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Neutron diffraction studies of temperature induced phase transitions in Rb_2KFeF_6 elpasolite

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Abstract. A neutron diffraction study of temperature induced phase transition in Rb_2KFeF_6 elpasolite has been performed. At room temperature the structure is cubic with space group $Fm\bar{3}m$. At $T = 170$ K a structural phase transition takes place. Space group and atom coordinates in this phase has been defined. The crystal structure is good refined by orthorhombic space group $Pmnn$. Possible models are discussed.

Introduction

Rb_2KFeF_6 fluoride belongs to compounds family with general chemical formula A_2BMF_6 (A, B – monovalent cations, M – trivalent cation). The space group of their cubic prototype is $Fm\bar{3}m$ ($Z = 4$). In this system two kinds of non-equivalent octahedral groups (BF_6 and MF_6) alternate along the three four-fold axes. The region of cubic lattice stability depends on tolerance factor [1]:

$$t = \frac{\sqrt{2}(r_{A^+} + r_{F^-})}{2r_{F^-} + r_{B^+} + r_{M^{3+}}}$$

where r_A , r_B , r_M and r_M are ion radii of A, B, F and M. $t = 1$ for ideal perovskite-type structure. BO_2 plane is under squeezed stresses and AO plane is under stretched stresses at the $t < 1$. Usually it leads to mutual turns of BO_6 octahedrons [2].

$Fm\bar{3}m$ symmetry is usually observed in the wide temperature region at the $0.88 < t < 1.0$. Distortion of the octahedral group takes place at the $t < 0.88$. This fact leads to crystal symmetry reduction.

Temperature dependence of phase transitions in crystals with high M^{3+} radius have been recently studied [3]. At the $M = \text{Sc, In, Lu}$ the consecution of two transitions $\text{Fm}\bar{3}\text{m} \rightarrow \text{I4}/\text{m} \rightarrow \text{P21}/\text{n}$ has been observed.

The structure of crystals with low M^{3+} ($M = \text{Cr, Ga, Fe}$) radius is still poorly known. These compounds usually demonstrate ferroelastic phase transition which corresponds considerable high changing in entropy ΔS .

We studied structure of the Rb_2KFeF_6 ($t = 0.885$; $\Delta S/R = 1.88$) at the wide temperature region.

Experimental

Rb_2KFeF_6 was prepared by solid-phase sintering with stoichiometric quantities of $\text{RbF} + \text{KF} + \text{FeF}_3$ mixture at the 700°C in the Institute of Solid State Chemistry of Bordeaux. Neutron diffraction experiments have been performed at the High Resolution Fourier Diffractometer HRFD and DN-2 diffractometer at the IBR-2 pulsed reactor in Frank Laboratory of Neutron Physics (Dubna) [4]. HRFD is a reverse time-of-flight diffractometer with a high resolution $\Delta d/d \sim 2.10\text{-}3$ in interplanar spacing region $0.5 < d < 4 \text{ \AA}$. Scattering angle is fixed at the $2\Theta = 152^\circ$. DN-2 is a multipurpose time-of-flight diffractometer with average resolution $\Delta d/d \sim 2\%$ and high flux up to $107 \text{ n/cm}^2\text{s}^2$. The data were analyzed by the Rietveld method using MRJA program [5].

Results

Figure 1 shows neutron diffraction pattern and the result of Rietveld refinement at the room temperature. Rb_2KFeF_6 has a cubic structure (space group $\text{Fm}\bar{3}\text{m}$) with $a = 8.865 \text{ \AA}$. We used several models for refining of atoms positions. The result is presented in table 1.

