $\text{WO}_3\text{F}_3^{3-}$ ions provides a possibility to form W–O...H–N hydrogen bonds. Structural data [4] provide N–H...O bonds lengths equal to 2.28 to 2.88 Å, that agrees with typical 2.88 Å value [6].

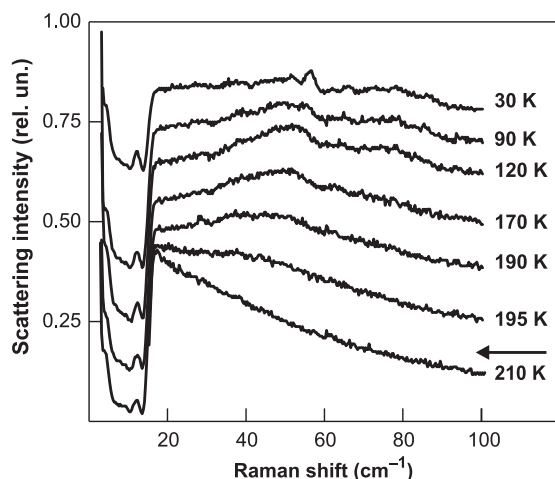


Figure 4. Transformation of low frequency lattice modes in A3 crystal under cooling.

Figure 4 shows considerable modification of low frequency lattice dynamics in this crystal. Wide central peak (its wing extends to about 100 cm^{-1}) drops below transition point; smooth maximum forms instead, that hardens under cooling and split into discrete lines far below transition point.

All observed modifications of A3 spectra confirm that this phase transition is connected with ordering processes and formation of W–O...H–N hydrogen bonds.

Phase transition in A2K crystal was found at 235 K according to calorimetry data [3]. This transition reveals itself in a splitting of 917 cm^{-1} line into doublet, yet its components stay wide. No drastic changes were found in the ranges of ammonium internal modes, and central peak stay wide down to 20 K. Seems that this transition doubles unit cell volume as well, as in A3 crystal, but it is not connected with ordering processes or hydrogen bonds formation.

Calorimetry [3] did not reveal phase transitions in C2A crystal down to 77 K. In this crystal (in contrast to A2K) ammonium ions are placed into O_h position that supposes their orientational disorder. Really, their lines seem widened slightly at room temperature, and deep cooling shows their fine structure: triple degenerated modes appear splitted into doublets – that supposes their uniaxial distortion. This process goes continuously, without transitional breaks down 15 K at least. It seems that deep cooling freezes dynamical disorder of ammonium ions, but lattice stay statically disordered at the long range.

4. Conclusions

Raman spectra of $(\text{NH}_4)_3\text{WO}_3\text{F}_3$, $\text{Cs}_2\text{NH}_4\text{WO}_3\text{F}_3$ and $(\text{NH}_4)_2\text{KWO}_3\text{F}_3$ oxyfluorides are obtained and analyzed for the first time, lines of NH_4^+ cations internal modes and W–O vibrations are identified. Experimental spectrum of $\text{WO}_3\text{F}_3^{3-}$ internal modes as compared with quantum chemistry simulations confirms that these anions are mainly found in *fac*-conformation. All molecular ions in the cubic phase are orientationally disordered, this is evidenced by wide internal lines and weak temperature dependence of these widths away from the transition point.

Cooling below the transition point in $(\text{NH}_4)_3\text{WO}_3\text{F}_3$ orders the anionic sublattice orientationally, this manifests in: substantial narrowing of W–O vibration lines; their splitting may be due to primitive cell doubling; formation of hydrogen bonds that leads to ammonium ions distortions; hardening of central peak and formation of discrete low frequency lattice spectrum.

Phase transition in $(\text{NH}_4)_2\text{KWO}_3\text{F}_3$ is not connected with ordering processes, though results in cell doubling as well.

Cooling down of $\text{Cs}_2\text{NH}_4\text{WO}_3\text{F}_3$ “freezes” dynamical disorder of ammonium cations, that shows in positional splitting of their internal modes, but the lattice stay disordered down to 15 K at least.

Acknowledgments

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