

THE CRYSTAL STRUCTURE OF SEARLESITE,  $\text{NaBSi}_2\text{O}_5(\text{OH})_2$ 

V. B. Kravchenko

Institute of Inorganic Chemistry, Siberian Branch, Academy of Sciences, USSR

Translated from *Kristallografiya*, Vol. 9, No. 2,

pp. 182-189, March-April, 1964

Original article submitted May 30, 1963

An x-ray structural investigation of searlesite,  $\text{NaBSi}_2\text{O}_5(\text{OH})_2$ , has been carried out. A new type of boron-silicon-oxygen layer has been found, which contains five-membered rings. A detailed description of the structure is given together with a comparison of the structure with those of certain other silicates.

To understand the geochemistry and mineralogy of boron it is essential to be acquainted with its crystallochemical properties and behavior under various physicochemical conditions, and so a study of the crystal structures of its natural compounds, in particular the borosilicates, is of undoubted interest.

We have determined [1] the crystal structure of searlesite,  $\text{NaBSi}_2\text{O}_5 \cdot \text{H}_2\text{O}$ , which is met with in some deposits of boron [2, 3, 4]. In our investigation we used platy mica-like crystals of searlesite from deposits at Green River, Wyoming, and acicular crystals from Cave Spring, Nevada, U.S.A. These specimens were kindly placed at our disposal by Prof. M. G. Valyashko. The unit cell constants and space group of searlesite had been previously determined by Fahey and Axelrod [2]. The mineral is monoclinic, with  $a=7.97$ ,  $b=7.05$ ,  $c=4.90$  Å;  $\beta=93^\circ 57'$ ;  $\rho_e=2.46$ ,  $\rho_c=2.46$ ,  $z=2$ . The absorptions were noticed only for the reflections  $0k0$  with  $k=2n+1$ . Of the two possible space groups,  $P2_1/m$  and  $P2_1$ , they chose the noncentrosymmetric group  $P2_1$ , in view of the presence of a piezoelectric effect.

The unit cell constants which we obtained agreed, within the limits of possible error, with those given above. The correctness of the choice of the noncentrosymmetric group was confirmed by a statistical analysis of the intensities of the reflections  $hk1$  and  $hk2$  [5], and by analysis of the Patterson projection on (001). Maxima with coordinates  $02y0$  must appear when there is a mirror plane perpendicular to the Y axis. On the  $P(u, v)$  projection (Fig. 1), only one small peak of this type is observed, which supports the view that a mirror plane is lacking.

The experimental material used in the structure determination consisted of photographs of the zero, first, second, third and fourth layer lines, obtained on rotation about the  $c$  axis, using as specimen an acicular crystal measuring  $\sim 0.05 \times 0.05 \times 0.5$  mm, and using a Weissenberg camera with Mo radiation; and also photographs of the zero and first three layer lines obtained on rotation about the  $b$  axis. Because of the perfect cleavage along (100) it was not possible to find a single crystal for the photograph along the  $b$  axis, and so an approximately parallel concretion of two crystals, measuring  $\sim 0.05 \times 0.3 \times 0.2$  mm, was used. In all, 1524 independent reflections were registered, of which 1258 were nonzero reflections. The small sizes of the crystals and the insignificant absorption (the linear attenuation coefficient was equal to  $\mu=9.1 \text{ cm}^{-1}$ ) meant that a correction for absorption was almost pointless. The intensities were measured visually using a blackening scale, consisting of 38 spots, and constructed using the same crystal. After introduction of corrections for the Lorentz and polarization factors, in the usual manner, the values of the moduli of the structure amplitudes were obtained.

Determination of the structure was begun with an analysis of the Patterson projection  $P(uv)$  along the short  $c$  axis (Fig. 1). This projection gave the following coordinates of the interatomic vectors for the pair of independent atoms A and B:  $x_A - x_B$ ,  $y_A - y_B$ ;  $x_A + x_B$ ,  $y_A - y_B + 1/2$ . Since the  $P(uv)$  projection is subject to the planar symmetry group  $Pmm$ , the interatomic vectors for a pair of atoms must lie at equal distances from the line  $y = 1/4$ .