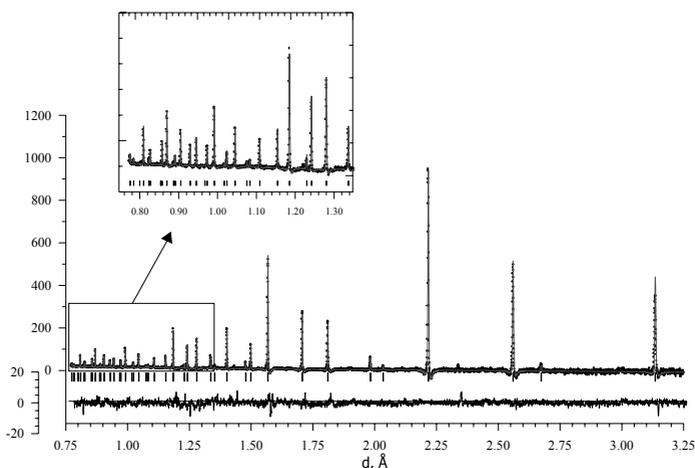


Figure.1. Neutron diffraction pattern and the result of Rietveld refinement of Rb_2KFeF_6 at $T = 290 \text{ K}$. The peak at $d = 2.34 \text{ \AA}$ is 111 peak from Al container.

In the first model (column a) we fixed atoms in the particular positions: Rb – 8c, Fe – 4a, K – 4b, F – 24e. In this assumption we obtain very high thermal factors and quite high value of χ^2 .

Table 1. Rietveld refinement data at the $T = 290$ K. a – all atoms fixed in particular positions; b – F in 24e, Rb displaced in [100] direction, c – Rb in 8c, F displaced in [110] direction (96k); d, e, f – F displaced in [110], Rb in [100], [110], [111] correspondingly.

		a	b	c	d	e	f
Rb	x	1/4	0.275(1)	1/4	0.272(1)	0.2656(4)	0.260(1)
	y	1/4	1/4	1/4	1/4	0.2656(4)	0.260(1)
	z	1/4	1/4	1/4	1/4	1/4	0.260(1)
	B, \AA^2	2.06(4)	0.74(7)	1.85(4)	0.85(3)	0.97(5)	1.19(5)
	Δ Rb, \AA	0	0.221(2)	0	0.195(2)	0.196(2)	0.154(2)
K	B, \AA^2	4.1(2)	1.19(6)	1.18(9)	1.15(7)	1.14(5)	1.2(1)
Fe	B, \AA^2	1.01(3)	0.66(4)	0.62(3)	0.64(4)	0.61.4	0.62(3)
F	x	0.218(1)	0.2163(2)	0.2164(2)	0.2164(2)	0.2164(2)	0.2163(2)
	y	0	0	0.0204(3)	0.0197(4)	0.0198(4)	0.0204(3)
	z	0	0	0.0204(3)	0.0197(4)	0.0198(4)	0.0204(3)
	B, \AA^2	4.5(1)	B ₁₁ =0.97(2) B ₂₂ =4.45(1) B ₃₃ =4.45(1)	B ₁₁ =0.89(1) B ₂₂ =1.69(1) B ₃₃ =1.69(1)	B ₁₁ =0.89(1) B ₂₂ =1.72(1) B ₃₃ =1.72(1)	B ₁₁ =0.89(1) B ₂₂ =1.70(1) B ₃₃ =1.70(1)	B ₁₁ =0.89(1) B ₂₂ =1.65(1) B ₃₃ =1.65(1)
	Δ F, \AA	0	0	0.154(3)	0.154(3)	0.154(3)	0.154(3)
	χ^2	5	2.2	2.4	2.2	2.2	2.2
	R _w , %	8.2	5.8	5.9	5.8	5.8	5.8

The t -factor value for Rb_2KFeF_6 is equal to 0.87. This value is lower than theoretically predicted boundary of cubic lattice stability [1]. According to group-theory analysis [6] distortions of initial $\text{Fm}\bar{3}\text{m}$ structure caused by octahedron or/and polar atoms displacements are possible. Data of [7] suppose the possibility of 4 positions of fluorine atoms in cubic phase (96k position). Therefore we performed refinements with fluorine atoms in 96k position and Rb – in 8c position (column c of the table 1), Rb is displaced along $[100]$ direction (column d of the table 2), Rb is displaced along $[100]$ direction (column e of the table 2), Rb is displaced along $[111]$ direction (column f of the table 1). The difference in refinement quality is very low and there is impossible to choose the only model based only on neutron diffraction data.

