

# Refined crystal structure of chkalovite $\text{Na}_2\text{Be}[\text{Si}_2\text{O}_6]$

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The crystal structure of the natural Na-Be silicate chkalovite  $\text{Na}_2\text{Be}[\text{Si}_2\text{O}_6]$  was elucidated in 1956 by Pyatenko and Bokii.<sup>1</sup> This repeat investigation arose from differences found on comparing the structures of Be chkalovite and the Zn analog  $\text{Na}_2\text{Zn}[\text{Si}_2\text{O}_6]$  (ref. 2) within the framework of the symmetry group  $C_{2v}^{19} = \text{Fdd}2$ , which replaces that proposed in ref. 1, namely  $\text{Fddd}$ , on the basis of crystallochemical considerations, since the R factor was too high (about 30%).

The specimens of natural chkalovite were obtained from the Fersman mineralogical museum. The intensities of 3285 independent nonzero reflections ( $I \geq 1.96 \sigma I$ ) were recorded by the  $2\theta : \theta$  method with a scan rate varying from 6 to 24° per minute by using a P1 Syntex automatic diffractometer with a spherical specimen of diameter 0.4 mm ( $\mu r = 0.17$ ,  $\lambda \text{ Mo K}\alpha$ , planar graphite monochromator  $\max(\sin \theta/\lambda) = 1.08 \text{ \AA}^{-1}$ ). No absorption corrections were applied.

The revised parameters of the orthorhombic F cell are  $a = 21.129 \pm 0.005$ ,  $b = 6.881 \pm 0.002$ ,  $c = 21.188 \pm 0.005 \text{ \AA}$ ;  $V = 3080.45 \text{ \AA}^3$ ,  $d = 2.66 \text{ g/cm}^3$ ,  $\rho = 2.68 \text{ g/cm}^3$ ;  $Z = 24$ , which agree well with those given in ref. 1.

The absences corresponded unambiguously with the space group  $\text{Fdd}2$ . The I was converted to  $|F_{hkl}|$  and

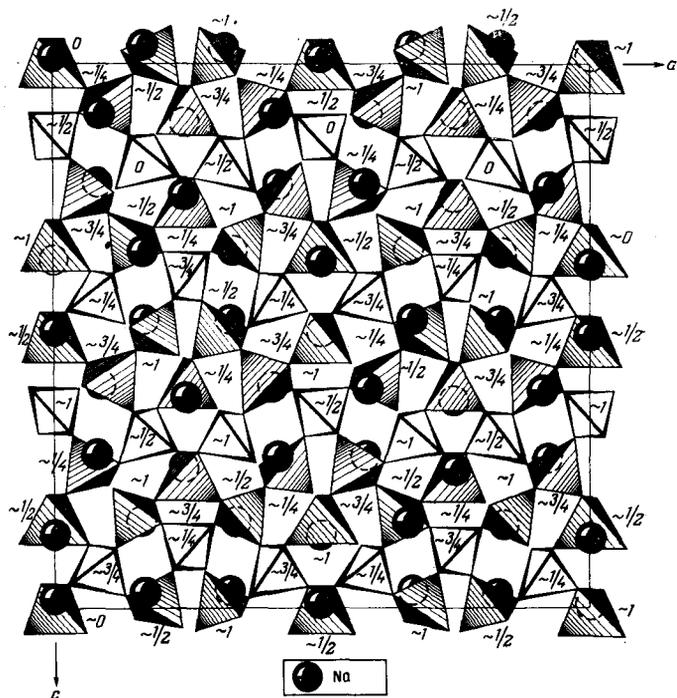


Fig. 1. Chkalovite  $\text{Na}_2\text{Be}[\text{Si}_2\text{O}_6]$ , xz projection, Si tetrahedra hatched.

then processed with the XTL Syntex specialized computing system.

The heavier Si and Na were revealed in the analysis, and also by comparison of the three-dimensional Patterson functions for  $\text{Na}_2\text{Be}[\text{Si}_2\text{O}_6]$  and the synthetic analog  $\text{Na}_2 \cdot \text{Be}[\text{Ge}_2\text{O}_6]$ . Electron-density distributions constructed from the Si and Na localized the O and Be. The resulting structural model was refined by the method of least-squares in the complete-matrix isotropic approximation to  $R_{hkl} = 7.0\%$  and in the anisotropic approximation to  $R_{hkl} = 5.9\%$ ; Table 1 gives the coordinates of the basal atoms with their standard deviations and individual temperature factors, while Table 2 gives the corresponding interatomic distances.

