Orientational disorder and phase transitions in ammonium oxofluorovanadates, $(\text{NH}_4)_3\text{VOF}_5$ and $(\text{NH}_4)_3\text{VO}_2\text{F}_4$

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Single crystals of $(\text{NH}_4)_3\text{VOF}_5$ and $(\text{NH}_4)_3\text{VO}_2\text{F}_4$ were obtained from aqueous fluoride solutions and phase transitions in these compounds were investigated using X-ray diffraction, differential scanning microcalorimetry (DSM) and vibrational spectroscopy. The room-temperature (RT) phases of these compounds belong to orthorhombic symmetry [*Immm* and *I222*, $Z = 6$, for $(\text{NH}_4)_3\text{VOF}_5$ and $(\text{NH}_4)_3\text{VO}_2\text{F}_4$, respectively] with similar unit-cell parameters and two independent vanadium atoms. Above RT [at 350 and 440 K for $(\text{NH}_4)_3\text{VOF}_5$ and $(\text{NH}_4)_3\text{VO}_2\text{F}_4$, respectively], the compounds undergo reversible phase transitions into high-symmetry dynamically disordered elpasolite-like (*Fm $\bar{3}m$* , $Z = 4$) structures with six and 12 spatial orientations of the vanadium octahedron for $(\text{NH}_4)_3\text{VOF}_5$ and $(\text{NH}_4)_3\text{VO}_2\text{F}_4$, respectively. The ligand atoms are distributed in a mixed (split) position of $24e + 96j$, one of the ammonium groups is disordered on the tetrahedron $32f$ site, but another one forms eight spatial orientations due to disorder of its hydrogen atoms in the $96j$ position. DSM and spectroscopic data enable the phase transition from high temperature to room temperature to be connected with the transition from isotropic orientations of the octahedron to its two different dynamic states.

1. Introduction

Vanadium oxide fluorides (VOFs) exhibit rich and extensive structural chemistry owing to the ability of vanadium to adopt different oxidation states and coordination environments, forming various basic building units (BBUs) that can be examined in varied systems (Adil *et al.*, 2010; Aidoudi *et al.*, 2011, 2014; Aldous & Lightfoot, 2009; Aldous *et al.*, 2007*a,b*; Chang *et al.*, 2016; DeBurgomaster *et al.*, 2010; Donakowski *et al.*, 2014; Gautier *et al.*, 2012, 2015; Senchyk *et al.*, 2012; Smith *et al.*, 2014; Yeon *et al.*, 2015). The formation of diverse VOFs with new BBUs can be expected to create unprecedented crystal structures giving rise to interesting physical properties. The presence of two distinct bonding motifs around the vanadium center (the V–O bond and the V–F bond) creates highly asymmetric local coordination spheres that will result in nonlinear optical behavior, such as second-harmonic generation, when the crystal structure is non-centrosymmetric (Donakowski *et al.*, 2012*a*, 2015; Stephens *et al.*, 2005; Welk *et al.*, 2007).

Ferroelectric and proton-conducting behaviors of a new vanadium oxide fluoride $(\text{NH}_4\text{K})_3\text{VO}_2\text{F}_4$ were recently reported (Patwe *et al.*, 2010). The compound belongs to a large structural family of elpasolites and crystallizes in an orthorhombic lattice (*Immm*) at ambient temperature, in a similar way to $(\text{NH}_4)_3\text{VO}_2\text{F}_4$ (Leimkühler & Mattes, 1986). The

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existence of the $\text{VO}_2\text{F}_4^{3-}$ ion in solution as well as in the solid state was established by nuclear magnetic resonance (^{51}V and ^{19}F NMR) (Gillespie & Rao, 1983) and electron paramagnetic resonance (EPR) (Adhyapak *et al.*, 1994; Rao *et al.*, 1982). The anion was speculated to have a *trans*-dioxo octahedral geometry. Nevertheless, infrared spectra of $\text{VO}_2\text{F}_4^{3-}$ indicated a *cis*-dioxo arrangement (Pausewang & Dehnicke, 1969). The crystal structure of $(\text{NH}_4)_3\text{VO}_2\text{F}_4$ (Leimkühler & Mattes, 1986) contains two independent $\text{VO}_2\text{F}_4^{3-}$ anions. One anion is rotationally disordered and the F^- and O^{2-} ligands can not be distinguished; however, the second anion is not disordered and exhibits a *cis*-dioxo arrangement. The crystal structure of $\text{Ag}_3\text{VO}_2\text{F}_4$ (Chamberlain *et al.*, 2010) as well as of a fully ordered $\text{K}_2\text{VO}_2\text{F}_3$ consisting of infinite chains of corner-sharing $[\text{VO}_2\text{F}_2\text{F}_{2/2}]^{3-}$ BBUs (Ryan *et al.*, 1971) support only a *cis*-configuration of the anion. In this respect, the return to a *trans*-dioxo anionic structure in the case of $(\text{NH}_4, \text{K})_3\text{VO}_2\text{F}_4$ (Patwe *et al.*, 2010) is not justified and the origin of four short distances assigned to the V—O bond is not clear and not consistent with the chemical formula of the compound. The incorporation of only one O atom into the coordination sphere of vanadium in the related VOF $(\text{NH}_4)_3\text{VOF}_5$ should simplify and clarify the situation. In the present study, the preparation and characterization of two structural analogs $(\text{NH}_4)_3\text{VO}_2\text{F}_4$ and $(\text{NH}_4)_3\text{VOF}_5$ with respect to their orientational disorder and phase transitions were undertaken.

Ammonium oxofluorovanadates $(\text{NH}_4)_3\text{VOF}_5$ and $(\text{NH}_4)_3\text{VO}_2\text{F}_4$ were previously assumed to be isostructural (Davidovich *et al.*, 1977). The crystal structure of the former was not determined, although a detailed single-crystal structure determination of the latter performed at room temperature has revealed the orthorhombic symmetry (space group *Immm*, $Z = 6$) (Leimkühler & Mattes, 1986). In accordance with the data of recent optic studies, $(\text{NH}_4)_3\text{VO}_2\text{F}_4$ undergoes four successive phase transitions with the following symmetry change: cubic *Fm* $\bar{3}m$ ($T_1 = 417$ K) $\rightarrow$ orthorhombic (I) *Immm* ($T_2 = 240$ K) $\rightarrow$ orthorhombic (II) ($T_3 = 211$ K, the space group was not defined) $\rightarrow$ monoclinic *P112/m* ($T_4 = 205$ K) $\rightarrow$ triclinic *P* $\bar{1}$ (Melnikova & Kocharova, 2009). The symmetry of all phases was suggested to be centrosymmetric. Calorimetric measurements performed in a wide temperature range confirmed the presence of four heat capacity anomalies at $T_1 = 438$, $T_2 = 244$, $T_3 = 210$ and $T_4 = 205$ K associated with the first-order phase transitions (Fokina *et al.*, 2009). Our recent vibrational spectroscopy data (Gerasimova *et al.*, 2017) indicate a rather dynamic nature of the phase transitions, especially well pronounced in the case of $(\text{NH}_4)_3\text{VOF}_5$.

