

Heat capacity and structure of $\text{Rb}_2\text{KMeO}_3\text{F}_3$ (Me: Mo, W) elpasolites

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ABSTRACT

X-ray and heat capacity measurements were performed on $\text{Rb}_2\text{KMoO}_3\text{F}_3$ and $\text{Rb}_2\text{KW}O_3\text{F}_3$ single crystals. A significant difference in the thermal parameters of atoms in 4a and 8c sites of $Fm-3m$ structure was found, which depended on the central atom. Calorimetric measurements have revealed the heat capacity anomalies at 195 and 67 K, respectively, in $\text{Rb}_2\text{KMoO}_3\text{F}_3$ and $\text{Rb}_2\text{KW}O_3\text{F}_3$. The standard molar enthalpy and entropy were determined. Entropy changes associated with phase transitions in oxyfluorides under study and related Rb_2KTiO_5 are discussed.

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1. Introduction

Interest in compounds $\text{A}_2\text{A}'\text{MeO}_x\text{F}_{6-x}$ containing six-coordinated quasi-octahedral species with fluorine/oxygen ligands is due to many factors. Firstly, some oxyfluorides belong to the well known family of crystals with perovskite-like structure exhibiting such useful properties as ferromagnetism, ferroelectricity and ferroelasticity. Secondly, they show chemical stability close to oxides. Thirdly, the low local symmetry of the six-coordinated anion offers wide possibilities of developing primarily noncentrosymmetric materials. And lastly, the crystal lattice symmetry of some oxyfluorides is a cubic one (sp. gr. $Fm-3m$, $Z = 4$) associated with structural disorder of two types. The former results from the fluorine/oxygen ligands disorder. The latter is connected with the relative orientations of the neighbouring octahedral units leading to cancelling the dipole moments of the separate octahedra. The cubic phase stability can be sometimes destroyed through the phase transitions of different physical nature.

According to [1], some elpasolite-like compounds $\text{A}_2\text{A}'\text{MeO}_x\text{F}_{6-x}$ with polar *fac* - units $[\text{MeO}_3\text{F}_3]$ (A, A': K, Rb, Cs; Me: Mo, W)

undergo two successive or single phase transitions depending on the relation between the size of monovalent cations. High temperature transformation is of ferroelectric–ferroelastic nature. Spontaneous polarization does not exhibit any changes at the low temperature ferroelastic transition detected in differential thermal analysis and X-ray experiments. In both transformations, structural distortions were supposed to be associated with rather small displacements of some atoms. For $\text{A}_3\text{MeO}_3\text{F}_3$ ($A = A'$) cryolites, this supposition was proved by a rather low value of the phase transition entropy $\Delta S \leq R \ln 2$. In spite of close ionic radii of the Mo (0.59 Å) and W (0.60 Å) atoms, molybdates compared to tungstates are characterized by higher temperature of the cubic phase stability and broader temperature range of the intermediate phase. It was supposed that these experimental facts could be associated with different degrees of the metal–oxygen bonds covalency in molybdates and tungstates [2].

It was also revealed that the stability of a cubic phase depends heavily on the combination of the monovalent cations. Indeed, elpasolites $\text{Cs}_2\text{KMeO}_3\text{F}_3$ (Me = Mo, W) and $\text{Cs}_2\text{NH}_4\text{WO}_3\text{F}_3$ remain cubic at least down to 80 K [1,3], $\text{Rb}_2\text{KW}O_3\text{F}_3$, $\text{Cs}_2\text{RbMeO}_3\text{F}_3$ and $(\text{NH}_4)_2\text{KMeO}_3\text{F}_3$ (Me: Mo, W) undergo one transformation [1,3,4], and only $\text{Rb}_2\text{KMoO}_3\text{F}_3$ exhibits the sequence of two transitions ($T_1 = 328 \pm 5$ K, $T_2 = 182 \pm 5$ K) [1]. Information on the heat capacity, entropy and susceptibility to hydrostatic pressure of elpasolites $\text{A}_2\text{A}'\text{MeO}_3\text{F}_3$ with monoatomic cations was absent for a long time.