The Si and Be atoms lie in almost regular tetrahedra with the usual separations; there are four sorts of Na: The nearest six O lie at the vertices of octahedra ( $\text{Na}_1\text{-O} = 2.263 - 2.668 \text{ \AA}$  for  $\text{O-O} = 2.563 - 3.901 \text{ \AA}$ ;  $\text{Na}_2\text{-O} = 2.475 - 2.593 \text{ \AA}$  for  $\text{O-O} = 2.625 - 3.930 \text{ \AA}$ ;  $\text{Na}_3\text{-O} = 2.229 - 2.898 \text{ \AA}$  for  $\text{O-O} = 4.363 - 2.613 \text{ \AA}$ ;  $\text{Na}_4\text{-O} = 2.285 - 3.132 \text{ \AA}$  for  $\text{O-O} = 2.619 - 4.707 \text{ \AA}$ ).

In accordance with ref. 1, the Si and Be tetrahedra in a ratio 2:1 are linked into a framework resembling that in  $\beta$ -cristobalite (Fig. 1). However, the classification of silicates causes chkalovite  $\text{Na}_2\text{Be}[\text{Si}_2\text{O}_6]$  to fall among the chain group. The repeating increment in the metachain  $[\text{Si}_6\text{O}_{18}]_\infty \dots -\text{Si}_1-\text{Si}_3-\text{Si}_2-\text{Si}_4-\text{Si}_3-\text{Si}_1-\dots$  has three independent angles:  $\text{Si}_1-\text{O}_3-\text{Si}_3 = 139^\circ, 81^\circ$ ,  $\text{Si}_2-\text{O}_1-\text{Si}_4 = 139^\circ, 22^\circ$ , and  $\text{Si}_3-\text{O}_4-\text{Si}_4 = 138^\circ, 36^\circ$  (Fig. 2).

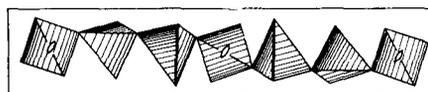


Fig. 2.  $\text{Na}_2\text{Be}[\text{Si}_2\text{O}_6]$ , chains of pyroxene type with  $[\text{Si}_6\text{O}_{18}]_\infty$  six-membered links.

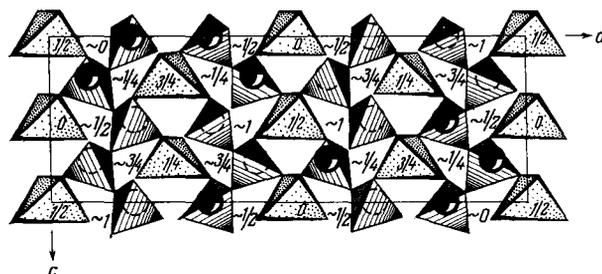


Fig. 3. Zn chkalovite  $\text{Na}_2\text{Zn}[\text{Si}_2\text{O}_6]$ , xz projection, Zn tetrahedra in special positions (on two-fold axes).

TABLE 1. Chkalovite  $\text{Na}_2\text{Be}[\text{Si}_2\text{O}_6]$ : Basal-Atom Coordinates and Individual Isotropic Temperature Factors