2. Experimental

2.1. Synthesis

A simple and convenient method of preparing vanadium fluorides or VOFs is a mechanochemical interaction of vanadium oxides or vanadates with ammonium hydrogen difluoride (NH_4HF_2 , m.p. 126°C) (Wani *et al.*, 1982; Wani & Rao, 1991*a,b*, 1993) when the reaction proceeds at ambient

conditions under grinding the initial components together. We used similar reactions for synthesis of $(\text{NH}_4)_3\text{VO}_2\text{F}_4$ and $(\text{NH}_4)_3\text{VOF}_5$:

Vanadium oxides V_2O_5 and V_2O_3 can be used instead of NH_4VO_3 and VF_3 as well. All starting substances were of reagent grade. The solid products were water-leached with addition of a small amount of hydrofluoric acid (40% HF by weight), filtered and evaporated slowly in air at room temperature. Well shaped octahedral single crystals of $(\text{NH}_4)_3\text{VOF}_5$ with bright-blue color were crystallized by slow evaporation of the solution obtained by aqueous dissolving of the stoichiometric quantities of $(\text{NH}_4)_3\text{VO}_2\text{F}_4$ and $(\text{NH}_4)_3\text{VOF}_5$:

The crystals obtained of both complexes, $(\text{NH}_4)_3\text{VO}_2\text{F}_4$ and $(\text{NH}_4)_3\text{VOF}_5$, were rinsed with ethanol under vacuum and air-dried. Their compositions were checked using powder X-ray diffraction and fully corresponded to the data presented in PDF-2 (Powder Diffraction File; Kabekkodu, 2007) [cards Nos. 084-1111 and 034-0882 for $(\text{NH}_4)_3\text{VO}_2\text{F}_4$ and $(\text{NH}_4)_3\text{VOF}_5$, respectively, which are very similar. Energy-dispersive X-ray analysis of $(\text{NH}_4)_3\text{VOF}_5$ has shown the ratio of O to F close to 1:5.

An attempt to synthesize elpasolite-like Na_2VOF_5 in accordance with the method by Stomberg (1986) was also made. Indeed, orange single crystals were recovered among others from a reaction mixture of V_2O_5 and NaF with 30% H_2O_2 and aqueous HF. However, their composition did not correspond to the above formula. Instead, a real cubic elpasolite $(\text{NH}_4)_2\text{NaVO}_2\text{F}_4$ was obtained.

2.2. Crystallographic determination

Single crystals of tetravalent [blue $(\text{NH}_4)_3\text{VOF}_5$] and pentavalent [orange $(\text{NH}_4)_3\text{VO}_2\text{F}_4$] VOFs of octahedral shape were non-merohedral microtwins. Such crystals were not suitable for X-ray diffraction. Among the bulk crystals, a small amount of plate-shaped crystals was present in quality close to single crystals, which were used for structural determinations. An Oxford Cryosystem Cobra temperature attachment was used for heating the crystals. Unfortunately, it did not allow raising the temperature above the phase transition (440 K) in the case of $(\text{NH}_4)_3\text{VO}_2\text{F}_4$. In the exposure time, the $(\text{NH}_4)_3\text{VOF}_5$ crystals were being darkened with a worsening quality, so the exposure time was minimal.

The crystal structure of $(\text{NH}_4)_3\text{VOF}_5$ was determined at 365 K [structure (I)], 296 K [structure (II)] and 193 K. No significant structural changes were found at 193 K relative to 296 K [except the increase of the thermal parameters U^{11} for V1 [0.057 (1) and 0.068 (1) $\text{\AA}^2$] and V2 [0.039 (1) and 0.069 (1) $\text{\AA}^2$]]. This means that the V atoms occupy not special but split positions at 296 K. The $(\text{NH}_4)_3\text{VO}_2\text{F}_4$ [structure (III)]

Table 1
Experimental details.

	Structure (I)	Structure (II)	Structure (III)
Crystal data			
Chemical formula	H ₁₂ N ₃ VOF ₅	H ₁₂ N ₃ VOF ₅	H ₁₂ N ₃ VO ₂ F ₄
<i>M_r</i>	216.07	216.07	213.07
Crystal system, space group	Cubic, <i>Fm</i> $\bar{3}$ <i>m</i>	Orthorhombic, <i>Immm</i>	Orthorhombic, <i>I</i> 222
Temperature (K)	365	296	296
<i>a</i> , <i>b</i> , <i>c</i> (Å)	9.0522 (4), 9.0522 (4), 9.0522 (4)	6.2986 (3), 9.1638 (4), 18.9044 (8)	6.2738 (3), 9.1388 (4), 18.8424 (8)
<i>V</i> (Å ³)	741.76 (10)	1091.15 (8)	1080.33 (8)
<i>Z</i>	4	6	6
<i>D_x</i> (Mg m ^{−3})	1.935	1.973	1.965
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α
<i>μ</i> (mm ^{−1})	1.38	1.41	1.41
Crystal size (mm)	0.30 × 0.25 × 0.12	0.19 × 0.19 × 0.13	0.20 × 0.20 × 0.12
Data collection			
Diffractometer	Bruker APEX-II CCD	Bruker APEX-II CCD	Bruker APEX-II CCD
Absorption correction	Multi-scan <i>SADABS</i>	Multi-scan <i>SADABS</i>	Multi-scan <i>SADABS</i>
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	1457, 111, 96	6473, 967, 837	6313, 1555, 1348
<i>R</i> _{int}	0.019	0.024	0.020
(sin <i>θ</i> /λ) _{max} (Å ^{−1})	0.797	0.712	0.698
Refinement			
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.025, 0.099, 1.01	0.046, 0.142, 1.00	0.044, 0.139, 0.98
No. of reflections	111	967	1555
No. of parameters	17	78	118
Δρ _{max} , Δρ _{min} (e Å ^{−3})	0.16, −0.45	0.77, −0.39	0.61, −0.44
Absolute structure	—	—	Refined as an inversion twin
Absolute structure parameter	—	—	0.45 (10)

Computer programs: *APEX2*, *SADABS*, *SAINT* (Bruker, 2008); *SHELXS97*, *SHELXL2014/7*, *SHELXTL* (Sheldrick, 2015).

crystals became microtwins at lower temperature (193 K), from which it was difficult to extract any information.

