N. M. MUSTAFAEV, V. V. ILYUKHIN, Academician N. V. BELOV

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N. M. MUSTAFAEV, V. V. ILYUKHIN, Academician N. V. BELOV

CRYSTAL STRUCTURE OF RUBIDIUM ORTHOFLUOROBERYLLATE γ-Rb_2BeF_4

Direct determination of the structures of orthofluoroberyllates was hindered chiefly by the absence of a sufficiently reliable method for obtaining single crystals ([1]). Therefore, in previously published works, conclusions about the structural analogy of orthofluoroberyllates of alkali cations and the corresponding silicates (as well as sulfates, chromates, etc.) were drawn on the basis of similar Debye diagrams ([2]), analogy in certain physical properties, and also crystallographic data; only in individual cases was a comparison of calculated and experimental structure factors carried out, and even then with very unsatisfactory values of the discrepancy coefficients (the coordinates used in modeling were taken by analogy with other compounds ([3,4])).

In light of the recent determinations of two layer structures, $BaSi_2O_5$ ([5]) and $RbBe_2F_5$ ([6]), the question of the identity of the structures of Rb fluoroberyllates and their silicate analogs according to Goldschmidt ([7,8]) should be approached with a certain degree of caution.

Of the three polymorphic modifications of Rb_2BeF_4, the γ-modification is the most stable at ordinary temperature up to 528°; the β-modification is stable in the interval 528–692°, and, finally, the α-form from 692° up to the melting temperature.

γ-Rb_2BeF_4 (readily separated from aqueous solutions, and also obtained by sintering equivalent quantities of 2MeF and BeF_2 ([10])) was first obtained as early as 1944 by Mukherjee ([9]) (from $RbNO_3$ and $(NH_4)_2BeF_4$). The crystals of γ-Rb_2BeF_4 are elongated along the axis [001] and have a characteristic tabular pseudohexagonal habit. The low refractive index of the biaxial (with a large angle of the optical axes), transparent and colorless specimens was determined by immersion: $N_{cp} = 1.383$; the specific gravity (pycnometer) is 3.64. Rb_2BeF_4 is characterized by distinct cleavage along (010) and a strong tendency to twin along (110) ([9]).

Among a small number of single crystals of Rb orthofluoroberyllate kindly provided by P. G. Grebenshchikov and N. A. Toropov, it was possible to select three almost isometric, unbounded fragments with dimensions $0.3 \times 0.3 \times 0.1$ mm. The parameters of the rhombic cell are: $a = 7.66$ Å, $b = 5.86$ Å, $c = 10.11$ Å; $Z = 4$, which are in good agreement with those given previously in ([2,10])

and differ somewhat from those for K_2BeF_4 ([11]). For the structure determination, three zero-level goniometric layer-line photographs around the axes a, b, c and one nonzero layer-line photograph $h1l$ were used (Mo$K\alpha$ radiation, $\max(\sin\theta/\lambda) = 0.720$ Å^{-1}). Statistical analysis of the structure factors F^2_{h1l} selected, fairly unambiguously, from the two Fedorov groups possible in the X-ray group $mmmPn - a$, the acentric $C^9_{2v} = Pn2_1a$.

The absence, in the Patterson projection $p(vw)$, of peaks along the axis $0v0$ made improbable the mirror plane m perpendicular to the y axis, and served as another confirmation of the absence of a center of symmetry.

Two crystallographically distinct heavy Rb atoms ($Z = 37$) were fixed unambiguously from the Patterson projections $p(uw)$ and $p(vw)$. Subsequent application of the heavy-atom method made it possible to locate all F atoms ($Z = 9$).

The coordinates of the independent atoms, refined by difference Fourier syntheses, at the final values of the discrepancy factor $R_{hol} = 13\%$ and $R_{0kl} = 8.9\%$, are given in Table 1 (the temperature coefficients B are respectively 1.0 Å^{-2} and 0.9 Å^{-2}).

In ordinary Be tetrahedra ([6,11,12]) the Be–F distances agree well with those known previously: 1.45-1.53 Å. The edges of these tetrahedra, F–F, likewise do not fall outside the normal limits: 2.42-2.50 Å.

In the recently solved structure of K orthofluoroberyllate ([11]), fairly convincing evidence was given that K_2BeF_4 is a fluoroberyllate model (according to Goldschmidt–Fersman ([7,8,13])) of the structure of the energy-cementing Ba orthosilicate Ba_2SiO_4. This model character (analogously to the better-known pair $KMnO_4$–$BaSO_4$) corresponds well to the ionic radii according to Ahrens ($r_K = 1.33$, $r_{Ba} = 1.34$ Å) ([14]), whereas according to Goldschmidt the larger Rb should have been regarded as the monovalent model for Ba (according to Goldschmidt $r_{Rb} = 1.49$ Å, $r_{Ba} = 1.43$ Å). And indeed, as was pointed out in ([6]), the model relation according to Goldschmidt is not fulfilled for the pair $BaSi_2O_5$–$RbBe_2F_5$ either (according to Ahrens $r_{Rb} = 1.47$ Å, $r_{Ba} = 1.34$ Å). Replacement of K ($r_K = 1.33$ Å) by the larger Rb ($r_{Rb} = 1.49$ Å) in the structure of Rb orthofluoroberyllate led, at first glance, to a paradoxical result: if Rb_2 (analogous to K_2 in K fluoroberyllate) is also placed in an eight-vertex polyhedron, then the other–Rb_1–is found in a distorted octahedron, whereas in K_2BeF_4 the atom K_1, like K_2, has 8-fold coordination. In the Rb_2 eight-vertex polyhedron all eight cation–anion distances deviate from the mean 2.78 Å

Fig. 1. Rb orthofluoroberyllate. Ribbons of Rb polyhedra of two kinds: eight-vertex polyhedra in the core of the ribbon and irregular octahedra on the teeth

Table 1

Figure 2

Figure 1: Figure 2

Atoms	x/a	y/b	z/c	Atoms	x/a	y/b	z/c
Rb_1	0.159	0.253	0.091	F_2	0.276	0.016	0.343
Rb_2	0.512	0.742	0.193	F_3	0.533	0.840	0.094
Be	0.235	0.249	0.402	F_4	0.793	0.252	0.956
F_1	0.313	0.442	0.333				

by less than 0.20 Å (2.61-2.96 Å), but the edges of the eight-vertex polyhedron F–F vary over wide limits: from 2.50 (the edge common with the BeF_4 tetrahedron) to 4.84 Å.