| Atom            | $x/a$     | $y/b$     | $z/c$     | $B_j$    |
|-----------------|-----------|-----------|-----------|----------|
| Si <sub>1</sub> | 0         | 0         | 0         | 0.16(2)  |
| Si <sub>2</sub> | 0         | 0.500     | 0.1601(1) | 0.14(2)  |
| Si <sub>3</sub> | 0.1500(1) | 0.0124(2) | 0.1754(1) | 0.15(1)  |
| Si <sub>4</sub> | 0.1837(1) | 0.5068(2) | 0.0118(1) | 0.15(1)  |
| Be <sub>1</sub> | 0.1685(3) | 0.018(1)  | 0.8259(3) | 0.39(7)  |
| Be <sub>2</sub> | 0         | 0         | 0.3649(4) | 0.53(11) |
| Na <sub>1</sub> | 0         | 0         | 0.5116(2) | 1.04(5)  |
| Na <sub>2</sub> | 0         | 0         | 0.1402(2) | 0.95(5)  |
| Na <sub>3</sub> | 0.1732(1) | 0.0047(4) | 0.0306(2) | 0.87(3)  |
| Na <sub>4</sub> | 0.1582(1) | 0.0112(4) | 0.6646(2) | 0.74(3)  |
| O <sub>1</sub>  | 0.0143(2) | 0.1886(5) | 0.7076(2) | 0.51(4)  |
| O <sub>2</sub>  | 0.1111(2) | 0.0852(5) | 0.1154(2) | 0.50(4)  |
| O <sub>3</sub>  | 0.1890(2) | 0.2014(5) | 0.2038(2) | 0.53(4)  |
| O <sub>4</sub>  | 0.1509(2) | 0.2050(5) | 0.4816(2) | 0.48(4)  |
| O <sub>5</sub>  | 0.2226(2) | 0.0697(5) | 0.5728(2) | 0.42(4)  |
| O <sub>6</sub>  | 0.1883(2) | 0.1997(5) | 0.8703(2) | 0.42(4)  |
| O <sub>7</sub>  | 0.1167(2) | 0.0843(5) | 0.7713(2) | 0.41(4)  |
| O <sub>8</sub>  | 0.0179(2) | 0.1883(5) | 0.0406(2) | 0.38(3)  |
| O <sub>9</sub>  | 0.0546(2) | 0.0808(5) | 0.4128(2) | 0.41(4)  |

Note: The standard deviations are given in parentheses.

TABLE 2. Chkalovite  $\text{Na}_2\text{Be}[\text{Si}_2\text{O}_6]$ : Interatomic Distances

| Si tetrahedra                       |           |                                     |           |                                 |           |                                 |           |
|-------------------------------------|-----------|-------------------------------------|-----------|---------------------------------|-----------|---------------------------------|-----------|
| Si <sub>1</sub> -O <sub>3</sub> (2) | 1.652 (4) | Si <sub>2</sub> -O <sub>1</sub> (2) | 1.669 (4) | Si <sub>3</sub> -O <sub>2</sub> | 1.594 (4) | Si <sub>4</sub> -O <sub>2</sub> | 1.658 (4) |
| O <sub>8</sub> (2)                  | 1.600 (3) | O <sub>6</sub> (2)                  | 1.591 (4) | O <sub>3</sub>                  | 1.653 (4) | O <sub>4</sub>                  | 1.658 (4) |
|                                     |           |                                     |           | O <sub>4</sub>                  | 1.652 (4) | O <sub>5</sub>                  | 1.593 (4) |
|                                     |           |                                     |           | O <sub>9</sub>                  | 1.598 (4) | O <sub>7</sub>                  | 1.608 (4) |
| Mean                                |           |                                     |           |                                 |           |                                 |           |
| Si-O                                | 1.626     | 1.630                               | 1.624     | 1.629                           |           |                                 |           |
| O-O                                 | 2.654     | 2.659                               | 2.650     | 2.656                           |           |                                 |           |
| Be tetrahedra                       |           |                                     |           |                                 |           |                                 |           |
| Be <sub>1</sub> -O <sub>2</sub>     | 1.636 (8) | Be <sub>2</sub> -O <sub>5</sub> (2) | 1.633 (6) |                                 |           |                                 |           |
| O <sub>6</sub>                      | 1.619 (7) | O <sub>9</sub> (2)                  | 1.635 (7) |                                 |           |                                 |           |
| O <sub>7</sub>                      | 1.655 (7) |                                     |           |                                 |           |                                 |           |
| O <sub>8</sub>                      | 1.633 (7) |                                     |           |                                 |           |                                 |           |
| Mean                                |           |                                     |           |                                 |           |                                 |           |
| Be-O                                | 1.636     | 1.634                               |           |                                 |           |                                 |           |
| O-O                                 | 2.670     | 2.666                               |           |                                 |           |                                 |           |

Note: The numbers of distances and standard deviations are given in parentheses.

The arrows denote the two types of Si on two-fold axes, which are perpendicular to the chain axis.

These chains (four in each  $c$  repeat period) lie in turn in the  $a/3 + b$  and  $a/3 - b$  directions in the  $ab$  plane,<sup>1)</sup> and they are linked into a framework by intermediate isolated Be tetrahedra.