Single-crystal X-ray diffraction data were collected using a Bruker KAPPA APEX-II diffractometer equipped with a graphite monochromator that emits Mo *K*α radiation (λ = 0.71073 Å). For data collections carried out at 296 K, 0.3° ω-scans were performed in a hemisphere of reciprocal space with an exposure time of 20 seconds per frame at a crystal–detector distance of 45 mm. For the data collection carried out at 365 K, using an Oxford Cryosystem Cobra attachment, 0.3° ω-scans were performed in the 1/8 sphere of reciprocal space with an exposure time of ten seconds per frame at a crystal–detector distance of 40 mm. Data collection, reduction and refinement of the lattice parameters were performed using the *APEX2* software package (Bruker, 2008). Structural determinations and refinements were performed with the *SHELXTL/PC* program (Sheldrick, 2015).

The structures were solved by direct methods with the analysis of electron-density distribution and refined against *F*² by the full-matrix least-squares method with anisotropic approximation. The H atoms of ammonium groups in the structures (II) and (III) were not determined whereas in (I) (at 365 K) they were localized from electron-difference syntheses. The H1 atoms around N1 form a tetrahedron with N–H bond distances of 0.89 Å whereas the H2 atoms around N2 form an octahedron with N–H bond distances of 0.92 Å. Next, the coordinates of the H atoms were calculated geometrically in accordance with the N1 disordering and the real geometry of N2H₄, and they were not refined. The structural information is

presented in Table 1, selected bond distances and angles are listed in Table 2.

2.3. Microcalorimetric measurements

The stability of the room-temperature phase of (NH₄)₃VOF₅ to the temperature change was examined using differential scanning microcalorimeter DSM-10 M (DSM). Calorimetric measurements were carried out in a wide temperature range 110–380 K in heating and cooling modes on a series of the samples obtained from different crystallizations. Powdered samples with a mass about 0.10 g were put into an aluminium sample holder. The heat flow through the sample and reference compound (Al₂O₃) was recorded *versus* temperature. Thermodynamic properties of (NH₄)₃VO₂F₄ were reported earlier by Fokina *et al.* (2009).

2.4. Spectroscopic measurements

Mid-infrared (400–4000 cm^{−1}) spectra were collected in a Nujol mull using a Shimadzu FTIR Prestige-21 spectrometer operating at 2 cm^{−1} resolution. In addition, the infrared spectra of (NH₄)₃VOF₅ and (NH₄)₃VO₂F₄ were recorded directly from the pure single crystal using an FTIR Bruker Vertex 70v spectrometer with the platinum ATR attachment.

The unpolarized Raman spectra were collected in a back-scattering geometry, using a triple monochromator Horiba Jobin Yvon T64000 Raman spectrometer operating in double

Table 2
Selected distances (Å) and angles (°) for (I)–(III).

(NH ₄) ₃ VOF ₅ (I)					
V1–O1 ⁱ	1.586 (3)	O1–F2	2.596 (2) × 8	F1–V1–F2	81.84 (2) × 4
V1–F2	1.843 (3) × 4	F2–F2A	2.579 (4) × 4	F2–V1–F2A	88.85 (1) × 4
V1–F1 ⁱⁱ	2.108 (3)	O1–V1–F2	98.16 (2) × 4	O1–V1–F1	180
				F2–V1–F2B	163.69 (5) × 24
(NH ₄) ₃ VOF ₅ (II)					
V1–O1	1.632 (2)	V2a–F5 ^{iv}	1.778 (4)	V2b–F8 ^{vi}	1.704 (5)
V1–F1 ⁱⁱⁱ	1.892 (2)	V2a–F6	1.776 (4)	V2b–F7	1.796 (9)
V1–F2A	1.893 (2)	V2a–F4 ^{iv}	1.910 (4) × 2	V2b–F8C ⁱⁱⁱ	1.874 (5)
V1–F3	1.915 (2) × 2	V2a–F5A	2.011 (4)	V2b–F8A	1.875 (5)
V1–F2 ⁱⁱⁱ	2.119 (2)	V2a–F6A ^{iv}	2.025 (4)	V2b–F7A ⁱⁱⁱ	1.887 (9)
				V2b–F8B ^v	2.031 (4)
O1–F1	2.674 (3)	F4–F5	2.682 (4) × 4	F7–F8	2.65 (1) × 4
O1–F3	2.660 (2) × 4	F4–F6	2.687 (4) × 4	F7–F8B	2.59 (1) × 4
O1–F2A	2.647 (2) × 2	F5–F6	2.678 (4) × 4	F8–F8A	2.62 (1) × 2
F2–F3	2.681 (2) × 4	F2–F2A	2.638 (3)	F8A–F8B	2.66 (1) × 2
O1–V1–F1	98.5 (1)	F4–V2a–F5	93.23 (5) × 2	F7–V2b–F8	98.3 (4)
O1–V1–F3	96.85 (5) × 2	F4–V2a–F6	93.50 (4) × 2	F7–V2b–F8A	92.3 (3)
O1–V1–F2A	97.1 (1)	F4–V2a–F5A	86.27 (5) × 2	F7–V2b–F8B	84.8 (3)
				F7–V2b–F8C	89.6 (4)
F2–V1–F1	82.40 (8)	F4–V2a–F6A	86.07 (4) × 2	F7A–V2b–F8	92.0 (3)
F2–V1–F3	83.16 (5) × 2	F5–V2a–F6	97.78 (7)	F7A–V2b–F8A	86.8 (3)
F2–V1–F2A	82.0 (1)	F6–V2a–F5A	89.78 (6)	F7A–V2b–F8B	84.9 (3)
				F7A–V2b–F8C	89.5 (4)
F1–V1–F3	88.63 (4) × 2	F5A–V2a–F6A	83.15 (5)	F8–V2b–F8A	94.2 (3)
F3–V1–F2A	89.52 (5) × 2	F6A–V2a–F5	89.29 (6)	F8A–V2b–F8B	85.6 (3)
				F8B–V2b–F8C	84.3 (3)
O1–V1–F2	179.13 (9)	F4–V2a–F4A	169.75 (9)	F8C–V2b–F8	95.7 (3)
F1–V1–F2A	164.44 (8)	F5–V2a–F5A	172.43 (8)	F7–V2b–F7A	169.8 (1)
F3–V1–F3A	166.29 (9)	F6–V2a–F6A	172.93 (9)	F8–V2b–F8B	176.9 (1)
				F8A–V2b–F8C	169.5 (2)
(NH ₄) ₃ VO ₂ F ₄ (III)					
V1–F2	1.671 (2)	V2a–F6	1.692 (3)	V2b–O7	1.644 (9)
V1–F1A ^{vii}	1.703 (2)	V2a–F5A ^{vii}	1.700 (3)	V2b–O9	1.659 (9)
V1–F2A ^v	1.756 (2)	V2a–F4	1.789 (4)	V2b–F7A ^v	1.810 (8)
V1–F3 ^{ix}	2.007 (2)	V2a–F4A ^v	1.980 (4)	V2b–F8 ^{vii}	1.889 (7)
V1–F1 ^{ix}	2.041 (1)	V2a–F5 ^x	2.042 (3)	V2b–F9A ^v	1.958 (9)
V1–F3A ^{viii}	2.076 (2)	V2a–F6A ⁱⁱⁱ	2.077 (3)	V2b–F8A ^{xi}	2.073 (6)
F1A–F2	2.610 (6) × 2	F4–F5A	2.634 (3) × 4	F7A–F7	2.64 (2)
F1A–F2A	2.624 (6) × 2	F4–F6	2.645 (3) × 4	F7A–F9	2.37 (2) × 2
F1A–F3A	2.641 (5) × 2	F5–F6	2.639 (3) × 4	F7A–F9A	2.61 (2) × 2
F1A–F3	2.653 (5) × 2			F7A–F8A	2.589 (9) × 2
F2–F3	2.635 (2) × 2			F8–F9	2.60 (2) × 2
F2–F2A	2.623 (3)			F8–F9A	2.74 (2) × 2
F3–F3A	2.643 (3)			F8–F8A	2.61 (2)
F1A–V1–F2	101.4 (3)	F4–V2a–F5A	98.01 (7)	F7A–V2b–F7	99.7 (6)
F1A–V1–F2A	98.7 (3)	F4–V2a–F6	98.86 (7)	F7A–V2b–F9	86.2 (7)
F1A–V1–F3	90.9 (2)	F4–V2a–F5	86.62 (5)	F7A–V2b–F9A	87.6 (7)
F1A–V1–F3A	88.1 (2)	F4–V2a–F6A	86.02 (5)	F7A–V2b–F8A	83.3 (3)
F1–V1–F2	89.4 (3)	F4A–V2a–F5A	91.07 (7)	F8–V2b–F7	94.0 (4)
F1–V1–F2A	86.5 (3)	F4A–V2a–F6	91.81 (7)	F8–V2b–F9	94.0 (7)
F1–V1–F3	81.5 (2)	F4A–V2a–F5	81.81 (5)	F8–V2b–F9A	90.7 (6)
F1–V1–F3A	80.2 (2)	F4A–V2a–F6A	81.35 (5)	F8–V2b–F8A	82.5 (4)
F2–V1–F3	91.1 (1)	F5A–V2a–F6	102.15 (5)	F7–V2b–F9	104.4 (8)
F2–V1–F2A	99.8 (1)	F5A–V2a–F6A	88.07 (4)	F9–V2b–F8A	93.7 (7)
F3–V1–F3A	80.66 (8)	F6–V2a–F5	89.44 (4)	F8A–V2b–F9A	80.2 (5)
F2A–V1–F3A	86.47 (9)	F5–V2a–F6A	79.70 (3)	F9A–V2b–F7	81.9 (6)
F1–V1–F1A	167.0 (1)	F4–V2a–F4A	164.18 (6)	F7A–V2b–F8	165.8 (4)
F2–V1–F3A	167.6 (2)	F5–V2a–F5A	166.63 (7)	F7–V2b–F8A	161.8 (6)
F2A–V1–F3	163.7 (2)	F6–V2a–F6A	167.86 (7)	F9–V2b–F9A	171.8 (1)

