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Abstract

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CRYSTAL STRUCTURE OF K-FLUOROBERYLLATE

$K_2BeF_4(Ba_2SiO_4)$

The extremely small size of crystals of cement silicates—which, probably, is also connected with their cement activity—has until now precluded the possibility of their structural study by the single-crystal method. In particular, until now we have not had a solved structure for the very simple and active cement compound Ba_2SiO_4. It was natural to turn to Goldschmidt' s "lightened" models of silicates, namely fluoroberyllates (^{1,2}), in the present case to K_2BeF_4, which most fully satisfies Goldschmidt' s "requirements" (Table 1).

Table 1

Ions	r, Å	Ions	r, Å
K^{1+}	1.33	Ba^{2+}	1.38
Be^{2+}	0.34	Si^{4+}	0.39
F^{1-}	1.33	O^{2-}	1.36

The closeness of the structures of these compounds was confirmed from powder data (^{3}) as early as 1942, but only recently did we obtain from B. P. Sobolev a considerable mass of crystalline K-fluoroberyllate, from which it was possible to select plates of size $\sim 0.3\times0.3\times0.1$ mm^3, suitable for single-crystal photography. It should be noted that within the specified mass of K_2BeF_4, needle-like and platy individuals occurred with equal frequency, but both morphological types gave identical Debyegrams.

The experimental material for the structural investigation consisted of rotation X-ray photographs about three axes of the orthorhombic crystal K_2BeF_4 and goniometric scans of three zero-layer lines. In all cases Mo K_α radiation was used.

The Laue class mmm and the cell parameters fixed by us,

$$a = 7.35\ \text{Å}, \quad b = 5.75\ \text{Å}, \quad c = 9.91\ \text{Å}$$

are in good agreement with the previous results (^{3}). With a specific gravity equal to 2.63, the cell contains 4 formula units ($z = 4$). The X-ray group $mmmPn{-}a$, following from the systematic extinctions, includes two Fedorov groups: the holohedral *Pnma* and the acentric $Pn2_1a$. The absence in the projection vw of peaks on the line $0v0$ immediately made the mirror plane $m = (010)$ doubtful. The final choice in favor of the acentric group $Pn2_1a$ was the result, at the concluding stage of analysis, of a comparison of the discrepancy factors of two close models for both projections $h0l$ and $0kl$: the *Pnma* variant gave 28 and 30%, and the $Pn2_1a$ variant 15.1 and 12.3%, respectively.

For solving the structure, two zero-layer scans, $h0l$ and $0kl$, proved sufficient, with intensities estimated by the now-routine method of blackening marks with a step of $\sqrt[4]{2}$ ($\max \sin\vartheta/\lambda = 0.783$ and 0.672 Å^{-1} for the two scans).

From the Patterson maps uw and vw it was possible to establish the coordinates of the heavier K atoms. The successive application of the heavy-atom method first in the centrosymmetric projection xz, and then also in the acentric yz, with the complications created by the absence of a center of symmetry in the structure ([4–8]), made it possible, from a series of syntheses of electron density, checked by Patterson maps, to localize all F and to refine the two sorts of K atoms. The lighter Be atoms were determined from difference Fourier syntheses.

Table 2 gives the refined coordinates of 7 independent atoms (20 parameters) of the structure at the indicated discrepancy factors. The temperature factors were $B = 1.1$ Å and $B = 0.6$ Å (for the projections $h0l$ and $0kl$, respectively).

The interatomic distances in Be-tetrahedra calculated from the coordinates in Table 2 do not go beyond the known limits: Be—F = 1.46-1.55 Å and F—F = 2.38-2.53 Å.

Among the 8 distances K_2—F, one is short, 2.42 Å, 6 are intermediate, equal to 2.67-2.85 Å, and one is longer, 2.96 Å. The mean K—F = 2.76 Å.

Similarly, for the K_1-polyhedron, 7 K—F distances are close to the mean, equal to 2.91 Å (2.86-3.00 Å), and one is shorter—2.69 Å. However, the K_1-polyhedron itself is looser than the eight-vertex polyhedron around K_2. The edge lengths of the K_1- and K_2-polyhedra vary over wide limits from 2.51 to 4.96 Å. The short edges are those which simultaneously are edges of the BeF_4-tetrahedra.

Table 2

Atoms	x	y	z
K_1	0.160	0.252*	0.088
K_2	0.0125	0.753*	0.307
Be	0.231	0.253	0.414
F_1	0.315	0.447	0.343
F_2	0.263	0.015	0.342
F_3	0.0257	0.266	0.414
F_4	0.200	0.758	0.055

Fig. 1. Crystal structure of olivine Mg2SiO4. Basic motif of distorted octahedra of two sorts: centrosymmetric along the axis of the ribbon and with a symmetry plane on the teeth

Figure 1: Fig. 1. Crystal structure of olivine Mg2SiO4. Basic motif of distorted octahedra of two sorts: centrosymmetric along the axis of the ribbon and with a symmetry plane on the teeth

Fig. 2. K-fluoroberyllate. Ribbon of large K-polyhedra of two sorts: axial—more distorted eight-vertex polyhedra—and fairly regular seven-coordinated cubes on the teeth

Figure 2: Fig. 2. K-fluoroberyllate. Ribbon of large K-polyhedra of two sorts: axial—more distorted eight-vertex polyhedra—and fairly regular seven-coordinated cubes on the teeth

* These "exact" parameter values are a consequence of the choice of origin (with an arbitrary, for this group, y coordinate) in the pseudocenter of symmetry determined by the holohedral group $P\,nma$.

