

## X-RAY DIFFRACTION STUDY OF LEUCOSPHEENITE

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The nature of the borosilicate  $\text{Na}_2\text{Ba}_2\text{Ti}_4\text{O}_4[\text{Si}_{16}(\text{Si}, \text{B})_8\text{O}_{56}]$  has been studied by x-ray diffraction. The parameters of the monoclinic lattices are  $a = 9.799 \text{ \AA}$ ,  $b = 16.840 \text{ \AA}$ ,  $c = 7.199 \text{ \AA}$ ,  $\beta = 93^\circ 22'$ ,  $Z = 1$ , space group  $\text{C2/m}$ . The structure was determined from three-dimensional data (840 reflections) and was refined to  $R = 0.135$  by the least squares method. A new silicon(boron)-oxygen radical - a two-level  $[\text{Si}_{16}(\text{Si}, \text{B})_8\text{O}_{56}]$  layer in which the Si and B atoms are only partially ordered and display the properties of isomorphous elements - has been established. The very large  $\text{Ba}^{2+}$  cations are located in holes in the two-level tetrahedral layer and have coordination number 10. The rest of the  $\text{Na}^+$  cations (coordination numbers 7 and 8) and Ti (coordination number 6) form single layers which alternate in the direction of the  $c$  axis with (Si, B) layers. Groupings of two Ti octahedra joined along an edge are present in the structure.

Leucosphenite is a rare natural borosilicate of sodium, barium, and titanium. Interest in its detailed study is dictated by its peculiar and complex chemical composition. Clarification of the role which boron and titanium play with respect to the silicon-oxygen radical of the structure is important, as well as establishment of the form and features of this radical. In a previous short communication [1], the x-ray diffraction characteristics of leucosphenite were given, along with a basic description of its structure without refined atomic coordinates.

The present communication gives the results of a complete x-ray diffraction study of the mineral after refinement of the structure by the least squares method. The conclusions given here are slightly different from the preliminary results.

Specimens from Yakutsk, obtained from A. F. Efimov and subjected to a complete chemical analysis [2], were used. The rare chemical purity of the Yakutsk leucosphenite, in which isomorphous impurities play an insignificant role as compared with the leading components, should be noted. Recalculation of the chemical analysis of Hey [3] gives the contents of major cations in the cell as

$\text{Na}_{7.65}\text{Ba}_{1.88}\text{Ti}_{3.86}\text{B}_{4.05}\text{Si}_{20.02}$ . The corresponding empirical formula of the mineral,  $\text{Na}_4\text{BaTi}_2\text{B}_2\text{Si}_{10}\text{O}_{30}$  ( $Z = 2$ ), agrees with that suggested in [2]. We emphasize the integral coefficient of the boron atoms, a circumstance which played an important role during the structure refinement.

Parameters of the monoclinic cell of leucosphenite are:  $a = 9.799 \pm 0.004 \text{ \AA}$ ,  $b = 16.840 \pm 0.006 \text{ \AA}$ ,  $c = 7.199 \pm 0.003 \text{ \AA}$ ,  $\beta = 93^\circ 22' \pm 04'$  (single-crystal diffractometer data). A three-dimensional set of experimental intensities (the 0-2 layer lines during rotation about the  $a$  axis and 0-3 layer lines during rotation about the  $c$  axis) were obtained on KFOR cameras with Mo radiation. The  $I(hkl)$  values were measured by comparison with a scale of blackening based on steps of  $2^{1/4}$ . During the evaluation of the  $F^2$  coefficients, only the LP factors were taken into account. Absorption was not allowed for in view of the small sizes of the grains (maximum cross section 0.25 mm). In all, the three-dimensional set of intensities contained 870 independent and nonzero reflections. Upon deciphering of the layer lines, only reflections with  $k = 2n$  were present in the  $0k0$  series, with

$h = 2n$  in the  $h0l$  series, and with  $(h + k) = 2n$  of the general type. The corresponding x-ray group,  $2/mC-/-$ , corresponds to three space groups:  $C_{2h}^3-C2/m$ ,  $C_2^3-C2$ , and  $C_S^3-Cm$ . The negative result of tests of the crystals for the piezoelectric effect (Crystal Physics Department of MGU), along with the statistical intensities, was the basis for preference of the centrosymmetric group  $C2/m$  as the initial working variant.

The base-centered cell of leucosphenite displays an interesting geometrical feature. If the diagonals of the  $C$  rectangle are chosen as the reference translation in the  $(001)$  plane, then a pseudohexagonal net with axial angle of  $60^\circ 24'$ , which is close to the ideal  $60^\circ$ , is formed. Diffraction patterns taken along the short  $c$  axis are also characterized by pseudohexagonal symmetry. All this reflects the unusual construction of leucosphenite, in which, as has already been noted [1], the silicon-oxygen motif can be derived from the mica radical.

In keeping with the chemical formula, in the unit cell of leucosphenite are located 2 atoms of Ba, 4 Ti, 8 Na, 20 Si, 4 B, and 60 O atoms. The position of the very heavy Ba in the group selected was determined unambiguously at the origin in the parameterless position  $(000)$ .

The  $P(xy)$  and  $P(yz)$  Patterson projections, constructed along the short  $c$  and  $a$  translations from 164  $hk0$  and 87  $0kl$  reflections, gave the first indication of the layer character of the leucosphenite structure. This circumstance, as the result of which multiple superpositions of the interatomic vectors were observed, precluded a successful interpretation of the corresponding two-dimensional syntheses. More substantial information was obtained from the  $P_1^{\sin, \cos}(xy)$  and  $P_1^{\sin, \cos}(yz)$  weighted Patterson projections, constructed from 292  $hk1$  reflections and 235  $1kl$  reflections. The Ti atoms, as well as 16 of the 20 Si atoms, were localized on these syntheses.