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Recently we studied the thermodynamic properties of $\text{Rb}_2\text{KMoO}_3\text{F}_3$ in the temperature range 85–345 K [5] and found some contradictions with the data presented in [1]. First of all, the symmetry of the rich series of the samples prepared by different methods was found to be cubic at room temperature. This result is in agreement with the data presented in [6] and is inconsistent with the rhombohedral symmetry found in [1]. The measurements of the heat capacity and dielectric constant revealed only one nonferroelectric phase transition at about 195 K [5], i.e., rather close to the temperature of ferroelastic transformation observed at $T_2 = 182 \pm 5$ K in [1]. It is necessary also to point out that, in the vicinity of phase transition, $\text{Rb}_2\text{KMoO}_3\text{F}_3$ exhibits a significant barocaloric efficiency which exceeds electro- and magnetocaloric efficiency in some materials considered as the prominent solid refrigerants [5].

In this paper we carried out single crystal structural investigation at room temperature and heat capacity measurements between 2 and 370 K on two related oxyfluorides: $\text{Rb}_2\text{KMoO}_3\text{F}_3$ and $\text{Rb}_2\text{KWO}_3\text{F}_3$.

2. Experimental

Fine-grained powders of $\text{Rb}_2\text{KMoO}_3\text{F}_3$ and $\text{Rb}_2\text{KWO}_3\text{F}_3$ were prepared by solid state synthesis:



High purity initial reagents $\text{KF} \cdot 2\text{H}_2\text{O}$, Rb_2CO_3 , MoO_3 , WO_3 , NH_4F and aqueous hydrofluoric acid (48% HF by weight) were used.

Anhydrous KF was obtained by evaporating $\text{KF} \cdot 2\text{H}_2\text{O}$ with the addition of etching acid. Then NH_4F was added to the remainder and a mixture was heated to 300 °C in a closed teflon crucible to remove the remaining water and alkali.



For additional decrease of oxygen and alkali content, KF was heated to 500 °C in a closed platinum crucible with the addition of CF_4 as a fluorine agent. Grinded powder was placed in platinum crucible with a cover and heated to 900 °C in the flow of dry nitrogen with a rate of 100 °C/h. Subsequent to exposure over 3 h at this temperature the sample was cooled with a rate of 50 °C/h. As a result, the transparent crystalline material was obtained.

Anhydrous RbF was obtained from Rb_2CO_3 by neutralization of HF and evaporating the solution at the excess of the etching acid. Successive thermal operations were identical to those for KF synthesis; however, at the last stage the substance was heated to 800 °C.

The mixtures of stoichiometric compositions $\text{KF} + 2\text{RbF} + \text{Me}(\text{Mo},\text{W})\text{O}_3$ were grinded under nitrogen flow, placed in platinum crucibles, and put in the hermetic ceramic reactors. Reactors were heated with a rate of 100 °C/h to 800 °C (Mo) and to 900 °C (W). After slow cooling, small colourless crystals of $\text{Rb}_2\text{KMoO}_3\text{F}_3$ and $\text{Rb}_2\text{KWO}_3\text{F}_3$ of about 1–3 mm in size were obtained.

The characterization of the samples synthesized was performed by chemical and X-ray analysis as well as by polarizing-optic observations. A good agreement of experimental data was found with the stoichiometry of compositions, optical isotropy and cubic elpasolite-like structure at room temperature.

X-ray single crystal data from $\text{Rb}_2\text{KWO}_3\text{F}_3$ and $\text{Rb}_2\text{KMoO}_3\text{F}_3$ were measured on a SMART APEX II diffractometer ($\text{MoK}\alpha$, $\lambda = 0.7106$ Å) at room temperature (298 K). The exposure time equal to 10 s for each frame was obtained by rotating the crystal

around the ω -axis on 0.5° with a fixed φ angle. Values of ω ranged between 0° and 182°. The 364 frames were measured for each fixed φ equal to 0°, 120° and 240°. Intensities of reflections were integrated in the framework of the standard program APEX II from Bruker. Multiscan absorption correction was performed by APEX II software. Subsequently, intensities of equivalent reflections were averaged. Structures of $\text{Rb}_2\text{KWO}_3\text{F}_3$ and $\text{Rb}_2\text{KMoO}_3\text{F}_3$ were solved by direct methods using the SHELXS program [7]. Refinements of structures by least-square minimization were carried out with SHELXL97 [8].