Symmetry codes: (i) z, x, y ; (ii) $-z, -x, -y$; (iii) $-x, -y, z$; (iv) $-x, -y, -z$; (v) $-x, y, -z$; (vi) $x, -y, z$; (vii) $-x + 1, -y, z$; (viii) $-x, -y + 1, z$; (ix) $x, y - 1, z$; (x) $x - 1, y, z$; (xi) $x - 1, -y, -z$.

subtractive mode, and detected by an liquid-nitrogen-cooled charge-coupled device. The spectral resolution for the recorded Stokes-side Raman spectra was set to $\sim 4 \text{ cm}^{-1}$ (this resolution was achieved with 1800 grooves mm^{-1} gratings and 100 mm slits). The microscope system based on an Olympus

BX41 microscope with an Olympus 50× objective lens, $f = 0.8 \text{ mm}$ with a numerical aperture of 0.75, provides a focal spot diameter of about $2 \mu\text{m}$ on the sample. Single-mode argon 514.5 nm from a Spectra-Physics Stabilite 2017 Ar⁺ laser of 5 mW on the sample was used as an excitation light source.

The intensity of the laser light was adjusted to avoid heating the sample.

3. Results and discussion

3.1. Calorimetric measurements

Heat flow through the $(\text{NH}_4)_3\text{VOF}_5$ sample and the reference compound (Al_2O_3) was recorded *versus* temperature. Three anomalies were revealed in the heat capacity behavior, $C_p(T)$, associated with a succession of phase transitions. Upon heating at a rate of 8 K min^{-1} , maxima of the $C_p(T)$ peaks were located at the temperatures $T_1 = 349(2)\text{ K}$, $T_2 = 230(1)\text{ K}$ and $T_3 = 221(1)\text{ K}$. All anomalies were found to be reproducible during the thermal cycling and accompanied by the following temperature hysteresis: $\delta T_1 \simeq 13\text{ K}$, $\delta T_2 \simeq 3\text{ K}$ and $\delta T_3 \simeq 7\text{ K}$. Thus, it can be argued that the phase transitions observed are first-order transformations.

After elimination of background from the experimental $C_p(T)$ data, the information on excess heat capacity, ΔC_p , connected with the phase transitions was obtained. The temperature dependence of ΔC_p is shown in Fig. 1. The enthalpy changes associated with the successive phase transitions were determined for a series of fresh samples by integration of the excess heat capacity temperature dependence $\Delta H_i = \int \Delta C_p(T) dT$. All values of ΔH_i were evaluated from the results obtained at the same temperature change rate of 8 K min^{-1} . Phase transition at T_1 is characterized by the enthalpy change $\Delta H_1 = 1500(150)\text{ J mol}^{-1}$.

The close position of ΔC_p peaks T_2 and T_3 (Fig. 1) prevents the correct determination of the individual enthalpy for the low-temperature transformations. The total enthalpy change was determined as $\Delta H_{2+3} = 1200(100)\text{ J mol}^{-1}$. The corresponding entropy changes at phase transitions are following: $\Delta S_1 = 4.5\text{ J mol K}^{-1} = 0.54R$ and $\Delta S_2 + \Delta S_3 = 5.2\text{ J mol K}^{-1} = 0.62R$, which indicate that these phase transitions are of order-disorder type. Interestingly, the total value of entropy changes ($1.16R$) in this case is approximately twofold lower than that

for $(\text{NH}_4)_3\text{VO}_2\text{F}_4$ ($\Sigma \Delta S_i = R \ln 7.7 = 2.02R$) (Fokina *et al.*, 2009).