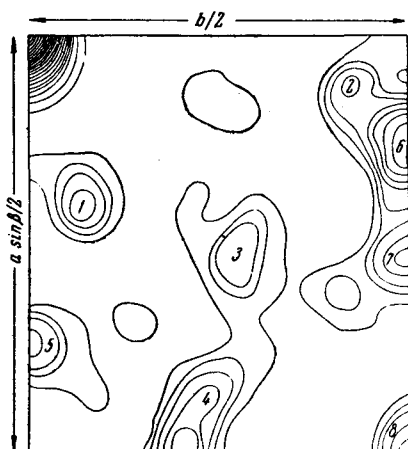


Fig. 1. Patterson projection on the (001) plane.

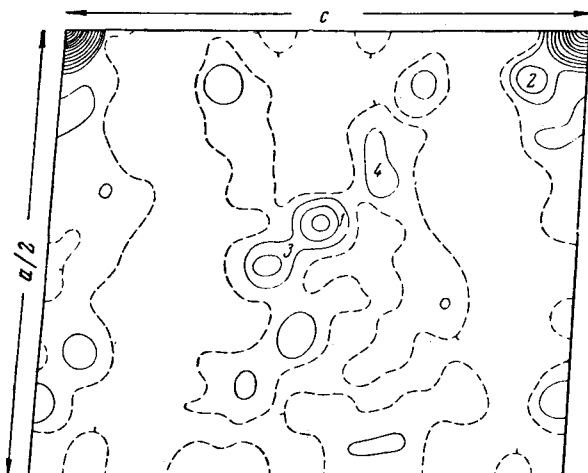


Fig. 2. Patterson projection on the (010) plane. The dashed lines are at the zero level.

In the first stage of the work it was necessary to determine the positions of the two heaviest atoms, the Si atoms, lying in independent parts of the unit cell (in the group  $P2_1$  only a general position of multiplicity 2 is possible).

Interpretation of the projection was aided by the following fact. The absence of a good cleavage along (010) suggests that the silicon atoms are interconnected along the  $b$  axis. Since the Si-Si distance here must not exceed  $2(\text{Si}-\text{O}) \approx 2 \times 1.65 = 3.30$  Å, then if we make the above assumption we must exclude from the analysis the peak 5 (Fig. 1), and with this we can include peaks 6, 7, and 8 (the shortest distance between atoms in these cases would be not less than  $b/2 = 3.52$  Å). There then remains

only two pairs of stronger peaks equidistant from  $y = 1/4$ , the maxima 1 and 2, and 3 and 4.

A comparison with the centrosymmetric projection along the twofold axis,  $P(uw)$ , immediately allows us to settle on the first pair of peaks. The two strong maxima 1 and 2 (Fig. 2), together with the weaker peaks 3 and 4, give a set of three peaks typical of a centrosymmetric pattern [6]. The  $x$  coordinates of the maxima 1 and 2  $P_1(uw)$ ,  $P_2(uw)$  and  $P_3(uw)$  confirmed that peaks 3 and 4 correspond to the vectors between silicon atoms related by a twofold screw axis.

The subsequent analysis of the projection on  $xy$  did not present any particular difficulties. For the peaks 1 and 2 (Fig. 1) a minimalization operation was carried out, which gave rough coordinates for 2 Si and 4 O (in the early stages the Na atom was not differentiated from the O atoms). A series of successive approximations of electron density allowed us to determine the coordinates of three more O atoms, to distinguish the Na atom among the O atoms, and to lower  $R(hk0)$  from its initial value of 39.5 to 26.8%. The positions of one further O atom and of the B atom remained undecided. Later work showed that in this projection they were overlapped by other atoms.