On the first stage, calorimetric investigations of $\text{Rb}_2\text{KWO}_3\text{F}_3$ and $\text{Rb}_2\text{KMoO}_3\text{F}_3$ were carried out in the temperature range 100–370 K using a DSM-10A differential scanning microcalorimeter. The powdered compounds were put in an aluminium sample holder. The experiments were performed in a helium atmosphere. The heating and cooling rates were fixed at 8 K/min.

More detailed heat capacity measurements on both oxyfluorides were performed by a relaxation method using a PPMS calorimeter (Quantum Design, Inc., San Diego, CA) in the temperature range of 2–300 K. The samples with the mass of about 30 mg ($\text{Rb}_2\text{KWO}_3\text{F}_3$) and 10 mg ($\text{Rb}_2\text{KMoO}_3\text{F}_3$) were glued to the sample puck using Apiezon N grease to ensure good thermal contact. The heat capacity of the addenda (puck plus grease) was measured in an individual experiment. The error in heat capacity was about 1% below 60 K and less than 0.5% above 100 K.

3. Results

In experiments with a differential scanning calorimeter we have not observed heat capacity anomalies associated with the ferroelectric phase transitions found in [1] at 291 K and 328 K for compounds $\text{Rb}_2\text{KWO}_3\text{F}_3$ and $\text{Rb}_2\text{KMoO}_3\text{F}_3$, respectively. Only one anomaly at 195 K was detected in molybdate connected with the nonferroelectric transformation studied by us in [5]. The decrease of the molybdate crystal symmetry below 195 K was proven also by the appearance of complicated optical twinning.

The results of calorimetric studies by PPMS are presented in Figs. 1 and 2. As for experiments with DSM-10A, the measured heat capacity of $\text{Rb}_2\text{KWO}_3\text{F}_3$ does not show the anomalous behaviour observed near 291 K in [1]. Instead, it exhibits a broad bump in the range ~ (55–100) K (Fig. 1). In $\text{Rb}_2\text{KMoO}_3\text{F}_3$ no anomalies were found other than a huge heat capacity peak at about 195 ± 1 K associated with phase transition from the cubic phase [5] (Fig. 2).

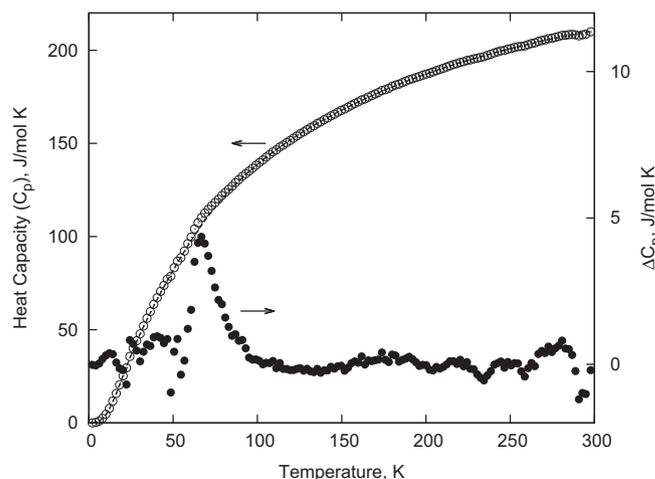


Fig. 1. Temperature behaviour of molar C_p and excess heat capacity ΔC_p of $\text{Rb}_2\text{KWO}_3\text{F}_3$. Solid line is a lattice heat capacity C_{lat} .

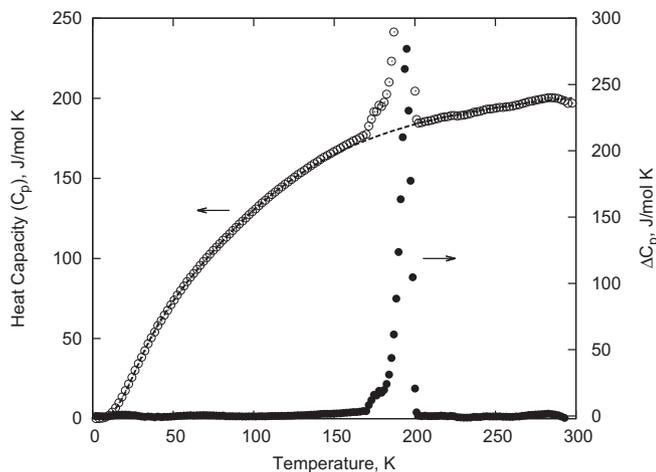


Fig. 2. Temperature behaviour of molar C_p and excess heat capacity ΔC_p of $\text{Rb}_2\text{KMoO}_3\text{F}_3$. Solid line is a lattice heat capacity C_{lat} .