3.2. Crystal structures

3.2.1. High-temperature crystal structure of $(\text{NH}_4)_3\text{VOF}_5$ [structure (I)]. The disordered elpasolite-like ($Fm\bar{3}m$, $Z = 4$) structure of $(\text{NH}_4)_3\text{VOF}_5$ (I) at 365 K (above T_1) is built from statistically disordered VOF_5 octahedra and two kinds of ammonium cations (Fig. 2a).

The crystal structure (I) with special positions for the V, N atoms and for F(O) in the 24e position was determined by a direct method and refined against F^2 by the full-matrix least-squares method with anisotropic approximation to $R_1 = 0.0853$. From the electron-density distribution of the F(O) atom (Fig. 3a), it follows that this atom occupies the 96j or mixed 24e + 96j position. In the former case (96j), the refinement led to $R_1 = 0.073$, whereas in the latter (24e + 96j), R_1 decreased to 0.0500. Therefore, the F(O) atoms are placed in the mixed 24e + 96j position as we described earlier (Udovenko *et al.*, 2003, 2017; Udovenko & Laptash, 2008a,b, 2011). Next, the additional refinement with the escape of the V atom from the octahedral center lowers R_1 to 0.0409. The electron-density distribution of the V atom (Fig. 3b) shows a

Figure 2
Disorder structure of $(\text{NH}_4)_3\text{VOF}_5$ (a) and isolated VOF_5 polyhedron (b) at 365 K. Green, blue and white balls are the F, N and H atoms, respectively (the central V atoms are not seen). Displacement ellipsoid plots are shown at the 50% probability.

Figure 3
Electron-density distribution of (a) the F1 atom in the (001) plane at $z = 0.20$ and (b) the V1 atom in the (001) plane at $z = 0$.

Figure 1
Excess heat capacity of $(\text{NH}_4)_3\text{VOF}_5$ obtained from DSM experiments.

disordering of the V atom octahedron occupying the 24e position (instead of the classical 4a position), which means six equivalent spatial orientations of VOF_5 . The reconstruction of a separate orientation (Fig. 2b) reveals the real polyhedron geometry with a short V—O bond of 1.586 (3), a long V—F_{trans} bond of 2.108 (3) Å and four V—F_{eq} bonds of 1.843 (3) Å (Table 2).

Here we must recognize that Stomberg (1986) was the first (to our best knowledge) to suggest this procedure (displacement of a central atom) for the case of elpasolite-like crystals, namely, for Na_2VOF_5 . Another thing is that he was, most probably, mistaken with the composition of the compound, as we will see below. He used initially a similar method to discern the O and F atoms in the disordered structure of Na_2NbOF_5 (Stomberg, 1984). Note please, the latter is not cubic but orthorhombic (*Pbcn*). It is clear that the displacement of the V atom in $\text{VO}_2\text{F}_4^{3-}$ towards the octahedron edge should result in 12 spatial orientations of the polyhedron (disordering of V on cuboctahedron), which can explain a twice as large value of ΔS at phase transitions in $(\text{NH}_4)_3\text{VO}_2\text{F}_4$ relative to that in $(\text{NH}_4)_3\text{VOF}_5$.

In accordance with our previous work (Udovenko *et al.*, 2017; Udovenko & Laptash, 2011), where the tetrahedral displacement of N1 from the 8c position was found, electron-density sections of N1 were constructed (Fig. 4). The sections show that N1 is displaced from the 8c position into 32f and disordered on tetrahedron.

Next, the real arrangement of N_2H_4 in structure (I) was established. Electron-density sections of N2 in the (001) plane with $z = 0.518$ and $z = 0.593$ were built [z coordinates of N2 and H2 were taken from the crystal structure of $(\text{NH}_4)_3\text{MoO}_3\text{F}_3$ (Udovenko & Laptash, 2008a) and $(\text{NH}_4)_3\text{AlF}_6$ (Udovenko & Laptash (2011))]. The H atoms were not specified (Fig. 5). It can be seen from Fig. 5(a) that the outer electron cloud of the N2 atom is deformed by the octahedron, whereas its internal cloud is spherical, which is inconsistent with the escape of N2 in the cube from the 4b position to the 32f position. The structural refinement with the displaced atom returns it to the initial position and the N2 atom therefore occupies the 4b position.

It follows from Fig. 5(b) that the H2 atoms are statistically distributed in the 96j position, and every vertex of the N_2Q_6 (Q is peak of electron density around N2) octahedron is surrounded by four H2 atoms with the side of the square equal

Figure 4
Electron-density distribution of N1 in $(\text{NH}_4)_3\text{VOF}_5$ in the (001) plane at (a) $z = 0.20$ and (b) $z = 0.30$. (c) Disordered arrangement of N_1H_4 displaced on tetrahedron from the 8c position into 32f.

to 0.42 Å. A superposition of electron densities from four H2 atoms in squares forms an octahedral surrounding of the N2 atom by the Q electron-density peaks (Fig. 5c). The final refinement of the structure in the space group $Fm\bar{3}m$ including H atoms reduced the R_1 value to 0.0247. The H atoms of N_2H_4 statistically occupy the 64j and 32f positions and form eight spatial orientations in the structure.

3.2.2. Room-temperature crystal structures of $(\text{NH}_4)_3\text{VOF}_5$ [structure (II)] and $(\text{NH}_4)_3\text{VO}_2\text{F}_4$ [structure (III)]. High-temperature modifications of $(\text{NH}_4)_3\text{VOF}_5$ and $(\text{NH}_4)_3\text{VO}_2\text{F}_4$ change their symmetry from cubic face-centered $Fm\bar{3}m$ to orthorhombic body-centered lattice with two possible space groups $Immm$ and $I222$ during the first phase transition on cooling to room temperature (RT). Two crystallographically independent vanadium atoms V1 and V2 [as was previously established by Leimkühler & Mattes (1986)] appear in structures (II) and (III). The axis vectors of the orthorhombic cell are as follows: $\mathbf{a} = 1/2(\mathbf{a}' + \mathbf{c}')$, $\mathbf{b} = \mathbf{b}'$, $\mathbf{c} = 3/2(-\mathbf{a}' + \mathbf{c}')$, where $\mathbf{a}'$, $\mathbf{b}'$, $\mathbf{c}'$ are the axes of the cubic cell (Fig. 6).