After finding the signs of the structure amplitudes for the  $xz$  projection an attempt was made to apply the Harker-Casper inequality, but this was unsuccessful because of the small number of large structure amplitudes (in all 5  $|u_{h0l}| \geq 0.5$  among 261 reflections). To determine the approximate coordinates of the atoms a minimalization was carried out for the maxima 3 and 4 (Fig. 2). On the pattern thus obtained, 2 Si peaks and six other strong peaks were distinguishable, and the  $x$  coordinates of the latter were in rough agreement with the values obtained for the O atoms in the  $xy$  projection. An attempt to work out the signs from these eight atoms led to the appearance of several new maxima on the electron density projection, and it was difficult to decide which were true maxima. By using normal and weighted Patterson projections and minimalized projections a choice was made of the five most reliable maxima, 2 Si, Na, and 2 O. Calculation of the signs from these five peaks, with fairly accurately determined coordinates, resulted in a more "ghost-free" electron density projection.

The subsequent refinement was carried out by the method of successive approximations. Apparently because of the poor quality of the crystal used for the  $b$  axis photographs, the reliability factor decreased only slowly; after five cycles of refinement

TABLE 1. Coordinates and Individual Temperature Factors of the Principal Atoms

Atom	x	y	z	B	Atom	x	y	z	B
Si <sub>I</sub>	0.1355	0.5902	0.2097	-0.17	O <sub>IV</sub>	0.309	0.490	0.308	0.27
Si <sub>II</sub>	0.0827	0.0167	0.3102	-0.13	O <sub>V</sub>	0.023	0.023	0.612	0.58
Na	0.440	0.000	0.981	0.96	OH <sub>I</sub>	0.356	0.280	0.694	0.51
O <sub>I</sub>	0.167	0.817	0.258	0.65	OH <sub>II</sub>	0.486	0.743	0.700	0.62
O <sub>II</sub>	0.085	0.543	0.898	0.58	B	0.371	0.298	0.409	0.07
O <sub>III</sub>	0.219	0.174	0.257	0.39					

it was equal to 30.3, and after five more it came down to 23.6% (taking into account the "zero" reflections, which were assigned half the intensity of the weakest spot on the film;  $\sin \theta/\lambda \leq 0.95$ ). The factor  $R(h0l)$  was equal to 20.6% when no account was taken of the unobserved reflections. It should be noted that one of the O atoms in this projection was overlapped by a Si atom, and its coordinates were determined very inaccurately. The determination of coordinates on the xz projection allowed the positions of the overlapping atoms on the xy projection to be found more precisely. The reliability factor for this projection, after refining, was 20.9% when the zero reflections were considered and 20.0% when they were not ( $\sin \theta/\lambda \leq 0.96$ ).

To confirm the correctness of the structure found, a complete three-dimensional Patterson synthesis was constructed. The calculations were made on a high-speed electronic computer using a program prepared by colleagues at the Computing Center of the Siberian branch of the Institute of Chemical Physics. The analysis showed that the coordinates obtained were in good agreement with the Patterson functions. The reliability factor for all nonzero reflections was 19.9% at this stage, with a general temperature factor of  $B = 0.20 \text{ \AA}^2$ .

The subsequent structure refinement was carried out by the method of least squares using all the three-dimensional data in a program also worked out in the above Computing Center. The refinement was carried out in stages. The order of refinement was: the temperature factor and normalization coefficient for each  $c$  axis layer line, the Si atom coordinates, the coordinates of the other atoms, the individual isotropic temperature factors for the Si atoms and then for the other atoms, and, once again, the coordinate parameters of all atoms. Table 1 gives the final values of the coordinates and individual isotropic temperature factors for all the 11 independent atoms in the structure. The negative values of  $B_j$  for the Si atoms and the low value of the general temperature factor ( $B = 0.16 \text{ \AA}^2$ ) are apparently tied up with the increase in intensity of weak reflec-

tions in the high-angle region. Similar behavior has also been observed in the refinement of silicate structures [7, 8].

