CRYSTALLOGRAPHY

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Abstract

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CRYSTAL STRUCTURE OF Na ORTHOFLUOROBERYLLATE

γ-Na_2BeF_4

Recently in our laboratory ([1,2]) the structures of the alkali orthofluoroberyllates K_2BeF_4 and Rb_2BeF_4 were solved, and it was shown that both can indeed serve, according to Goldschmidt-Fersman ([3,4]), as model structures for orthosilicate Ba_2SiO_4, the K compound being quite close, while the Rb compound is somewhat distorted. In the solved structures—very probably in Ba_2SiO_4 and presumably in Sr_2SiO_4*—an olivine-like (Mg_2SiO_4) motif is well expressed, but with considerable deviations—distortions associated with the "large size" of the cations K and Rb, and also Ba, in comparison with Mg. As for the Ca orthosilicate of analogous formula, namely Ca_2SiO_4, three modifications are known for it, one of which—larnite, γ-Ca_2SiO_4—repeats the olivine structure especially accurately: Ca in it is located in octahedra, and the environment of each O^{2-} anion strictly corresponds to the olivine environment, despite the increase in the size of the Ca octahedron with the standard dimensions of the $[SiO_4]$ tetrahedron.

In accordance with this, solving the structure of γ-Na_2BeF_4 is of interest; as Table 1 shows (the ionic radii of "parallel" atoms are given according to Goldschmidt and, in parentheses, according to Ahrens; the latter have better justified themselves in comparing Ba_2SiO_4 with the models K_2BeF_4 and Rb_2BeF_4), it should be a perfect model of the structure of Ca orthosilicate.

Table 1

Na^+	Be^{2+}	F^-	Ca^{2+}	Si^{4+}	O^{2-}
0.98(0.97)	0.35(0.34)	1.33(1.33)	1.04(0.99)	0.39(0.42)	1.32(1.32)

The absence of direct structural data for γ-Na_2BeF_4 is connected with the great difficulty of obtaining single-crystal samples. It should be noted, however, that on the basis of Debyegrams, using the closeness of the unit-cell parameters, the authors ([6]) came to the conclusion that the structure of γ-Na_2BeF_4 is built according to the olivine type. We obtained the possibility of directly solving the structure thanks to the kindness of B. P. Sobolev and Yu. P. Dikov, who placed

Fig. 1. Crystal structure of γ-Na_2BeF_4 on the (001) plane

Figure 1: Fig. 1. Crystal structure of γ-Na_2BeF_4 on the (001) plane

at our disposal single crystals of Na orthoberyllate—the product of hydrothermal synthesis. Of the three modifications $(\gamma-, \delta-, x)$ of Na_2BeF_4, the rhombic γ-phase seemed the most promising with respect to model connection with larnite (δ is trigonal and x is monoclinic). Among the large mass of crystalline γ-Na_2BeF_4, it was nevertheless possible to isolate only one crystallite, of tenths-of-a-millimeter dimensions, suitable for single-crystal photography. With Laue class mmm, the cell parameters $a = 10.181$ Å, $b = 5.61$ Å, $c = 4.447$ Å do not agree with previously published data ($^{6-8}$). A density of 2.48 corresponds to a content in the cell of $Z = 4$ formula units. The X-ray group $mmm\,Pn{-}a$, following from systematic absences, covers two Fedorov groups: $Pnma$ and $Pn2_1a$, of which the acentric $Pn2_1a$ was chosen, since in the final result it made it possible to reduce the discrepancy factor R to a significantly better value.

In the reduced symmetry, the first relatively significant difference from γ-Ca_2SiO_4 appeared; this seemed interesting to us in connection with the previously noted "fundamental" asymmetry of the tetrahedral Be atoms as compared with Si (^{9}). At the same time, lowering the symmetry led to an increase in the number of structural parameters (20 in γ-Na_2BeF_4, as compared with 9 in the olivine structure of γ-Ca_2SiO_4).