The structure of Be chkalovite may be compared with that of Zn "chkalovite" recently elucidated<sup>2</sup> (Fig. 3), which reveals the reasons why the latter has only one axis triplicated with respect to the  $\beta$ -cristobalite, while Be chkalovite has two such axes. Neither structure has a (001) symmetry plane but (100) and (010) diamond planes are retained. In Zn chkalovite, the replacement of Si by Zn in every third layer along the  $a$  axis allows (100) to remain a diamond plane with alternation of  $d'$  and  $d''$ , these being enclosed in the crossing  $[\text{Si}_4\text{O}_{12}]_\infty$  chains. The lateral (010) =  $ac$  plane cannot contain short-linked chains, since it contains Zn tetrahedra intersecting the layers, and so that the  $a$  axis has to be triplicated in accordance with Buerger's rule<sup>3</sup> to retain the diamond feature in (010).

In Be chkalovite, each third layer of Si along the  $c$  axis is replaced by Be, and to keep the (010) plane of the diamond type the parameter is tripled, but there are no such analogous factors for the  $a'$  parameter and tripling here should be ascribed<sup>4</sup> to insufficient symmetry of the Be atoms in their tetrahedra.

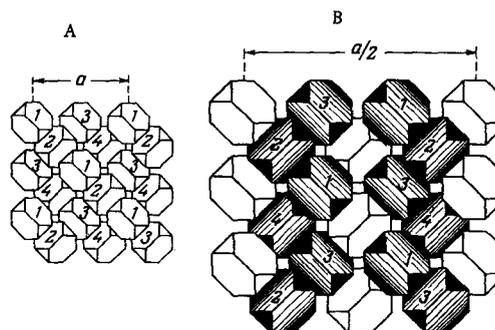


Fig. 4. Laves polyhedra in: A)  $\beta$ -cristobalite; B) Be chkalovite. Population of these in the ratio 2:1 trebles the  $a$  repeat while retaining the diamond plane (1, 2, 3, 4).

In the first description of Be chkalovite, the structure of  $\beta$ -cristobalite was represented as a packing of large Laves polyhedra of the  $MgCu_2$  type,<sup>5</sup> with appropriately fitted Si tetrahedra, but with the figures with 12 vertices themselves empty (Fig. 4A). Replacement of one-third of the  $Si^{4+}$  by  $Be^{2+}$  causes two thirds of the polyhedra to be filled by Na atoms; the ones remaining empty are those which have edges in common with the Be tetrahedra along the c axis (Fig. 1). Then Buerger's rule triples (Fig. 4B) one of the repeat distances in the original cristobalite cell.

Comparison of the structures of the similar Zn and Be chkalovites  $Na_2Zn[Si_2O_6]$  and  $Na_2Be[Si_2O_6]$  (and also  $Na_2Zn[SiO_4]$ , ref. 6, and  $Na_2Be[SiO_4]$ , ref. 7) shows that the analogy in behavior between Be and Zn observed in mineralogy does not, strictly speaking, go further than the simplest structures: bromellite  $BeO$ —zincite  $ZnO$ , phenakite  $Be_2[SiO_4]$ —willemite  $Zn_2[SiO_4]$ , and is altered in a characteristic fashion in complex structures.

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obtaining the experimental data.

<sup>1</sup>) These are former oblique translations in the centered face of the initial cubic structure of  $\beta$ -cristobalite; the present triplicated  $ab$  face of chkalovite contains three parallel parts of the metachain with four tetrahedra in each. The chain emerging from  $x, y = 0$  reaches the level  $x = 1$  only for  $y = 3b$ .

<sup>1</sup>Yu. A. Pyatenko, G. B. Bokif, and N. V. Belov, Dokl. Akad. Nauk SSSR, 108, No. 6 (1956).

<sup>2</sup>E. L. Belokoneva, Yu. K. Egorov-Tismenko, et al., Kristallografiya, 14, 1060 (1969) [Sov. Phys.—Crystallogr., 14, 918 (1970)].

<sup>3</sup>M. J. Buerger, Am. Mineral., 39, 600 (1954).

<sup>4</sup>N. V. Belov, Min. Sborn. L'vov. Univ., No. 16, 29 (1962).

<sup>5</sup>N. V. Belov, Structures of Ionic Crystals and Metallic Phases [in Russian], Izd. AN SSSR, Moscow (1947).

<sup>6</sup>V. V. Ilyukhin, A. V. Nikitin, and N. V. Belov, Dokl. Akad. Nauk SSSR, 171, 1325 (1966) [Sov. Phys.—Dokl., 11, 1035 (1967)].

<sup>7</sup>G. F. Plakhov, M. A. Simonov, and N. V. Belov, Dokl. Akad. Nauk SSSR, 218, 335 (1974) [Sov. Phys.—Dokl., 19, 556 (1975)].

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