The reliability factor calculated from the coordinates in Table 1 was equal to 13.9% for all nonzero reflections and 19.5% for all reflections. The factors, with and without consideration of the zero reflections respectively, were 15.8 and 15.3% for the  $hk0$  zone, 19.3 and 16.9% for the  $h0l$  zone ( $\sin \theta/\lambda \leq 0.95$ ; the "zero" reflections were assigned half the intensity of the weakest reflection on the x-ray photograph).

All the atoms lie in general twofold positions. The structure possesses 32 parameters. The  $y$  coordinate of the Na atom was chosen as the origin for the Y axis.

Figure 3 shows a projection of the structure on the (001) plane, and Fig. 4 a projection on (100). A characteristic feature of the structure is the presence of boron-oxygen-silicon layers lying parallel to (100). The oxygen-silicon tetrahedra form  $[\text{Si}_2\text{O}_5]_{2\infty}$  layers containing six-membered rings. Three tetrahedra in the ring are orientated with their corners pointing in the same direction, along the  $b$  axis, and the three others are arranged so that they have one edge approximately parallel, and another edge approximately perpendicular, to the  $b$  axis. Each tetrahedron in the layer has one corner left free. The B atom is bonded with two such free corners of tetrahedra orientated in opposite directions, and its coordination is brought up to tetrahedral by two hydroxyl groups, which are not part of the oxygen-silicon arrangement (formula  $\text{O} + \text{H}_2\text{O}$ ).

The features of the structure emerge clearly from an examination of the method of connection of the cation and anion units. The basis of the structure can be considered as made up of infinite columns of deformed Na octahedra (Fig. 3), threaded on a twofold screw axis and connected together through shared edges. Two neighboring octahedra share one edge each with the same  $\text{BO}_2(\text{OH})_2$  tetrahedron. The marked elongation of neighboring octahedra by the boron-oxygen tetrahedron results in movement

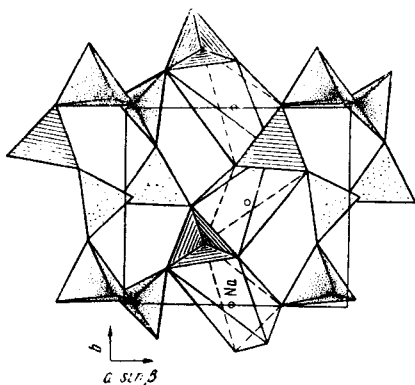


Fig. 3. Projection of the crystal structure of searlesite on the (001) plane. The columns of Na octahedra are shown. The  $\text{BO}_2(\text{OH})_2$  tetrahedra are striated.

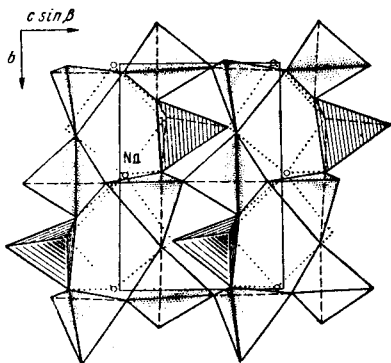


Fig. 4. Projection of the crystal structure of searlesite on the (100) plane. Only one tetrahedron layer is shown. The  $\text{BO}_2(\text{OH})_2$  tetrahedra are striated.

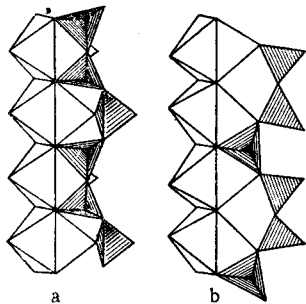


Fig. 5. The two methods of attaching the triple-tetrahedron chains to the Ca octahedra in wollastonite (according to [11]).

apart of the opposite corners of the octahedra, making them a very convenient distance apart for the attachment of a  $\text{Si}_2\text{O}_7$  group. These diorthogroups and the boron-oxygen tetrahedra are connected into chains of composition  $\text{BSi}_2\text{O}_7(\text{OH})_2$ , analogous to the triple-tetrahedron chains (Dreierkettes [9]) in wollastonite [10]. In wollastonite,  $\text{Ca}_3\text{Si}_2\text{O}_7$ , these chains are attached to infinite columns of Ca octahedra in two ways (Fig. 5a and 5b [11]). In searlesite the second method is used. Here the difference is clearly seen between the  $\text{Si}_2\text{O}_7$  diorthogroups and isolated  $\text{SiO}_4$  tetrahedra in wollastonite and the  $\text{BO}_2(\text{OH})_2$  in searlesite.