In the Rb_1 octahedron, six Rb–F distances remain within narrow limits of about 3.00 Å, with the F–F edges of the distorted octahedron ranging from 2.61 to 5.20 Å (the seventh and eighth anions with $d > 3.10$ Å we excluded from the first coordination sphere).

The not very substantial difference only in the M_I polyhedra ([11]) did not lead to significant structural changes in the motif of γ-Rb_2BeF_4 in comparison with the motif in K_2BeF_4.

Although the ionic radius of Rb is greater than that of K (by approximately 10%) and substantially exceeds (almost twofold) the ionic radius of the cation Mg, which is the principal one in olivine (Mg_2SiO_4), the olivine features of K_2BeF_4 are preserved here as well: the relatively more compact Rb_2 polyhedra, joining by faces, form the principal core of the olivine-like ribbon (Fig. 1), while the looser

Rb_1 octahedra form its serrations. Mutual linkage of the ribbons is achieved through the vertices of octahedra located along their serrations.

In accordance with the smaller coordination number, the Rb_1 octahedra on the serrations can be attached to the polyhedra of the main backbone of the ribbon only along one face, but not along two, as was the case for K_1 in K_2BeF_4.

Fig. 2. Alternation, in the Rb_2SO_4 motif, of Rb polyhedra and SO_4 tetrahedra

Comparison of the crystal structure of γ-Rb_2BeF_4 with the previously determined (from powders) structures of Rb_2SO_4 and Rb_2CrO_4 ([15], [16]) makes it possible to develop the earlier considerations ([11]) concerning the prevailing role of large cations M in the microarchitecture of the structure M_2BX_4, with a passive role of the complex "anion" BX_4.

Fig. 3. MII backbones in ribbons of M_2BX_4 structures: **a** –Rb_2SO_4 and **b** –Rb_2BeF_4; and chains of MI polyhedra that determine the connection of ribbons with one another: **c** –Rb_2SO_4 and **d** –Cs_2SO_4

Figure 3

Figure 2: Figure 3

As in Rb_2SO_4, so also in Rb_2CrO_4, the cation MII(Rb_2) is not located in the eight-vertex polyhedron that has already become familiar to us, but in a seven-vertex polyhedron at an average distance MII–X = 2.90 Å (anions farther away than $d > 3.20$ Å we excluded from the coordination sphere), and it is precisely these seven-vertex polyhedra (the tendency of Rb toward sixfold coordination is apparent; cf. $RbBe_2F_5$ ([6])) that constitute the backbone of the ribbon (Fig. 3, a). On the serrations of the ribbon (Fig. 3, b) there are loose Rb_1 nine-vertex polyhedra (average $d = 3.17$ Å).

Within the mirror plane (all the compounds indicated belong to the space group *Pnma*) translationally identical ribbons are connected already along the edges of these nine-vertex polyhedra, whereas in K_2BeF_4 and γ-Rb_2BeF_4 they are connected only through vertices. A decrease in the coordination number

For the MII cation somewhat activates the BX4 complexes: the connection of the ribbon rods, located at different levels (0.25 and 0.75), is accomplished by means of SO4 and CrO4 tetrahedra (Fig. 2).

On the whole, however, we see an almost complete similarity of the structural motifs of all three Rb compounds, despite the chemical dissimilarity of the B cation; and in the series Rb2BeF4 –Rb2SO4 –Rb2CrO4 one may a priori expect, if not mixed solid solutions, then at least epitaxial two-dimensional ones.

The transition to the larger monovalent cation Cs (Cs2SO4, CsCrO4) (17, 18) is of interest from the point of view of establishing the upper limits of preservation of the structural motif: a) upon further replacement of the cation M in the series: K ($r_K = 1.33$ Å), Rb ($r_{Rb} = 1.49$ Å), Cs ($r_{Cs} = 1.65$ Å), with one and the same central (in the tetrahedron) atom, and b) upon changing this central atom (Be $\rightarrow$ S $\rightarrow$ Cr).

Consideration of the nearest anionic environment of the loose cation Cs makes it possible to distinguish a group of five O atoms, which are situated at distances close to the sum of the ionic radii $r_{Cs} + r_O = 3.01$ Å. The presence of such a "first" coordination group of five anions is characteristic both for Cs2 (2.75–3.10) and for Cs1 (2.87–3.10 Å).

Coordination five is very meager for large Cs, and more distant anions also have to be brought in to complete the coordination sphere. For Cs2 these are three O atoms at distances of 3.30–3.52 Å, and for Cs1 –five with distances of 3.36–3.59 Å in the structure of Cs2SO4 and 3.25–3.83 Å in the chromate Cs2CrO4.

A considerable increase of the coordination number to 10 (Fig. 3a) nevertheless does not lead to a change in the basic olivine-like motif, despite the very greatly increased radii from Mg to Cs.

Institute of Crystallography
Academy of Sciences of the USSR

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Note: Figure translations are in progress. See original paper for figures.