For the initial determination of the structure, it proved sufficient to have two zero-level photographs $hk0$ and $h0l$ with intensities measured from blackening marks (interval $\sqrt[4]{2}$, Mo K_α radiation, $(\sin\theta/\lambda)_{\max} = 0.84$ and 1.02 Å^{-1} on the two photographs).

An attempt to determine the signs of the structure amplitudes by direct methods gave no results because of the small number of independent reflections (in the orthorhombic structure there are, *a priori*, half as many of them as in the monoclinic one). The solution was found from analysis of Patterson maps, supported by the expected rough analogy with the motif of γ-Ca_2SiO_4. The latter was important in distinguishing Na atoms from (isoelectronic in the ionic state) F atoms. The principal points were the fixing of two Na atoms, first in the acentric projection $hk0$ and then in the centrosymmetric $h0l$, followed by further determination of the F atoms up to the identification of the lightest atom, Be. The final discrepancy factors were: $R_{hk0} = 11.2\%$ $(B = 0.35)$ and $R_{h0l} = 12.6\%$ $(B = 0.5)$.

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* Infrared spectral data do not allow the structures of Sr_2SiO_4 and Ba_2SiO_4 to be fully identified (^{5}).

Fig. 2. Crystal structure of γ-Na_2BeF_4 in polyhedra

Figure 2: Fig. 2. Crystal structure of γ-Na_2BeF_4 in polyhedra

Fig. 3. Ribbons of Na_1 (a) and Na_2 (b) in the structure of γ-Na_2BeF_4.

Figure 3: Fig. 3. Ribbons of Na_1 (a) and Na_2 (b) in the structure of γ-Na_2BeF_4.

Fig. 1. Crystal structure of γ-Na_2BeF_4 on the (001) plane

Fig. 2. Crystal structure of γ-Na_2BeF_4 in polyhedra

The adopted coordinates are given in Table 2.
The interatomic distances corresponding to these coordinates are:
Be—F = 1.46-1.55 Å, with edges of the Be tetrahedron F—F = 2.48-2.57 Å.

Table 2

Atoms	x/a	y/b	z/c	Atoms	x/a	y/b	z/c
Na_I	0.000	0.002	0.020	F_{II}	0.158	0.473	0.749
Na_{II}	0.233	0.748	0.503	F_{III}	0.083	0.259	0.276
Be	0.172	0.238	0.646	F_{IV}	0.059	0.732	0.750
F_I	0.158	0.033	0.751				

The Na—F distances are close to the mean value (Na—F = 2.08—2.18 Å), 2.13 Å.

It is convenient to compare the structures of orthofluoroberyllates Na_2BeF_4 with Ca-orthosilicates, since between Ca_2SiO_4 and artificial Na_2BeF_4 there exists (according to the literature data) isotypism in all modifications ([8]).

With such a consideration, for γ-Na_2BeF_4 (Fig. 1) we arrive at the classical description of the olivine structure ([10–12]). The basis of the structure of γ-Na_2BeF_4 is a closest double-layer packing of F atoms, in which 1/2 of the octahedral voids are occupied by Na and 1/4 of the tetrahedral voids by Be.

Fig. 3. Ribbons of Na_1 (a) and Na_2 (b) in the structure of γ-Na_2BeF_4.

It is clear that the very similar structural parameters of $[SiO_4]$ and $[BeF_4]$ should not cause any special changes in the structural motif, but the replacement of Mg (0.74) by the comparatively large Na (0.98) would seem, to some extent, to have had to affect the general structural motif in γ-Na_2BeF_4. However, in contrast to larger cations (K, Rb, Cs, ⋯), which require an increase in coordination numbers (up to 9), in the structure of γ-Na_2BeF_4 the coordination number of the large Na remains equal to 6. Possibly for this reason, no "defects" characteristic of olivine are observed in the structure of γ-Na_2BeF_4 (as is evidenced by the F—F distances).

In the structure, two types of Na-octahedra are clearly distinguished (Fig. 2). Octahedra of Na_I are situated as if isolated at the beginning and at 1/2a, being joined by $[BeF_4]$-tetrahedra (Fig. 3a), and play a cementing role between ribbons of Na_{II} octahedra running parallel to the c axis (Fig. 3b).

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