Condensation of these chains into a infinite layer is achieved in searlesite with the aid of a twofold screw axis passing approximately through the vertices of the diorthogroup tetrahedra. This results in an infinite layer of composition  $[\text{BSi}_2\text{O}_5(\text{OH})_2]_{2\infty}$  containing five-membered rings (Fig. 4). Each five-membered ring is made up of four oxygen-silicon tetrahedra and one boron-oxygen tetrahedron. The oxygen-silicon tetrahedra do not have free corners, while the two free corners of the boron-oxygen tetrahedron are occupied by OH groups. In this method of condensation the oxygen-silicon tetrahedra of neighboring triple-tetrahedron chains in a layer are connected up parallel to the  $c$  axis into metasilicate chains, which differ from those in pyroxenes in having a different pitch to the tetrahedron screw and a shorter repeat distance (4.9 Å instead of  $\sim 5.2$  Å). A similar situation was noted [12] in another layer silicate with large cations, namely sanbornite,  $\text{BaSi}_2\text{O}_5$  [13]. The  $b$  and  $c$  lattice constants of the searlesite layer are thus closely related in their scheme of formation. A somewhat reduced  $b$  constant along the axis of the triple-tetrahedron chain (7.05 Å compared to 7.27 Å in wollastonite) is connected with the replacement of a  $\text{SiO}_4$  tetrahedron with the smaller  $\text{BO}_2(\text{OH})_2$  tetrahedron.

It is interesting to compare searlesite with another layer silicate containing five-membered rings [14], namely melilite,  $(\text{Ca}, \text{Na})_2[(\text{Mg}, \text{Al})(\text{Si}, \text{Al})_2\text{O}_7]$  [15]. Belov has shown [16] that the melilite layer is formed on condensation of symmetrized wollastonite chains (Fig. 6a), also through the medium of a twofold screw axis. The difference from searlesite is that the  $2_1$  axis connects, not the vertices of the two diorthogroup tetrahedra, but a vertex of one of the single tetrahedra and one of the vertices of the diorthogroup tetrahedra. In this case there is formed, perpendicular to the axis of the triple-tetrahedron chain, not a metasilicate chain but a chain exactly similar to the original, in accordance

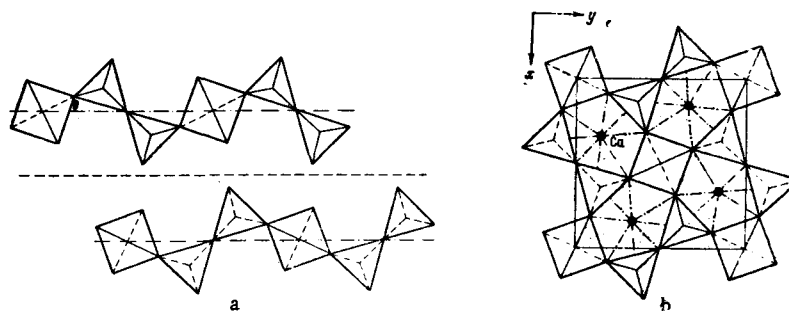


Fig. 6. a) Symmetrized wollastonite chains, cut from a melilite layer (after [16]); b) the melilite layer (after [15]).

with the tetragonal symmetry of the mineral. The tetrahedra of the diorthogroup in the melilite layer each have one free corner, all pointing in the same direction. The single (third) tetrahedron does not have a free corner. It is somewhat larger in size than the diorthogroup tetrahedra.