To get information about the anomalous heat capacity associated with phase transitions it was necessary to find the temperature dependence of the lattice contribution to the heat capacity $C_{\text{lat}}(T)$. A good agreement between experimental results and data fitted in a wide temperature range using traditional equation

$$C_{\text{lat}}(T) = A_1 D(\Theta_D/T) + A_2 E(\Theta_{E1}/T), \quad (1)$$

which combines Debye $D(\Theta_D/T)$ and Einstein $E(\Theta_{E1}/T)$ functions, was found only for $\text{Rb}_2\text{KMoO}_3\text{F}_3$. As to $\text{Rb}_2\text{KWO}_3\text{F}_3$, it was necessary to add one more Einstein's term $A_3 E(\Theta_{E2}/T)$ to (1). The characteristic Debye's and Einstein's temperatures were estimated as follows: $\Theta_D = 116$ K, $\Theta_{E1} = 262$ K, $\Theta_{E2} = 796$ K and $\Theta_D = 158$ K, $\Theta_{E1} = 403$ K, respectively for $\text{Rb}_2\text{KWO}_3\text{F}_3$ and $\text{Rb}_2\text{KMoO}_3\text{F}_3$. The behaviour of $C_{\text{lat}}(T)$ is shown by solid lines in Figs. 1 and 2. The difference between the experimental heat capacity and interpolated lattice part was less than 1%. It must be stressed that there is no physical meaning associated with the fitting parameters in (1).

Using the excess heat capacity $\Delta C_p(T) = C_p(T) - C_{\text{lat}}(T)$ we determined the phase transition parameters. Excess values of

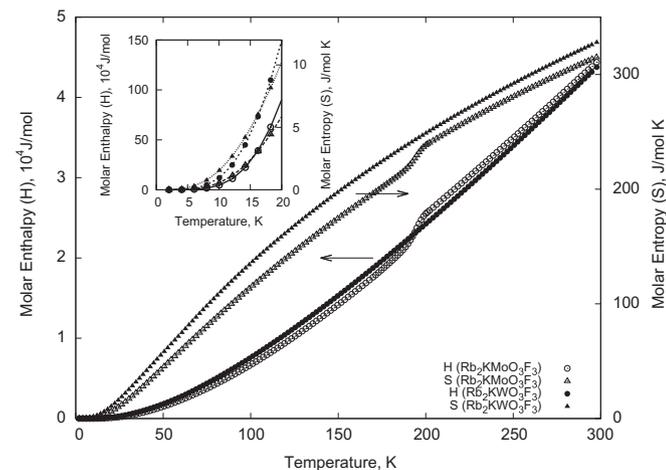


Fig. 3. Temperature dependences of molar enthalpy H and entropy S for $\text{Rb}_2\text{KMeO}_3\text{F}_3$ (Me: W, Mo) crystals. Insert shows the low temperature behaviour of molar enthalpy and entropy.

Table 1
Molar enthalpy and entropy of oxyfluorides for selected temperatures.

T, K	$\text{Rb}_2\text{KMoO}_3\text{F}_3$		$\text{Rb}_2\text{KWO}_3\text{F}_3$		T, K	$\text{Rb}_2\text{KMoO}_3\text{F}_3$		$\text{Rb}_2\text{KWO}_3\text{F}_3$	
	H, kJ/mol	S, J/mol K	H, kJ/mol	S, J/mol K		H, kJ/mol	S, J/mol K	H, kJ/mol	S, J/mol K
10	0.004	0.55	0.011	1.51	160	15.88	185.7	17.03	208.48
20	0.09	5.8	0.15	10.22	170	17.63	196.3	18.77	219.06
30	0.36	16.6	0.51	24.66	180	19.53	207.1	20.56	229.68
40	0.84	30.1	1.08	40.92	190	21.82	219.5	22.38	239.12
50	1.49	44.6	1.83	57.42	200	25.50	238.4	24.24	248.65
60	2.29	59.3	2.73	73.79	210	27.37	247.5	26.12	257.85
70	3.23	73.7	3.80	90.29	220	29.25	256.2	28.04	266.77
80	4.28	87.7	4.98	106.09	230	31.14	264.6	29.99	275.22
90	5.44	101.3	6.25	121.06	240	33.04	272.8	31.96	283.80
100	6.69	114.5	7.61	135.29	250	34.97	280.6	33.95	291.95
110	8.03	127.3	9.03	148.87	260	36.92	288.3	35.97	299.87
120	9.46	139.7	10.52	161.83	270	38.88	295.7	38.01	307.58
130	10.97	151.7	12.07	174.22	280	40.87	302.9	40.08	315.09
140	12.54	163.4	13.67	186.10	290	42.87	309.9	42.16	322.40
150	14.18	174.7	15.33	197.51	300	44.84	316.6	44.25	329.48

