CRYSTAL STRUCTURE OF RUBIDIUM DI(META)-FLUOROBERYLLATE $\mathrm{RbBe_2F_5}$

1961

SovietRxiv

Fig. 1. Crystal structure (plan) of Rb-di(meta)-fluoroberyllate with alternating layers (of the brucite type) of Rb octahedra and pseudohexagonal nets $[Be_2F_5]_{\infty,\infty}$. The pseudo-orthorhombic cell and the pseudohexagonal primitive cell are indicated.

Figure 1: Fig. 1. Crystal structure (plan) of Rb-di(meta)-fluoroberyllate with alternating layers (of the brucite type) of Rb octahedra and pseudohexagonal nets $[Be_2F_5]_{\infty,\infty}$. The pseudo-orthorhombic cell and the pseudohexagonal primitive cell are indicated.

Abstract

Full Text

CRYSTALLOGRAPHY

V. V. ILYUKHIN and Academician N. V. BELOV

CRYSTAL STRUCTURE OF RUBIDIUM DI(META)-FLUOROBERYLLATE $RbBe_2F_5$

The study of the composition, properties, and fine structure of fluoroberyllate systems and of their particular representatives is of great importance not only in connection with the practical use of individual compounds for obtaining pure metals and their alloys, but also because of the peculiar, more narrowly scientific interest which fluoroberyllates have, according to Goldschmidt—Fersman, as "weakened models" of silicates. In these models such a fundamental drawback of silicates—for analytical and physical chemistry—as insolubility in water and in the simplest solvents recedes into the background or disappears altogether.

Fig. 1. Crystal structure (plan) of Rb-di(meta)-fluoroberyllate with alternating layers (of the brucite type) of Rb octahedra and pseudohexagonal nets $[Be_2F_5]_{\infty,\infty}$. The pseudo-orthorhombic cell and the pseudohexagonal primitive cell are indicated.

Of the series of known ortho-, meta-, and di(meta)-fluoroberyllates* the least studied remain the latter, with the formula $MeBe_2F_5$, where Me denotes alkali elements: Li, Na, K, Rb, Cs. Up to now it has not been possible (^{1}) to obtain the Li and Na compounds in quantities and in sufficiently pure form to permit their X-ray study; moreover, the Li-, Na-, and K-compounds decompose before the melting point (^{2}), and thus one can deal only with the Rb- and Cs-di(meta)-fluoroberyllates.

Most reports on fluoroberyllate systems come from the Moscow laboratory of A. V. Novoselova ($^{2-4}$) and the Leningrad laboratory of N. A. Toropov and R. G. Grebenshchikov ($^{1,5-7}$). The latter kindly placed at our disposal mica-like single-crystal plates of $RbBe_2F_5$.

Fig. 2. Frontal projection (onto the xz plane) of the structure of $RbBe_2F_5$

Figure 2: Fig. 2. Frontal projection (onto the xz plane) of the structure of $RbBe_2F_5$

The crystals are biaxial, with the low refractive indices characteristic of fluoroberyllates: $N_{\text{av}} = \frac{1}{2}(N_g + N_p) = 1.332$ (^{7}), with very small birefringence ($\simeq 0$). The crystallographic study revealed perfect cleavage along (001) and, in this plane (001), striation at an angle of 120°, with which the pseudohexagonality characterizing the morphology of the crystals is evidently associated. The specific gravity is 2.809 (pycnometric). The crystals are slightly hygroscopic and on heating undergo polymorphic transformations (^{1}). The γ-modification of $RbBe_2F_5$, stable under ordinary conditions, is characterized by a tendency toward polysynthetic twinning.

Initially the crystals were assigned monoclinic symmetry $2/m\,C--/--$ (three possible space groups: $C\,2/m$, $C\,2$, Cm). A cell with parameters $a = 7.99$ Å; $b = 4.70$ Å; $c = 6.12$ Å; $\beta \simeq 90°$ ($a : b = 1.71 \simeq \sqrt{3}$) contains 2 formula units of $RbBe_2F_5$.

However, the absence of planes (lines) of symmetry on the x-ray goniometric photographs of the side zones $0kl$ and $hk0$ indicated a lower symmetry—triclinic. The corresponding—refined—cell in the same setting C (which was retained because of the closeness of three angles to 90°) is characterized by the parameters: $a = 7.98$ Å, $b = 4.69$ Å, $c = 6.12$ Å, $\alpha = 89°40'$, $\beta = 91°$, $\gamma = 90°27'$ ($a : b \simeq \sqrt{3}$). Reduction to the standard (according to Delaunay and the International Tables (^{8})) cell with three obtuse angles gives $a = 4.69$ Å, $b = 4.61$ Å, $c = 6.12$ Å, $\alpha = 90°27'$, $\beta = 90°20'$, $\gamma = 120°48'$; $a \simeq b$, $\alpha \simeq \beta \simeq 90°$, $\gamma \simeq 120°$, i.e., the pseudo-orthohexagonal cell is replaced by a pseudohexagonal primitive one.