The existence of a large number of isomorphous melilite compounds is due to the extensive possibilities of replacing the cations in the single tetrahedra [replacement of the formula (Mg, Al) by Zn, Fe, Be, Co, Ca, etc.]. It is an interesting point that, in the synthetic boron analog of melilite,  $\text{CaB}_2\text{SiO}_7$ , the boron apparently occupies the single tetrahedra and one of the diorthogroup tetrahedra [17], thus making the second diorthogroup oxygen-silicon tetrahedron a "special" tetrahedron. The difference in anion arrangements between searlesite and melilite is easy to explain, in the face of their undoubted similarities, by the different layout of their cations (in accordance with the principles of the second division of silicate crystallochemistry [11]); in searlesite the Na octahedra form infinite columns along the  $\underline{b}$  axis, while in melilite the eight-cornered Ca polyhedra give infinite networks parallel to (001), leading to the higher symmetry of the tetrahedral layer. The balance of valences in the structure of searlesite is shown in Table 2.

The  $\text{O}_{\text{III}}$  and  $\text{O}_{\text{I}}$  atoms are bonded to one Na atom, and the  $\text{OH}_{\text{I}}$  and  $\text{OH}_{\text{II}}$  groups to two. The interatomic distances in the  $\text{SiO}_4$  tetrahedra are:  $\text{Si}-\text{O}$  1.59–1.65 Å (average value 1.61 Å);  $\text{O}-\text{O}$  from 2.55 to 2.72 Å (average value 2.64 Å); the  $\text{B}-\text{O}$  distances in the  $\text{BO}_2(\text{OH})_2$  tetrahedron, 1.47 and 1.52 Å; the  $\text{B}-\text{OH}$  distances are 1.41 and 1.49 Å; the B atom is displaced from the center of the tetrahedron towards the oxygen of the  $\text{OH}_{\text{I}}$  group; the  $\text{O}-\text{O}$  and  $\text{O}-\text{OH}$  edges are 2.35–2.45 Å (average value 2.40 Å);  $\angle \text{Si}_{\text{I}}-\text{O}_2-\text{Si}_{\text{II}}$   $143^\circ 12'$ ;  $\angle \text{Si}_{\text{I}}-\text{O}-\text{Si}_{\text{II}}$   $148^\circ 51'$ ;  $\angle \text{B}-\text{O}_{\text{III}}-\text{Si}_{\text{II}}$   $142^\circ 51'$ ;  $\angle \text{B}-\text{O}_{\text{IV}}-\text{Si}_{\text{I}}$   $128^\circ 28'$ . The

$\text{Na}-\text{O}$  distances in the octahedron are 2.31, 2.36, 2.48, 2.53, 2.69 and 2.74 Å; the  $\text{O}-\text{O}$  edge varies from 2.40 to 4.81 Å. Opposite the face of the octahedron formed by the two largest edges there lies, at a distance of 2.94 Å from the Na atom, the  $\text{O}_{\text{I}}$  oxygen of the diorthogroup. If this is included in the coordination sphere of Na, the balance of valences for the  $\text{OH}_{\text{I}}$  and  $\text{OH}_{\text{II}}$  groups becomes even closer to unity, but for the  $\text{O}_{\text{I}}$  atom an excess appears in the sum of valence forces, making it  $2\frac{1}{7}$ . The coordination polyhedron of Na is then a trigonal prism with a semioctahedron on one of its faces, and the  $\text{O}-\text{O}$  edges of this polyhedron vary more widely, from 2.40 to 3.92 Å.

The accuracy of determination of the atomic coordinates was evaluated from the usual formulas of Vainshtein [18], using coefficients taken from Porai-Koshits' book [19]. The values of the standard deviations for the atomic coordinates were:  $\text{Si}-0.0026$ ;  $\text{Na}-0.0034$ ; for  $\text{O}-0.0053$ , and for  $\text{B}-0.010$  Å. The probable errors in the interatomic distances were:  $\text{Si}-\text{O}=0.0059$ ;  $\text{Na}-\text{O}=0.0063$ ;  $\text{O}-\text{O}=0.0077$  and  $\text{B}-\text{O}=0.011$  Å.

