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Crystal structure of anhydrous alum $RbFe^{3+}(SeO_4)_2$

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Summary. The compound $RbFe(SeO_4)_2$ was prepared hydrothermally by reaction of Rb_2CO_3 and $FeC_2O_4 \cdot 2H_2O$ with H_2O and H_2SeO_4 at 490 K. Single crystal X-ray methods revealed isotypy with $KAl(SO_4)_2$. $RbFe(SeO_4)_2$ crystallizes in space group P321; $Z = 1$; $a = 5.005(1)$ Å, $c = 8.548(2)$ Å, $V = 185.4$ Å^3; 781 unique data up to 80 °2θ; R, $R_w = 0.045$, 0.042. The structure is best described as sheets of $[Fe(SeO_4)_2]^-$ parallel (001), interconnected by Rb^+. FeO_6 trigonal prims and SeO_4 tetrahedra have bond lengths of 1.99 Å and 1.63 Å, respectively. The Rb atom is [6 + 6] coordinated with Rb–O distances of 3.04 Å and 3.48 Å.

Keywords. $RbFe(SeO_4)_2$; Crystal structure; Crystal chemistry.

Die Kristallstruktur des wasserfreien Alauns $RbFe^{3+}(SeO_4)_2$

Zusammenfassung. Die Verbindung $RbFe(SeO_4)_2$ wurde hydrothermal dargestellt durch Reaktion von Rb_2CO_3 und $FeC_2O_4 \cdot 2H_2O$ mit H_2O und H_2SeO_4 bei 490 K. Einkristallröntgenmethoden belegten die Isotypie mit $KAl(SO_4)_2$ $RbFe(SeO_4)_2$ kristallisiert in der Raumgruppe P321; $Z = 1$; $a = 5.005(1)$ Å, $c = 8.548(2)$ Å, $V = 185.4$ Å^3; 781 unabhängige Daten bis 80 °2θ; R, $R_w = 0.045$, 0.042. Die Struktur läßt sich am besten als Schichten von $[Fe(SeO_4)_2]^-$ parallel (001) beschreiben, die durch Rb^+ verbunden sind. FeO_6 trigonale Prismen und SeO_4 Tetraeder weisen Bindungslängen von 1.99 Å bzw. 1.63 Å auf. Das Rb-Atom ist [6+6] koordiniert mit Rb–O Abständen von 3.04 Å und 3.48 Å.

Introduction

Anhydrous alum compounds are characterized by the general formula $Me^{1+}Me^{3+}[X^{6+}O_4]_2$ with Me^{1+} = Na, K, Rb, Cs, Ag, NH_4, Tl; Me^{3+} = Al, Sc, V, Cr, Mn, Fe, Ga, Rh, In, Tl and X^{6+} = S, Se, Cr, Mo, W. Based on the atomic arrangement, these compounds may be classified into several groups. Among them, two structure concepts are commonly found: a) compounds related to the structure type of yavapaiite, $KFe(SO_4)_2$, (C2/c) and (b) compounds isotypic with $KAl(SO_4)_2$, crystallizing in P321. The present work concentrates on anhydrous alum compounds of trigonal symmetry.

The crystal structures of some sulfate representatives were determined by powder methods in the space group P321 already in 1928 [1]. Further powder investigations [2, 3] established the lattice constants of 18 sulfate and 10 selenate compounds, obviously belonging to the same structure type, and a single crystal study of $KAl(SO_4)_2$ [4] confirmed the structural arrangement proposed in [1]. Meanwhile, a steadily increasing number of "anhydrous alum compounds" has been described to crystallize in some other trigonal space groups [cf. 5].

In the course of systematic investigations on kieserite-type compounds [6, 7] also systems containing iron or manganese as well as sulfur or selenium and in addition monovalent cations were studied, for a survey on these oxosalts cf. [8]. Among them are $NaFe^{3+}(SeO_4)_2$ [9], isotypic with monoclinic yavapaiite, $KFe(SO_4)_2$, $KMn^{3+}(SeO_4)_2$ [10] (triclinic distorted yavapaiite type) and $RbFe(SeO_4)_2$. The present paper describes $RbFe(SeO_4)_2$, a representative of the $KAl(SO_4)_2$ structure type. The lattice parameters of the title compound were already given in [3].

Experimental

Rb_2CO_3 and $FeC_2O_4 \cdot 2H_2O$ were mixed with H_2O subsequently adding H_2SeO_4 conc. in excess. This solution was heated in Teflon-lined steel autoclaves of 50 cm^3 capacity (filling rates of approx. 20%) up to 490(5) K, kept at this temperature for about one week and then cooled to room temperature within 12 hours. As a result, yellowish transparent platelets of $RbFe(SeO_4)_2$ up to 0.5 mm in size had grown exhibiting the crystallographic forms {00.1}, {10.1} and subordinate {10.0}.