The number of formula units (Z) increases from 4 to 6. The structure contains four independent V1 atoms in the 4j position and two independent V2 atoms in the 2d position (space group $Immm$), the coordination environment of which is a superposition of $\text{V}2a\text{X}_6$ and $\text{V}2b\text{X}_6$ octahedra with a population of 0.5. Disordered $\text{V}2b\text{X}_6$ octahedra have two spatial orientations. At the first stage of structural refinement in the

Figure 5
Electron-density distribution of the N2 in $(\text{NH}_4)_3\text{VOF}_5$ in the (001) plane at (a) $z = 0.518$ and (b) $z = 0.593$. (c) Disordered arrangement of H atoms in N_2H_4 .

Figure 6
The projection of structure (II) along the b axis (N atoms are not shown). The axes $\mathbf{a}'$, $\mathbf{b}'$, $\mathbf{c}'$ are the axes of the cubic cell.

Table 3

Analysis of structural refinement (**bond** distances are given in Å).

<i>Immm</i>	
(NH ₄) ₃ VOF ₅ (II)	(NH ₄) ₃ VO ₂ F ₄ (III)
Unsplit positions V1 (0, 0.5, 0.317); V2 (0, 0.5, 0) V1–X = 1.760 × 2 + 1.907 × 2 + 2.001 × 2 V2a–X = 1.892 × 2 + 1.900 × 2 + 1.905 × 2 V2b–X = 1.823 × 2 + 1.870 × 4 R = 0.0488 for 837 (<i>F</i> ₀), 74 parameters	Unsplit positions V1 (0, 0.5, 0.317); V2 (0, 0.5, 0) V1–X = 1.698 × 2 + 1.871 × 2 + 2.040 × 2 V2a–X = 1.860 × 2 + 1.879 × 2 + 1.884 × 2 V2b–X = 1.801 × 2 + 1.837 × 4 R = 0.0610 for 818 (<i>F</i> ₀), 74 parameters
Split positions V1 (0.027, 0.5, 0.318); V2 (0.019, 0.514, 0) V1–X = 1.632 + 1.892 + 1.893 + 1.915 × 2 + 2.119 V2a–X = 1.776 + 1.778 + 1.910 × 2 + 2.011 + 2.025 V2b–X = 1.704 + 1.796 + 1.874 × 2 + 1.887 + 2.031 R = 0.0462 for 837 (<i>F</i> ₀), 78 parameters	Split positions V1 (0, 0.519, 0.315); V2 (0.028, 0.521, 0) V1–X = 1.693 + 1.712 × 2 + 2.044 × 2 + 2.007 + 2.045 V2a–X = 1.686 + 1.697 + 1.888 × 2 + 2.043 + 2.077 V2b–X = 1.584 + 1.796 + 1.833 + 1.877 + 1.911 + 2.092 R = 0.0511 for 818 (<i>F</i> ₀), 79 parameters
<i>I222</i>	
(NH ₄) ₃ VOF ₅ (II)	(NH ₄) ₃ VO ₂ F ₄ (III)
Unsplit positions V1 (0, 0, 0.318); V2 (0, 0, 0) V1–X = 1.759 × 2 + 1.909 × 2 + 2.002 × 2 V2a–X = 1.900 × 2 + 1.893 × 2 + 1.899 × 2 V2b–X = 1.821 × 2 + 1.863 × 2 + 1.884 × 2 R = 0.0478 for 1368 (<i>F</i> ₀), 114 parameters	Unsplit positions V1 (0, 0, 0.314); V2 (0, 0, 0) V1–X = 1.698 × 2 + 1.873 × 2 + 2.041 × 2 V2a–X = 1.855 × 2 + 1.877 × 2 + 1.884 × 2 V2b–X = 1.786 × 2 + 1.826 × 2 + 1.869 × 2 R = 0.0589 for 1348 (<i>F</i> ₀), 108 parameters
Split positions V1 (0.026, 0.005, 0.318); V2 (0.019, 0.014, –0.005) V1–X = 1.637 + 1.867 + 1.891 + 1.896 + 1.965 + 2.113 V2a–X = 1.766 + 1.774 + 1.781 + 1.986 + 2.016 + 2.029 V2b–X = 1.694 + 1.744 + 1.868 + 1.911 + 1.969 + 1.979 R = 0.0436 for 1368 (<i>F</i> ₀), 117 parameters	Split positions V1 (0.0087, 0.0186, 0.315); V2 (0.027, 0.021, 0.0051) V1–X = 1.671 + 1.703 + 1.756 + 2.007 + 2.041 + 2.076 V2a–X = 1.692 + 1.700 + 1.789 + 1.980 + 2.042 + 2.077 V2b–X = 1.644 + 1.659 + 1.810 + 1.889 + 1.958 + 2.073 R = 0.0443 for 1348 (<i>F</i> ₀), 118 parameters

space group *Immm*, *R*₁ was 0.0488 and 0.0610 for (II) and (III), respectively (Table 3).

Two short distances in the environment of the V1 atom in (III) (V–X = 1.698 Å) correspond to the V–O bonds and are analogous to distances of 1.676 and 1.706 Å in the structure of Ag₃VO₂F₄ (Chamberlain *et al.*, 2010). The V–O and V–F distances in the V2a and V2b octahedra are averaged, and the F and O atoms statistically occupy the same positions. In the environment of the V1 atom in (II), two short V–X distances

Figure 7

Electron-density distribution of the V1 in (II) (a) and in (III) (b) in the (001) plane at *z* = 0.317.

of 1.760 Å are also present, but there should be one short distance corresponding to the V–O bond. Therefore, the O atom is statistically located in two positions, and the distance 1.760 Å is equal to the mean value of the V–O and V–F bond lengths. We can see the same, for example, in the case of a hybrid VOF, α-[H₂NH₂(CH₂)₂NH₂]VOF₄, where the non-bonding (terminal) fluorine and oxygen atoms are disordered, having an average length of 1.744 Å on one of the sites (which corresponds to 56% O and 44% F) and an average length of 1.783 Å on the other site (which corresponds to 44% O and 56% F) (Aidoudi *et al.*, 2011).

The local octahedral environment around the V atom is highly distorted, as is typical for V^{IV} in oxyfluorides; in particular the terminal vanadyl V=O group and *trans*-F have, respectively, short and long lengths (Aldous, Goff *et al.*,

2007). The V=O bond length is typically ~1.6 Å, whereas the V–F_{trans} bond length is ~2.1–2.2 Å and V–F_{eq} are typically ~1.9 Å (Lu *et al.*, 2013; Aidoudi *et al.*, 2014). For the VOF₅^{2–} anion, the V=O bond length is typically ~1.60 Å, while V–F_{trans} and V–F_{eq} lengths are typically about 2.10 and 1.80 Å, respectively (Gautier *et al.*, 2015). The dioxo vanadium fluoride anion has been observed as an ordered dimeric [V₂O₄F₆]^{4–} BBU in monoclinic structures of Na₂[M(H₂O)₂(V₂O₄F₆)] (*M* = Co²⁺, Ni²⁺ and Cu²⁺) with the V1–O1 and V1–O2 distances of 1.606–1.627 and 1.664–1.702 Å, respectively (Donakowski *et al.*, 2012b). The V–O distance in *cis*-dioxo vanadium fluoride of the ordered K₂VO₂F₃ is 1.636 Å and the terminal V–F distances are 1.862 and 1.914 Å (Ryan *et al.*, 1971).