Fig. 2. Frontal projection (onto the xz plane) of the structure of $RbBe_2F_5$

The presence of the piezoelectric effect and the statistical analysis of the structure factors (^{9}) (which led to a non-centrosymmetric distribution in two projections, yz and xz) exclude all symmetry groups except $P1$ (or $C1^1$ in the adopted pseudo-orthohexagonal setting).

A direct consequence of the non-centrosymmetric arrangement of the atoms, with a comparatively small deviation from centrosymmetric, were the diffuse peaks in the Patterson syntheses $p(xz)$ and $p(yz)$. The method of integral characteristics (^{10,11}), as applied to the two-dimensional Patterson function,

---

* Compounds with the radical Be_2F_5 are now called difluoroberyllates by chemists; however, mineralogists prefer to call compounds with Si_2O_5 dimetasilicates, deriving their formation from metasilicate radicals SiO_3 according to the equation $2SiO_3 - O = Si_2O_5$.

Fig. 3

Figure 3: Fig. 3

made it possible first to identify part of the Rb—F peaks and then the remaining ones, and thereby led to approximate coordinates of Rb and F.

The difference Patterson synthesis (projection xz), in which only the maxima Rb—Be and F—Be should remain, made it possible to determine the coordinates of two kinds of Be atoms. Refinement was carried out by successive syntheses of electron density for the non-centrosymmetric projections xz and yz.

Table 1

Coordinates of the basis atoms* in the structure of $RbBe_2F_5$

Atoms	x	y	z	Atoms	x	y	z
Rb	0	0	0	F_4	25.0	33.4	52.5
F_1	16.7	49.4	17.5	F_5	31.9	00.4	80.0
F_2	-2.5	49.5	47.0	Be_I	15.0	54.5	41.3
F_3	20.0	83.4	46.7	Be_{II}	31.0	5.0	56.3

* In hundredths of the cell axes.

Table 1 gives the coordinates of 7 basis atoms (21 parameters) for the cell $C1$. The accuracy of determining some coordinates was limited by

taking into account the overlap of peaks and the absence of a center of symmetry in the structure. Discrepancy coefficients: $R_{h0l} = 11.5\%$ (88 nonzero reflections); $R_{0kl} = 11.7\%$ (58 nonzero reflections).

In the tetrahedra BeF_4, which did not give rise to doubt, the interatomic distances do not go beyond the limits Be—F = 1.43-1.48 Å; F—F = 2.33-2.41 Å. In the likewise clearly distinguished RbF_6 octahedra, the Rb—F distances remain within the narrow limits 2.82-3.08 Å, but the octahedra themselves are flattened (Fig. 3) along the pseudohexagonal axis (cf. the Ca-octahedra in milarite [12]), and therefore the edges of the octahedra split into two kinds: horizontal, 4.61-4.69 Å, and lateral, 3.55-3.6 Å. Within each group, the distances thus remain within very narrow limits.

Fig. 3. Agreement in the motif of $RbBe_2F_5$ of Rb-octahedra with “diorthogroups” of two Be-tetrahedra

In accordance with the principles of the crystal chemistry of silicates that are being developed in our laboratory [13], the basis of the structure of Rb-difluoroberyllate should be considered to be a close-packed brucite-like (phlogopite-like) layer of Rb-octahedra parallel to (001). In the (centered) pseudoorthohexagonal cell such a layer is represented by only two Rb atoms

Fig. 4

Figure 4: Fig. 4

—one at the vertices of the cell and the other at its center (Fig. 1). Identical brucite-like layers are separated from one another along the z axis by the translation $c = 6.12$ Å (Fig. 2).

Between the layers of Rb-octahedra extends a net of fluoroberyllate tetrahedra with a hexagonal motif, which in projection corresponds completely to the well-known silica-oxygen nets in sheet silicates, in particular in phlogopite. But whereas in sheet di-(meta)-silicates the nets of Si-tetrahedra are usually polar and their tetrahedra, by their vertices, point only in one direction toward the layer of octahedra, in Rb-di(meta)-fluoroberyllate the nets are two-sided and are connected at once with two brucite-like layers of octahedra (Fig. 2). Each six-membered ring in the net consists of tetrahedra of the "dioptase type" [14], i.e., three of its tetrahedra point in one direction along the z axis, and three in the other.

Thus, in the fluoroberyllate analogue—the model of a di(meta)-silicate—there are no layers of empty polyhedra that are so characteristic of talc, kaolinites, and chlorites in general, nor the layers, characteristic of micas, of very sparsely populated octahedra with alkali cations. The perfect cleavage of fluoroberyllate is evidently associated with the weakness of the bonds in the octahedra around the large but loose (small charge, large radius) Rb cation. The striation in the cleavage planes in three directions, parallel to the three directions of columns of octahedra that can be distinguished in the close-packed brucite-like layer, indicates a cleavage break precisely along these layers [15].