Single crystal data collection was done on a Stoe AED2 four-circle diffractometer; crystal parameters and details of refinement procedures are given in Table 1. The obtained lattice parameters

Table 1. Summary of crystal data, X-ray measurements and structure refinements for $RbFe(SeO_4)_2$

a[Å]	5.005(1)
c[Å]	8.548(2)
V[Å^3]	185.4
space group	P321
formula units per cell	1
ρ_{calc}[gcm^{-3}]	3.83
μ(MoKα)[cm^{-1}]	191.3
transmission factors	0.15–0.60

Equipment: Stoe four-circle diffractometer AED2; graphite monochromatized MoKα-radiation; programs Multan 87 [11] and Shelx76 [12]

Data collection: 2θ-ω scans; 35 steps/reflection, increased for α_1-α_2 splitting; 0.03° and 0.5–2.0s/step; 2*5 steps for background measurement; 3 standard reflections each 120 min; $2\theta_{max} = 80°$; 295 K

lattice parameter refinement	54 reflections ($31° < 2\theta < 40°$)
measured reflections	4319
h, k, l_{max}	9 9 16
unique data set	781
data with $F_0 > 3\sigma(F_0)$	730
number of variables	21
R	0.045
$R_w(w = 2.33/[\sigma(F_0)]^2)$	0.042

agree well with the data in the literature ($a = 4.997$ Å, $c = 8.531$ Å [3]). Intensities were corrected for Lorentz and polarization effects as well as for absorption according to the shape of the crystal. The crystal structure was solved in the space group P321 by direct methods (Multan 87). The structure parameters (atomic positions according to [4]) were refined by full-matrix least-squares techniques, the results are listed in Table 2. Complex scattering factors were taken from the International Tables for X-ray Crystallography [13]. A determination of the absolute configuration revealed minor differences only between the final structure and it's inverted one. Selected interatomic distances and bond angles for $RbFe(SeO_4)_2$ are compiled in Table 3.

Table 2. Structural parameters of $RbFe(SeO_4)_2$ with e.s.d.'s in parentheses. U_{ij} are given in pm^2. The anisotropic displacement factor is defined as $\exp[-2\pi^2\Sigma_i\Sigma_j U_{ij}h_ih_ja_i^*a_j^*]$

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rb	0	0	0	214(3)	214(3)	312(6)	107(2)	0	0
Fe	0	0	1/2	90(3)	90(3)	140(6)	45(2)	0	0
Se	1/3	2/3	0.2968(1)	85(2)	85(2)	137(3)	43(1)	0	0
O1	1/3	2/3	0.1114(7)	307(18)	307(18)	123(24)	154(9)	0	0
O2	0.0435(9)	0.7045(8)	0.3614(6)	113(14)	102(14)	328(25)	69(12)	−31(15)	−72(16)

Table 3. Interatomic bond lengths [Å], bond angles [°] (with e.s.d.'s in parentheses) and intrapolyhedral O–O distances (given in brackets) in $RbFe(SeO_4)_2$

			[Å]
Rb–O1	6 ×		3.042(2)
Rb–O2	6 ×		3.478(5)
Fe–O2	6 ×		1.990(4)
		[°]	[Å]
O2–Fe–O2	3 ×	74.2(2)	[2.400(8)]
O2–Fe–O2	6 ×	88.2(2)	[2.769(4)]
O2–Fe–O2	3 ×	122.5(2)	[3.489(6)]
O2–Fe–O2	3 ×	143.1(2)	[3.775(6)]
			[Å]
Se–O1	1 ×		1.585(6)
Se–O2	3 ×		1.649(3)
⟨Se–O⟩			⟨1.633⟩
		[°]	[Å]
O1–Se–O2	3 ×	109.5(2)	[2.642(7)]
O2–Se–O2	3 ×	109.4(2)	[2.692(4)]

Results and Discussion

The title compound belongs to the $KAl(SO_4)_2$ structure type (space group P321), a listing of isotypic phases with references is given in Table 4. The structure consists of sheets parallel (001), built up by $Me^{3+}O_6$ polyhedra sharing corners with XO_4 tetrahedra (Figs. 1, 2). These sheets are separated by the Me^{1+} cations in height $z/c = 0$ such that the Me^{3+} and Me^{1+} cations are alternately arranged along [001].

In $RbFe(SeO_4)_2$ a distorted trigonal prism (torsion angle approximately 13.5°) around ferric iron has a mean Fe–O bond length of 1.99 Å which is well in the range known for Fe^{3+} in octahedral coordination. Three O–O distances within the prism are rather short (2.40 Å), especially as they are not part of a common edge with another polyhedron. The Rb atom is bound to six equidistant oxygen atoms (3.042 Å), six additional oxygen atoms (3.478 Å, which form two common faces with FeO_6 prisms) complete the coordination figure (distorted hcp, the equatorial