We can observe similar distances in our structures (II) and (III), which were solved by displacing the V atom from its original positions in the space groups *Immm* and *I222* (Table 3). The displacement of the V atoms along the *a* and *b* axes for (II) and (III), respectively, is indicated by the corresponding electron-density sections of these atoms (Fig. 7), as well as the increased values of *U*¹¹ for V1 and V2 in (II) at 193 K relative to 296 K. As a result, *R*₁ decreased from 0.0488 to 0.0461 for (II) and from 0.0610 to 0.0511 for (III).

The V1 atoms became disordered in two orientations (dumbbells), as in the case of Ag₃VO₂F₄ (Chamberlain *et al.*, 2010), and V2 atoms were disordered in four orientations

(square). One short V1—O distance of 1.632 Å emerged in the V1 environment in (II), and in the V2a and V2b environments there were two averaged V—O and V—F distances. The V2bOX₅ octahedra had two spatial orientations. In structure (III), one of distances in the V2b octahedron seemed rather short (V—X = 1.584 Å), so the structural refinements were also performed in the space group *I222*. The results of the refinement without the displacement of the V atoms were close to those in the *Immm* group (Table 3). Taking into account the displacement of vanadium atoms, *R*₁ decreased slightly from 0.0478 to 0.0436 during the refinement of (II), so we settled on the symmetrical space group *Immm*. In the case of (III), *R*₁ decreased significantly from 0.0589 to 0.0443. The V1 atoms also became disordered in two orientations (dumbbells), and the V2 atoms were disordered in four orientations (tetrahedron). Thus, the asymmetrical space group *I222* is more preferable for (III).

Following from Table 3, the O atom in the V1OX₅ octahedron occupies one site in structure (II) with a V—O distance of 1.632 Å, whereas in V2aOX₅ and V2bOX₅, it is distributed in two positions (Fig. 8).

Two O atoms in (III) (*I222*) are distributed in the V1O₂F₄ and V2aO₂F₄ octahedra in three positions, whereas in the V2bO₂F₄ octahedron they occupy two positions (Fig. 9).

Both structures contain four independent N atoms, and two of them (N3 and N4) half occupy their positions. The disorder of these nitrogen atoms is due to the disordered environment of the V2 atom, between which they are located. The H atoms were not determined. In the nearest environment of nitrogen atoms in (NH₄)₃VOF₅, the F7 atom locates at 2.627 Å from N2, and in (NH₄)₃VO₂F₄, the F9 atom lies at 2.661 Å from N2.

Analyzing the structural data of (NH₄)₃VO₂F₄ (Leimkühler & Mattes, 1986), it should be noted that a weak peak at the electron density was assigned erroneously by the authors to

Figure 8
Isolated coordination polyhedra VOF₅ in (II).

Figure 9
Isolated coordination polyhedra VO₂F₄ in (III).

Figure 10
Difference electron-density distribution of the F4 atom in the (010) plane at *z* = 0.093 in the (NH₄)₃VO₂F₄ structure in space group *Immm* (a) and *I222* (b).

the F6 atom. This peak does not emerge when the population of the F8 atom is doubled. Also, the F4 atom (in our case F8) was located in a general position. However, analysis of the difference electron-density section showed that the F4 atom occupies the *8l* position (0, *y*, *z*) but not the general 16*o* position (*x*, *y*, *z*) (Fig. 10a). The F4 atom was not specified in the calculation. In the (NH₄)₃VOF₅ structure, the equivalent thermal parameter of the F4 atom at 193 K [0.06 (1) Å²] is two times smaller than that at 296 K [0.12 (1) Å²]. In space group *I222*, this atom is not split (Fig. 10b); therefore, the F4 atom is not split at 296 K. For this reason, the authors could not correctly describe the environment of the V2 atom, which is a superposition of two octahedra.

The (NH₄,K)₃VO₂F₄ structure was even more incorrectly determined (Patwe *et al.*, 2010). Four short V—X distances for each polyhedron (1.651–1.704 Å) are present instead of two. Paired two and all four of them for V2O₂F₄ and V1O₂F₄, respectively, are in *trans*-position to each other. The reason for this is the wrong use of the position coordinates of the disordered anions from the parent cubic phase *Fm* $\bar{3}$ *m* as their initial coordinates for *Immm*. The sharp difference between the *cis*- and the *trans*-structure of the anion is easily revealed by vibrational spectroscopy.

3.3. Vibrational spectra

The infrared spectrum of (NH₄)₃VOF₅ (Fig. 11a) clearly shows two states for the VOF₅^{3−} (*C*_{4v}) octahedron at room temperature (two stretching vibrations of the V—O bond at 948 and 933 cm^{−1}) and the infrared spectrum of (NH₄)₃VO₂F₄ demonstrates a *cis* configuration of the VO₂F₄^{3−} anion (*C*_{2v}), deconvolution of which in the range 850–1000 cm^{−1} shows four lines in accordance with two states of this anion as it was also considered in our recent publication (Gerasimova *et al.*, 2017).

Temperature transformations of the V—O stretching part of Raman spectra of (NH₄)₃VOF₅ are shown in Fig. 11(b). One broad line is observed at 350 K (above the first phase transition point) that corresponds to a single dynamically disordered state of the VOF₅ octahedron in a cubic elpasolite-like structure (isotropic reorientations). The RT spectrum contains two peaks corresponding to two independent octahedral states in the orthorhombic (*Immm*) structure. Four lines below 230 K (after the second phase transition) indicate the presence of at least four independent VOF₅ polyhedra with different V—O bond lengths, which means the ordering

of dynamically disordered octahedra but not complete in accordance with the ΔS value ($R \ln 3.2$ from $R \ln 6$) at these phase transitions. Further cooling increases the number of lines to at least seven, which indicates about seven different local units of VOF_5 (at 50 K) meaning full ordering of the octahedral sublattice (Gerasimova *et al.*, 2017). Thus, we can assume dynamic disorder in our complexes connected with isotropic orientations of octahedra in cubic phase and two different octahedral reorientations in orthorhombic phases.