enthalpy $\Delta H = 2700 \pm 150$ J/mol and entropy $\Delta S = 14.6 \pm 0.8$ J/mol K $\approx \ln 6$ connected with phase transition in $\text{Rb}_2\text{KMoO}_3\text{F}_3$ estimated by integration of the $\Delta C_p(T)$ and $(\Delta C_p/T)(T)$ functions, agree well with the values obtained in [5]. As observed in Fig. 1, an excess heat capacity of $\text{Rb}_2\text{KWO}_3\text{F}_3$ exists in the temperature range between 50 and 100 K. The maximum value of ΔC_p is rather low, namely about 4% compared to C_{lat} , and centred at about 67 K. The excess enthalpy in tungstate is equal to $\Delta H = 80 \pm 14$ J/mol. Thus the entropy change is also very small: $\Delta S = 1.2 \pm 0.2$ J/mol K.

To calculate the molar enthalpy and entropy we integrated the molar heat capacity data according to the known equations:

Table 2
Crystal data, data collection and refinement.

Crystal data	$\text{Rb}_2\text{KWO}_3\text{F}_3$	$\text{Rb}_2\text{KMoO}_3\text{F}_3$
Chemical formula	$\text{Rb}_2\text{KWO}_3\text{F}_3$	$\text{Rb}_2\text{KMoO}_3\text{F}_3$
M_r	498.89	410.98
Space group, Z	$Fm-3m$, 4	$Fm-3m$, 4
a , Å	8.9402(5)	8.9406(8)
V , Å ³	714.56(1)	714.66(1)
D_x , Mg/m ³	4.637	3.82
μ , mm ⁻¹	30.29	15.95
Size, mm	0.2 × 0.2 × 0.2	0.25 × 0.25 × 0.25
Data collection		
Wavelength	MoK α , $\lambda = 0.7106$ Å	
Measured reflections	1631	1729
Independent reflections	77	74
Reflections with $I > 2\sigma(I)$	76	63
Absorption correction	Multiscan	Multiscan
R_{int}	0.045	0.0359
$2\theta_{\text{max}}$, °	59.32	59.32
h	-11 → 12	-12 → 11
k	-11 → 12	-11 → 11
l	-12 → 12	-11 → 11
Refinement		
$R[F^2 > 2\sigma(F^2)]$	0.0228	0.0183
$wR(F^2)$	0.0618	0.0489
No. of parameters	8	8
S	1.042	1.039
Weight	$w = 1/[\sigma^2(F_o^2) + (0.0256P)^2 + 40P]$, where $P = \max(F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0119P)^2 + 14.27P]$, where $P = \max(F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\text{max}}$	<0.001	<0.001
$\Delta\rho_{\text{max}}$, e/Å ³	1.01	0.33
$\Delta\rho_{\text{min}}$, e/Å ³	-0.83	-0.31
Extinction correction coefficient (SHELX97)	0.0034(4)	0.0059(6)

Table 3
Coordinates of atoms (X, Y, Z), occupancy (q) and thermal parameters (U).