Table 4. Summary on anhydrous alums, isotypic with $KAl(SO_4)_2$ and references

Sulfates		Selenates	
Compounds	Refs.	Compounds	Refs.
K - Al	[1, 2, 4, 14]		
- Cr	[2, 14]		
Rb - Al	[2, 14]	Rb - Al	[3]
- Sc	[15]		
- V	[16]		
- Cr	[2, 14]		
- Fe	[2, 14]	- Fe	[3]
- Ga	[2, 14]	- Ga	[3]
Cs - Al	[2, 14]		
- Sc	[15]		
- V	[16]		
- Cr	[2, 14]		
- Fe	[2, 14]	Cs - Fe	[3]
- Ga	[2, 14]		
Tl - Al	[2, 14]	Tl - Al	[3]
- Sc	[17]		
- V	[17]		
- Cr	[2, 14, 17]		
- Fe	[2, 14, 17]	- Fe	[3]
- Ga	[2, 17]	- Ga	[3]
NH_4 - Al	[2, 14]	NH_4 - Al	[3]
- Sc	[15, 17]		
- V	[18]		
- Cr	[2, 14]		
- Fe	[2, 14, 17]	- Fe	[3]
- Ga	[2, 17]	- Ga	[3]

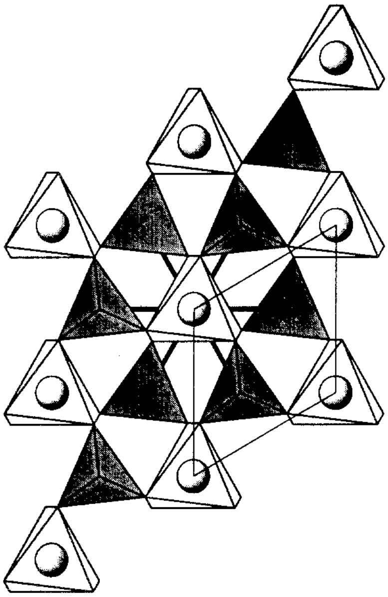

Fig. 1. Crystal structure of RbFe(SeO$_4$)$_2$ in a projection parallel to [001]. The figure was drawn with the program ATOMS [19]. The Rb atoms are indicated as large circles

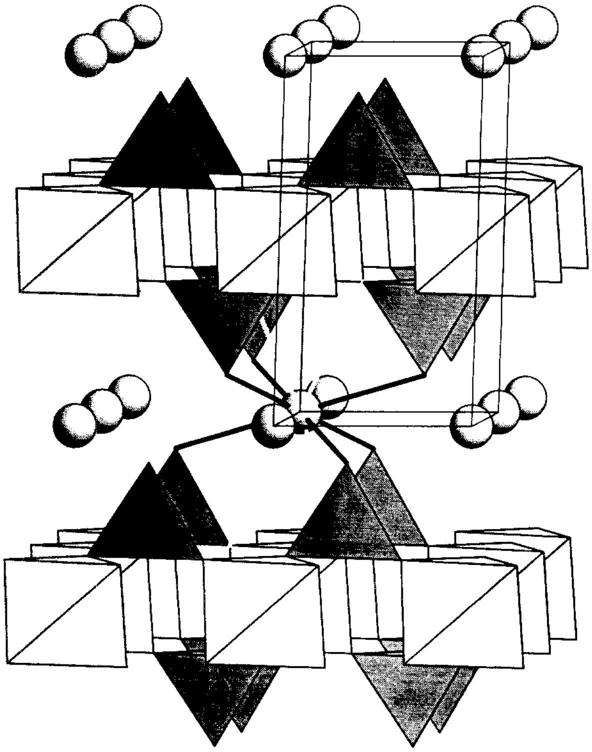

Fig. 2. Drawing of RbFe(SeO$_4$)$_2$ projected slightly inclined to [100]. For one Rb atom the six short Rb–O bonds are shown in dark lines

oxygens are considerably nearer and not coplanar). Each RbO$_{12}$ polyhedron has common edges with six neighbouring RbO$_{12}$ groups and six SeO$_4$ tetrahedra. The tetrahedral SeO$_4$ anion has one relatively short Se–O distance (1.585 Å) to the oxygen atom O1, which is not part of the Me^{3+}O$_6$ trigonal prism.

It is worth noting that the KAl(SO$_4$)$_2$ structure type is known only for sulfates and selenates and especially among those with large monovalent cations. Unfortunately, in many cases only the lattice parameters (obtained by powder methods) are cited and it is not finally proven that they crystallize in space group P321, which is only inferred from the similarity of the powder pattern. Further trigonal anhydrous alums are described in the space groups $P\bar{3}c1$ and $P\bar{3}m1$ [20], R32 [21] and $R\bar{3}$ [22], represented by $KFe(MoO_4)_2$, $KAl(MoO_4)_2$, $RbTl(SO_4)_2$ and $KV(SO_4)_2$, respectively. As already pointed out by [22], these structure types are similar with respect to the arrangement of $Me^{3+}(XO_4)_2$ layers linked by monovalent cations. The differences are caused by the environment of the trivalent cation (octahedral or trigonal prismatic), and further by the type of linkage between $Me^{3+}O_6$ polyhedra and XO_4 tetrahedra. A determining factor may be seen in the ratio of sizes of the involved ions. Some compounds are reported to exist in more than one modification. For a more detailed view on the relationships of anhydrous alums (including also yavapaiite- and some more structure types) the reader is referred to [5].

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