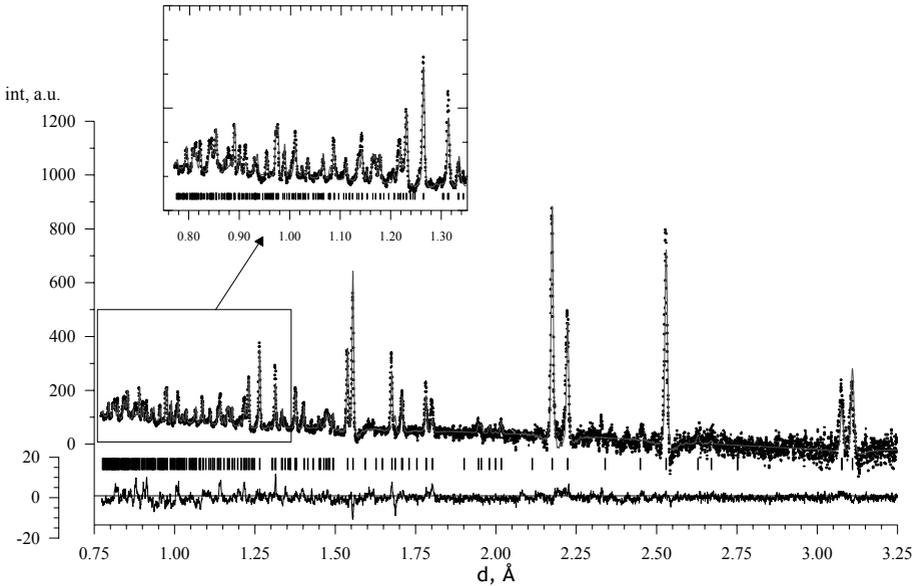


Figure 2. Neutron diffraction pattern and the result of Rietveld refinement of Rb_2KFeF_6 at $T = 10\text{ K}$.

Figure 2 shows neutron diffraction pattern and the result of Rietveld refinement at the temperature $T = 10\text{ K}$, which is much lower than the temperature of structural phase transition ($T \sim 170\text{ K}$ [3]). The crystal structure precisely described in the frame of $\text{Pm}\bar{3}\text{m}$ space group with the $a = 6.1567(3)\text{ \AA}$, $b = 6.1508(3)\text{ \AA}$, $c = 8.8942(3)\text{ \AA}$, $\chi^2 \sim 2.34$. Detail information is shown in the table 2. This result is corresponds with possible variants of phase transitions predicted in [8].

Table 2. Rietveld refinement data at the $T = 10$ K.

atom	position	x	y	z	$B_{\text{iso}}, \text{\AA}^2$
Rb	4f	0	0.5	0.2644(1)	0.76(2)
K	2b	0	0	0.5	0.3(1)
Fe	2a	0	0	0	0.4(1)
F	4e	0	0	0.2155(2)	0.7(1)
F	4g	0.2319(2)	0.2079(2)	0	0.6(1)
F	4g	0.7681(2)	0.2079(2)	0	0.6(1)

Discussion

Phase transitions in elpasolites family depend on two main factors: electron structure of M^{3+} cation and value of the tolerant factor t . Determinating factor for non-Jahn-Teller cations like Fe^{3+} is a tolerant factor.[2, 3]. It is equal 0.87 in the case of Rb_2KFeF_6 . This value is lower than the theoretical boundary of crystal lattice stability. This fact allows us to suppose that fluorine atoms are disorder in 4 equivalent positions (96k) in the initial cubic phase at room temperature. Strong anisotropy of thermal vibrations of fluorine atoms confirms this assumption. Rb is also displaced from the 8c position in the cubic phase, but we cannot precisely define a direction of displacement from the our data (see columns d, e, f in the table 1). From the other side all atoms are ordered in the low-temperature phase. According to our data, the turn of octahedrons around of an fourth order axis on 2.8 degree takes place. FeF_6 octahedrons turn counter-clockwise and KF_6 octahedrons turn clockwise.

Conclusions

We have performed neutron diffraction study of the Rb_2KFeF_6 crystal structure at the 10 and 290 K. At the room temperature the structure can be described in the frame of Fm3M space group. Disordered in 4 equivalent positions fluorine atoms are responsible for lattice instability which leads to structural phase transition at $T = 170$ K. According to our data we can conclude that phase transition connects mainly with a superposition of two mechanisms: ordering of fluorine atoms and displacement of rubidium.

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