Atom	X	Y	Z	q	U, Å ²
Rb ₂ KWO ₃ F ₃ , T = 298 K a ₀ = 8.9402(5) Å					
W (4a)	0	0	0	1	U ₁₁ = U ₂₂ = U ₃₃ = 0.0250(6)
Rb (8c)	1/4	1/4	1/4	1	U ₁₁ = U ₂₂ = U ₃₃ = 0.0267(6)
K (4b)	1/2	0	0	1	U ₁₁ = U ₂₂ = U ₃₃ = 0.0138(9)
F/O (24e)	0.2121(9)	0	0	0.5	U ₁₁ = 0.012(3) U ₂₂ = U ₃₃ = 0.059(4)
Rb ₂ KMoO ₃ F ₃ , T = 298 K a ₀ = 8.9406(8) Å					
Mo (4a)	0	0	0	1	U ₁₁ = U ₂₂ = U ₃₃ = 0.0324(6)
Rb (8c)	1/4	1/4	1/4	1	U ₁₁ = U ₂₂ = U ₃₃ = 0.0327(6)
K (4b)	1/2	0	0	1	U ₁₁ = U ₂₂ = U ₃₃ = 0.0168(7)
F/O (24e)	0.2118(6)	0	0	0.5	U ₁₁ = 0.018(3) U ₂₂ = U ₃₃ = 0.060(3)
Rb ₂ KMoO ₃ F ₃ , T = 343 K a ₀ = 8.946(5) Å [9]					
Mo (4a)	0	0	0	1	U ₁₁ = U ₂₂ = U ₃₃ = 0.0346(6)
Rb (8c)	1/4	1/4	1/4	1	U ₁₁ = U ₂₂ = U ₃₃ = 0.0380(6)
K (4b)	1/2	0	0	1	U ₁₁ = U ₂₂ = U ₃₃ = 0.0213(7)
F/O (24e)	0.2105(7)	0	0	0.5	U ₁₁ = 0.0219(3) U ₂₂ = U ₃₃ = 0.066(3)

$$H(T) = \int_0^T C_p(T) dT = \int_0^T C_{lat}(T) dT + \Delta H(T), \quad (2)$$

$$S(T) = \int_0^T \frac{C_p(T)}{T} dT = \int_0^T \frac{C_{lat}(T)}{T} dT + \Delta S(T). \quad (3)$$

Obtained data is presented in Fig. 3 and in Table 1 at regular intervals of temperatures.

It was shown above that the room temperature structures of both oxyfluorides are cubic ones. Main information about crystal data, data collection and refinement is summarized in Table 2. Matrices of orientation and cell parameters of compounds under study were calculated and refined by 152 reflections. Space group *Fm-3m* was defined by analysis of extinction rules and statistics of all reflections intensities. Oxygen and fluorine atoms were refined with the same coordinates and equal thermal parameters. The sum of their occupancies was equal to 1. Thermal parameters of all atoms were refined anisotropically. However, strong anisotropic moving was found only for O(F) atoms (Table 3). As a result, the structures were finally refined with small *R*-factors (Table 2).

Table 4
Main interatomic distances.

Rb ₂ KWO ₃ F ₃	d, Å	Rb ₂ KMoO ₃ F ₃	d, Å	d, Å [9]
W–O(F)	1.896(5)	Mo–O(F)	1.893(5)	1.883(6)
Rb–O(F)	3.179(6)	Rb–O(F)	3.179(6)	3.183(1)
K–O(F)	2.574(5)	K–O(F)	2.577(5)	2.591(6)

The main interatomic distances are presented in Table 4. In Tables 3 and 4 one can see also the results of structural refinement performed on Rb₂KMoO₃F₃ at 343 K in [9]. Taking into account the thermal expansion, we have found that the difference between the values of the unit cell parameters obtained in the present paper and [9] does not exceed 0.05%.