It is convenient to describe the structure of K_2BeF_4 (Ba_2SiO_4) by comparing it with the well-known orthosilicate motifs of forsterite (olivine) Mg_2SiO_4 and low-temperature γ-Ca_2SiO_4.

In an ideal representation, the olivine structure is a closest hexagonal (two-layer) packing of O atoms, in which half of the octahedral voids are occupied by Mg (Fe) and one quarter of the tetrahedral voids by Si. Because of the comparatively large size of the Mg cations, its octahedra are considerably distorted, as shown in Fig. 1, where in the serrated ribbon motif the division of Mg-octahedra into two sorts is clearly evident: centrosymmetric ones in the middle row and those with a mirror plane on the teeth.

Fig. 1. Crystal structure of olivine Mg_2SiO_4. Basic motif of distorted octahedra of two sorts: centrosymmetric along the axis of the ribbon and with a symmetry plane on the teeth.

Fig. 2. K-fluoroberyllate. Ribbon of large K-polyhedra of two sorts: axial —more distorted eight-vertex polyhedra and fairly regular seven-coordinated cubes on the teeth.

The clearly distinguished triangular pits serve as bases for the Si-tetrahedra, while the vertices of these tetrahedra rest on the no less clearly distinguished junctions of three octahedra. The same basic motif of serrated ribbons is preserved also in K_2BeF_4 (Ba_2SiO_4), which is analogous in gross formula but more "large-cationic" ; in the ribbon (Fig. 2) two sorts of K-polyhedra also appear: central (K_2) and on the teeth (K_1). Both are correspondingly greatly enlarged because of the size of the K (Ba) cation in comparison with Mg (with BeF_4-tetrahedra approximately the same as SiO_4-tetrahedra). The increase

Figure 3

Figure 3: Figure 3

Figure 4

Figure 4: Figure 4

the coordination number is achieved in an obvious way: F atoms from the teeth of neighboring ribbons take part in the environment of K (the polyhedron itself is looser), and by this the outer K_1-polyhedra are transformed into fairly regular geometrical figures—Thomson (twisted) cubes with only very slightly broken (along intersecting diagonals) square bases. In Fig. 2, with the line of sight parallel to the *b* axis, the junctions of three K-polyhedra, into which the vertices of BeF_4-tetrahedra abut, stand out clearly (cf. the structure of Mg_2SiO_4). On comparison with Fig. 3 it is also not difficult to find the small triangular voids —the bases of BeF_4 tetrahedra, the vertices of which abut into the junctions of three polyhedra of the lower layer. Along the *a* axis (Fig. 3) Thomson "cubes" alternate with BeF_4-tetrahedra in such a way that with one cube the Be-tetrahedron has a common edge, and with another only a common vertex. This motif appears very characteristically in a series of alkali and alkaline-earth sulfates.

Fig. 3. Alternation, in the (cement) motif of K_2BeF_4 (Ba_2SiO_4), of Thomson cubes with K cations and BeF_4- (SiO_4)-tetrahedra

Be-tetrahedra also have a common edge "on the side" with K_1-polyhedra from the teeth of neighboring ribbons. By one more edge (parallel to the *y* axis) the Be-tetrahedron is connected with K_2-polyhedra of a somewhat different form, but also quite characteristic for the same series of sulfates (silicates).

Fig. 4. K-fluoroberyllate. Framework of K_1-eight-vertex polyhedra of the type specifically described in the text

In Fig. 4 the "top" and "bottom" of the K_1-polyhedron are well expressed (in K_1-polyhedra joined by a horizontal glide plane): a pentagonal (5 + 1 vertex) pyramid, at the center of whose base K_1 is located, while on the opposite side there is a somewhat shortened edge with the 7th and 8th atoms (common with the Be-tetrahedron).

The "swelling" of the cation polyhedron (in the role of K_2) is characteristically manifested with the further increase of the ionic radius from K to Ba and NH_4. In the structures K_2SO_4, $KBaPO_4$, and $(NH_4)_2BeF_4$ (9–11), cations of two kinds are likewise clearly distinguished: M_2—forming the inner rods of the ribbons, and M_1—playing the role of teeth. In these structures the M_2-polyhedra are eight-vertex polyhedra similar to K_2, but the coordination number of M_2 increases to 9, and the polyhedron itself becomes (for example, in $KBaPO_4$) a combination of a distorted triangular prism with three irregular semioctahedra.

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