The physical features of searlesite, i. e., perfect cleavage on (100), and the mica-like nature of some specimens, are explained easily by the presence in the structure of boron-silicon-oxygen layers and by the weak bonds in the Na polyhedra connecting the layers. On the differential thermal analysis curve of searlesite [20], only one endothermic effect was noted, at  $\sim 480^\circ$ , accompanied by a loss in weight. This high-temperature effect is due to the hydroxyl groups present in the structure, and not to molecules of water, as suggested earlier.

The author is deeply indebted to G. B. Bokii for valuable advice and observations during the course of the work, to M. G. Valyashko for the gift of the searlesite specimens, to A. Likek and his laboratory colleagues (of the Institute of Tech-

TABLE 2. Balance of Valences in the Searlesite Structure

Atom	Si <sub>I</sub>	Si <sub>II</sub>	B	Na	Sum of valence forces
O <sub>I</sub>	1	1	—	—	2.00
O <sub>II</sub>	1	1	—	—	2.00
O <sub>III</sub>	—	1	0.75	0.17	1.92
O <sub>IV</sub>	1	—	0.75	0.17	1.92
O <sub>V</sub>	1	1	—	—	2.00
OH <sub>I</sub>	—	—	0.75	0.33	1.08
OH <sub>II</sub>	—	—	0.75	0.33	1.08

nical Physics of the Czechoslovakian Academy of Sciences, Prague), to B. L. Tamopolskii, L. E. Maksimova, V. I. Andrianov, and Z. A. Safina (this branch of the Institute of Chemical Physics) and to F. A. Brusentsev (of this Institute) for help in carrying out the calculations.

## LITERATURE CITED

- V. B. Kravchenko and G. B. Bokii Dokl. AN SSSR, 143, 690 (1962).
- J. J. Fahey and J. M. Axelrod, Amer. Mineralogist, 34, 1014 (1950).
- W. F. Foshag, Amer. Mineralogist, 19, 268 (1934).
- C. Milton, E. C. T. Chao, and J. M. Axelrod, Amer. Mineralogist, 45, 188 (1960).
- A. J. C. Wilson, Acta crystallogr., 2, 318 (1949).
- Kh. S. Mamedov and N. V. Belov, Dokl. AN SSSR, 106, 462 (1956).
- D. R. Peacor and M. J. Buerger, Amer. Mineralogist, 47, 539 (1962).
- M. J. Buerger, Ch. W. Burnham, and D. R. Peacor, Acta crystallogr., 15, 583 (1962).
- F. Liebau, Acta crystallogr., 12, 177 (1959).
- Kh. S. Mamedov and N. V. Belov, Dokl. AN SSSR, 107, 463 (1956).
- N. V. Belov, The Crystal Chemistry of Silicates with Large Cations, No. II in the V. I. Vernadskii Lectures [in Russian], Izd. AN SSSR, Moscow (1961).
- V. V. Ilyukhin and N. V. Belov, Kristallografiya, 6, 847 (1961) [Soviet Physics—Crystallography, Vol. 6, p. 685].
- R. M. Douglass, Amer. Mineralogist, 43, 517 (1958).
- G. B. Bokii, Crystal Chemistry [in Russian], Izd. MGU (1960).
- J. V. Smith, Amer. Mineralogist, 38, 643 (1953).
- N. V. Belov, Mineralog. sb. L'vovsk. geol. obsh. pri univ., 15, 22 (1961).
- H. Bauer and N. Jahr, Mineral., 6, 127 (1962).
- B. K. Vainshtein, Zh. éksperim. i teor. fiz., 27, 44 (1954).
- M. A. Porai-Koshits, A Practical Course of X-Ray Structural Analysis [in Russian], Izd. MGU (1960).
- R. D. Allen, U. S. Geol. Surv. Bull., 1036k, 196 (1957).

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-to-cover English translations appears at the back of this issue.