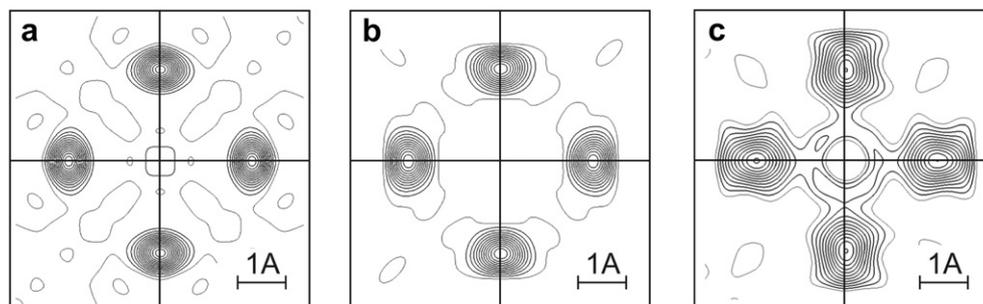
4. Discussion

It is interesting to compare the behaviour of the molar enthalpy *H*(*T*) and entropy *S*(*T*) of Rb₂KMoO₃F₃ and Rb₂KWO₃F₃ in the temperature range studied (Fig. 3). Taking into account the error of measurements, the values of standard molar enthalpy at 298.15 K for molybdate *H*_{298.15} = 44.5 ± 0.3 kJ/mol and tungstate *H*_{298.15} = 43.8 ± 0.3 kJ/mol are almost equal. On cooling through phase transition, the molar enthalpy of Rb₂KMoO₃F₃ becomes lower. In contrast, it was found that the entropy of tungstate exceeds the *S* value in molybdate in a wide temperature range. This difference increases distinctly below the phase transition point in Rb₂KMoO₃F₃ and then is reduced progressively to zero at very low temperatures (insert in Fig. 3).

In accordance with the results of X-ray studies, the structure of Rb₂KWO₃F₃ remains cubic at least until the lowest experimental temperature of about 100 K. We have no way of performing X-ray investigations below 100 K and therefore there is no information about the relation between heat capacity anomaly in Rb₂KWO₃F₃ and possible structural transformation. On the other hand, it is necessary to point out that recent preliminary Raman investigations on Rb₂KWO₃F₃ didn't show any strong difference in spectra at room temperature and at 10 K [10]. One can suppose that if the heat capacity anomaly observed in tungsten oxyfluoride associates with some phase transition, so will negligible displacements of atoms.

As for Rb₂KMoO₃F₃, the cubic structure transforms into a pseudo-tetragonal one at 195 K [5]. Strong complicated twinning in the low temperature phase of molybdate prevented the solving of the question concerning its real distorted symmetry.

In accordance with Table 4, interatomic distances in Rb₂KWO₃F₃ and Rb₂KMoO₃F₃ are almost the same. However, the thermal parameters in both oxyfluorides are close to each other only for F/O as well as potassium (Table 3). The relation between K–O(F) distances (Table 4) and the sum of ionic radii of these atoms (2.71–2.78 Å) means that namely this is the reason for the smallest thermal parameter for the potassium ion which is the lightest metal ion. At the same time, the *U*_{ii} values for atoms in 4a and 8c positions in the molybdenum compound significantly exceed those for Rb₂KWO₃F₃. This means that the oxyfluorides under study are characterized by different degrees of anharmonicity of Rb and Me atom vibration which can be determined as $\delta \approx \langle x^2 \rangle / a_0^2$ (where *x* is an amplitude of atom vibration) [11].

**Fig. 4.** Difference sections through MeO_xF_{6-x} in Rb₂KWO₃F₃ (a), Rb₂KMoO₃F₃ (b) and Rb₂KTiO₅ [12] (c).

Let us compare the results obtained with the same for related $\text{Rb}_2\text{KTiOF}_5$ [12]. Similarly to $\text{Rb}_2\text{KMoO}_3\text{F}_3$ this oxyfluoride undergoes a strong first order nonferroelectric phase transition at 215 K followed by large value of entropy change $\Delta S \approx R \ln 8$. According to X-ray investigations, the largest thermal parameters are also characteristic for atoms in 8c (Rb) and 4a (Ti) crystallographic sites [12].

Fig. 4 shows the difference sections of electron density through WO_3F_3 , MoO_3F_3 and TiOF_5 polyhedra. One can see that the electron density distributions for F/O atoms in $\text{Rb}_2\text{KWO}_3\text{F}_3$, $\text{Rb}_2\text{KMoO}_3\text{F}_3$ and $\text{Rb}_2\text{KTiOF}_5$ are similar in appearance. On the other hand, in spite of the large difference between U_{11} and $U_{22} = U_{33}$ values (Table 3 and [12]), there is no evidence of the F/O atoms disordering.

5. Conclusion

The results obtained in this paper show that in spite of close size of the Mo and W atoms, $\text{Rb}_2\text{KMoO}_3\text{F}_3$ and $\text{Rb}_2\text{KWO}_3\text{F}_3$ are characterized by significant differences in the temperature of the cubic phase stability as well as the mechanism of phase transitions. One can suppose that fluorine-oxygen ligands are not critical atoms and order-disorder transformations in $\text{Rb}_2\text{KMoO}_3\text{F}_3$ and $\text{Rb}_2\text{KTiOF}_5$ [12] can be associated with the strong anharmonic vibrations of atoms occupying 8c and 4a sites of a cubic phase.

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