3.4. The Na_2VOF_5 elpasolite

Stomberg (1986) reported the elpasolite-like $Fm\bar{3}m$ crystal structure of Na_2VOF_5 . The O and F ligands occupy the 24e position. In the electron-density map, Na2 (8c site, half occupancy) appeared with a peak height of only half the magnitude of that observed for Na1 (4b site). The V atom was located in the 24e site with occupancy of 1/6. No chemical analysis or vibrational spectroscopy data were given. We repeated the synthesis, keeping the original proportions of the components and obtained several crystal phases. The main phase was NaHF_2 as a large excess of NaF was used. Orange

crystals of $(\text{NH}_4)_2\text{NaVO}_2\text{F}_4$ were obtained. We used vanadium(V) oxide (V_2O_5) of reagent grade which contained ammonium. In industrial practice, a method of extracting vanadium from solutions by precipitation of ammonium metavanadate is widely used. Pure vanadium(V) oxide is obtained by calcination of ammonium metavanadate. The infrared spectrum of our orange crystals contained the NH_4^+ stretching and bending vibrations at 3300–2850 and 1425 cm^{-1} , respectively, and the V–O stretches at 905 and 870 cm^{-1} indicating that the anion is *cis*- VO_2F_4 .

It should be noted that $\text{Na}_3\text{MO}_x\text{F}_{6-x}$ ($x = 0\text{--}3$) compounds are of low symmetry (mainly, monoclinic, isotypic with cryolite Na_3AlF_6), whereas $\text{A}_2\text{NaMO}_x\text{F}_{6-x}$ ($\text{A} = \text{alkali metal or ammonium}$; $x = 0\text{--}3$) are cubic elpasolites. Thus, Na_3VF_6 is monoclinic (Alter & Hoppe, 1975), whereas elpasolite-type $(\text{NH}_4)_2\text{NaVF}_6$ is cubic, $a = 8.485 \text{ \AA}$ (Massa, 1976). Refined parameters for both compounds are given by He *et al.* (2009). The lattice constants for the Na_3VF_6 compound are $a = 5.510 (6)$, $b = 5.725 (8)$, $c = 7.948 (6) \text{ \AA}$, $\beta = 90.410 (8)^\circ$ in the space group $P2_1/n$, and $a = 8.5001 (2) \text{ \AA}$ for $(\text{NH}_4)_2\text{NaVF}_6$ in space group $Fm\bar{3}m$.

Na_3VOF_5 also has a monoclinic structure ($a = 5.49$, $b = 5.69$, $c = 7.93 \text{ \AA}$, $\beta \simeq 90^\circ$) (Pausewang, 1971). The cryolite $\text{Na}_{3-\delta}\text{VO}_{1-\delta}\text{F}_{5+\delta}$ was recently prepared, which crystallizes in the monoclinic system $P2_1/n$: $a = 5.5403 (2)$, $b = 5.6804 (2)$, $c = 7.9523 (2) \text{ \AA}$, $\beta = 90.032 (7)^\circ$ (Nava-Avendaño *et al.*, 2015). However, K_2NaVOF_5 ($a = 8.28 \text{ \AA}$) and $\text{Rb}_2\text{NaVOF}_5$ ($a = 8.44 \text{ \AA}$) (Pausewang, 1971) are cubic elpasolites.

$\text{Na}_3\text{VO}_2\text{F}_4$ is monoclinic ($P2_1/c$; $a = 5.51$, $b = 5.69$, $c = 7.93 \text{ \AA}$, $\beta \simeq 90^\circ$; $Z = 2$), whereas $\text{K}_2\text{NaVO}_2\text{F}_4$ ($a = 8.27 \text{ \AA}$) and $\text{Rb}_2\text{NaVO}_2\text{F}_4$ ($a = 8.44 \text{ \AA}$) are cubic elpasolites (Pausewang & Dehnicke, 1969).

Phase stabilities of the $\text{A}_2\text{BMO}_x\text{F}_{6-x}$ elpasolites are governed by the tolerance factor t in terms of the sizes of A, B and M (Pausewang & Rüdorff, 1969; Massa & Babel, 1988; Flerov *et al.*, 1998), $t = [(2)^{1/2}(R_A + R_X)/(R_B + R_M + 2R_X)]$, where R_A , R_B , R_M and R_X are the ionic radii of the corresponding ions in the general formula. The tolerance factor for these elpasolite-like cubic compounds ranges from 0.87 to 1.00. We estimated the t values for Na_2VOF_5 and $(\text{NH}_4)_2\text{NaVO}_2\text{F}_4$ to be 0.76 and 0.96, respectively. Consequently, the former compound can not be cubic. The X-ray powder data for the latter were reported by Wani *et al.* (1982) which coincide with our data and those reported by Stomberg (1986). Note also that all $(\text{NH}_4)_2\text{NaM}^{\text{III}}\text{F}_6$ ($M^{\text{III}} = \text{Al, Fe, Ga, In, Cr, V}$) are cubic elpasolites (Mi *et al.*, 2008).

4. Conclusions

Crystal-structure determination of $(\text{NH}_4)_3\text{VOF}_5$ and $(\text{NH}_4)_3\text{VO}_2\text{F}_4$ at room temperature was severely complicated by orientational disorder. This disorder has a dynamic nature as our DSM and vibrational spectroscopy data show, which is inconsistent with the EPR (electron paramagnetic resonance) spectroscopy data of the γ -irradiated polycrystalline $(\text{NH}_4)_3\text{VO}_2\text{F}_4$ (Rao *et al.*, 1982) indicating C_{4v} symmetry (*trans*-configuration) of the $\text{VO}_2\text{F}_4^{3-}$ anion. Two types of octets represent a rigid and a dynamic form of the anion. Our

Figure 11
(a) Infrared room-temperature spectra of $(\text{NH}_4)_3\text{VO}_2\text{F}_4$ and $(\text{NH}_4)_3\text{VOF}_5$ and (b) temperature dependence of Raman spectra of $(\text{NH}_4)_3\text{VOF}_5$.

preliminary EPR data of $(\text{NH}_4)_3\text{VO}_2\text{F}_4$ are similar to those of the γ -irradiated sample. We suspect that the crystal lattice of $(\text{NH}_4)_3\text{VO}_2\text{F}_4$ can contain a small amount of the VOF_5^{3-} (C_{4v}) anion. Two different anionic forms in $(\text{NH}_4)_3\text{VOF}_5$ and $(\text{NH}_4)_3\text{VO}_2\text{F}_4$ are connected with different dynamic orientations of the anions (most likely, around twofold and fourfold octahedral axes in the exact ratio of 2:1), which undergo on heating to the single state of isotropic orientations of octahedra with 12 and six spatial equivalent orientations for $\text{VO}_2\text{F}_4^{3-}$ and VOF_5^{3-} , respectively. The real geometry of polyhedra is clearly detected in the high-temperature phase and is partially observed at room temperature.

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