Fig. 4. Projection xz of the structure of sanbornite $BaSi_2O_5$. Cells with the origin at a Ba atom and at a center of symmetry are indicated

A layer of tetrahedra pointing in two directions along the pseudohexagonal axis can hardly be called two-storied; it is rather one-and-a-half-storied—

···with which the size c in the fluoroberyllate is considerably reduced in comparison with c in typical three-story dimetasilicates (6.12 Å as against ~ 7.0 Å).

As indicated above, the fluoroberyllate net characteristic of $RbBe_2F_5$, in projection, does not differ from all known silica nets of the pseudohexagonal type. These same nets are usually represented as the product of condensation of metasilicate—pyroxene—chains. But in the latter all tetrahedra face in one direction toward the (brucite) layer of octahedra, whereas in the chain $[BeF_3]_\infty$ that can be singled out from the net in $RbBe_2F_5$, the tetrahedra alternately face in different directions. This apparently minor difference, in addition to the fact that it allows the net of tetrahedra to be bonded at once with two layers of octahedra, acquires profound meaning in the light of the ideas of the second chapter of *Crystal Chemistry of Silicates* [13], in which not a single SiO_4 tetrahedron is usually associated with the edges of large cations (even if it has been cut out of a chain), but rather a pair of tetrahedra—the Si_2O_7 group. In Fig. 3 it is easily established that above one edge in the lid of the large Rb octahedron (with length $a = 4.69$ Å) there are indeed two Be tetrahedra (or, according to Goldschmidt, the edge of the Rb octahedron is commensurate with twice the edge of the Be tetrahedron). Thus the structure of $RbBe_2F_5$ is a model of a silicate from the second chapter of *Crystal Chemistry of Silicates*. Turning to the well-known representations of sheet silicates, for example phlogopite, we shall see that in the latter, for one silica ring there are, in the corresponding layer, three Mg octahedra, whereas in $RbBe_2F_5$, for one fluoroberyllate ring (of the "dioptase" type) there is only one Rb octahedron.

In the preceding account we compared the only known di(meta)-fluoroberyllate by structure with the only Goldschmidt-Fersman di(meta)-silicates known, namely with micas and chlorites, and therefore the structures being compared differed in their formulas. A formal analogue of $RbBe_2F_5$ is the recently investigated sanbornite $BaSi_2O_5$ [16], and indeed a considerably greater similarity may be noted between them, although one cannot speak of an analogy. In sanbornite, despite its smaller radius, Ba has sevenfold coordination, and already the layers of Ba polyhedra are wavy. The half-period along the z-axis, $c/2 = 6.77$ Å, differs comparatively little from the period c in the fluoroberyllate, and in the silicate we likewise have a net $[Si_2O_5]_{\infty,\infty}$, linking the upper Ba layer with the lower one, i.e., the silica net is also wavy; but in each of its six-membered rings (Fig. 4) four Si tetrahedra face to one side and two to the other (in the adjacent ring, conversely). In such a wavy silica net, the diorthogroups Si_2O_7 characteristic of the second chapter of *Crystal Chemistry of Silicates* are especially sharply distinguished, and the whole net is characterized not by hexagonal but by rectangular rhombic symmetry.

Received
14 VII 1961

CITED LITERATURE

1. N. A. Toropov, R. G. Grebenshchikov, ZhNKh, 6, 4, 920 (1961).
2. A. V. Novoselova, *Usp. khim.*, 28, 33 (1959).
3. A. V. Novoselova, Yu. P. Simanov, E. I. Yarembash, ZhFKh, 26, 9, 1245 (1952).
4. O. N. Breusova, A. V. Novoselova, Yu. P. Simanov, DAN, 118, 935 (1958).
5. N. A. Toropov, R. G. Grebenshchikov, ZhNKh, 1, 12, 2686 (1956).

6. N. A. Toropov, R. G. Grebenshchikov, ZhNKh, 1, 7, 1619 (1956).
7. R. G. Grebenshchikov, DAN, 114, 316 (1957).
8. V. N. Delaunay, *Zs. Kristallogr.*, 84, 132 (1933); *Intern. Tables for X-Ray Crystallogr.*, 1, 1952, p. 530.
9. G. A. Sim, *Acta Crystallogr.*, 11, 123 (1958).
10. B. K. Vainshtein, ZhETF, 27, 44 (1954).
11. V. V. Ilyukhin, S. V. Borisov, *Zhurn. strukturn. khim.*, 1, 1, 80 (1960).
12. N. V. Belov, T. N. Tarkhova, DAN, 69, No. 3 (1949); *Tr. Inst. kristallogr.*, issue 6, 83 (1951).
13. N. V. Belov, *Crystal Chemistry of Silicates with Large Cations*, Second Lecture in Memory of V. I. Vernadsky, Publishing House of the Academy of Sciences of the USSR, 1961.
14. N. V. Belov, V. P. Butuzov, N. I. Golovastikov, DAN, 87, No. 6 (1952).
15. N. V. Belov, *Structure of Ionic Crystals*, Publishing House of the Academy of Sciences of the USSR, 1947.
16. R. M. Douglass, *Am. Miner.*, 43, 517 (1958).

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.