Upon the transition to the electron density synthesis it was established that the  $\sigma(xy)$  and  $\sigma(yz)$  projections, constructed with only the Ba atoms being taken into account, practically reiterate the corresponding Patterson syntheses. Specifically, as the result of their location in the cell, attraction of the Ti and Si atoms did not change the signs of the equatorial structure amplitudes and did not introduce new information into the two-dimensional electron density distribution.

The  $P(xyz)$  three-dimensional distribution function confirmed the positions found earlier for Ti and

part of the Si, and the information obtained in this manner proved to be sufficient for the successful construction of a three-dimensional electron density synthesis. All cations, as well as a significant portion of the O atoms, were localized on the  $\rho(xyz)$  cross sections. A subsequent approximation of  $\rho(xyz)$ , constructed with the atoms so found being taken into consideration, completed the stage of isolation of the rough structure model. The divergence factor for total thermal correction,  $B = 1.7$ , amounted to 17.4%.

In the model obtained, the largest cations,  $Ba^{2+}$ , are located at the lattice points of a base-centered cell. The Ti atoms and two kinds of Na in one plane at the level  $z = c/2$  form a single layer of cations which are average with respect to radius. The small tetrahedral  $Si^{4+}$  and  $B^{3+}$  equally occupy the three general eightfold positions between  $Ba^-$  and the Ti, Na layers at levels  $z \approx c/4$  and  $3c/4$ .

The B atoms statistically replace Si in the centrosymmetric variant examined. The concrete nature of this replacement underlay further clarification in the process of structure refinement. Furthermore, in connection with the ambiguous determination of the space group and the integral Si:B ratio noted above in the formula for leucosphenite (exactly four B atoms per cell), the model may not be uniquely possible. An alternative variant lies in the complete ordering of Si and B, which would occur as the result of lowering of the symmetry of the structure to  $Cm$  or  $C2$  with decomposition of each eightfold complex of group  $C2/m$  into two fourfold ones. In accordance with what has been said, three different models were analyzed during the refinement of the structure of leucosphenite: 1) complete statistical distribution of Si and B in all three eightfold positions with tetrahedral cations; 2) partial ordering, i.e., statistical substitution of Si by B in only one of the positions mentioned, and 3) complete ordering of Si and B. The last variant was broken up into two self-consistent cases in accordance with the two possible acentric groups  $Cm$  and  $C2$ .

The silicon(boron)-oxygen motif of the structure, which is described in detail in [1], is reproduced in Fig. 1B. A portion of its component tetrahedra is denoted in the figure by gray triangles (one eightfold position), and the other, the remaining one, by white triangles (corresponding to two eightfold positions). In the deciphering process, it was noted that the atoms in the "gray" tetrahedra have lower scattering power than those in the "white" tetrahedra. Both on the Patterson projections and the electron density syntheses, a

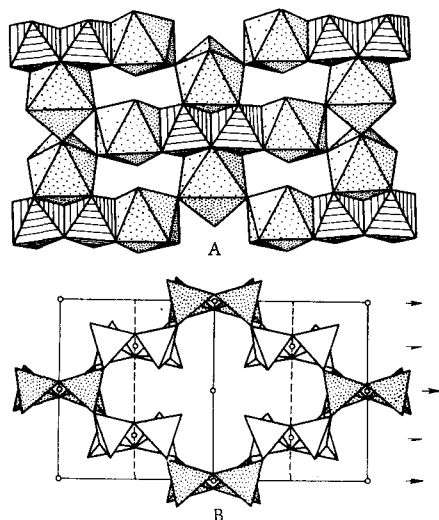


Fig. 1. The leucosphenite structure in  $xy$  projection. A) Layer of Ti and Na polyhedra; B) motif of Si (B) tetrahedra.

weaker peak corresponded to the first atom than corresponded to the second. This was the basis for assuming that the maximum number of B are concentrated in the "white" tetrahedra. Therefore, the idea of partial or complete ordering of Si and B is associated with just this feature of the eightfold positions. In the case of complete ordering, half of the "gray" tetrahedra should be occupied by Si, and half should be occupied only by B. In this case, the corresponding four-member ring is found to be composed of two different diortho groups:  $\text{Si}_2\text{O}_7$  and  $\text{B}_2\text{O}_7$  (compare danburite). The dumbbells of the latter may be horizontal or vertical, depending on whether the symmetry is  $C_m$  or  $C_2$ .

During refinement of the structure in the Computing Center, Academy of Sciences of the USSR on a BESM-3M computer in accordance with the program of B. L. Tarnopol'skii and V. I. Andrianov, a three-dimensional block of intensities was used from which the very strong reflections at low angles  $\theta$ , which were subject to the greatest influence of secondary extinction, had been excluded. Two complete cycles of refinement of the positions and

thermal parameters were carried out for each of the calculated variants, after which the values of interatomic distances and valence angles were given on the printout.

From the data of Table 1 it follows that the best R factor corresponds to Model 1, i.e., to statistical distribution of B with respect to all three eightfold positions occupied by tetrahedral cations. For the purpose of additional confirmation of this variant, a special cycle of refinement of the multiplicities of the cations in the positions mentioned was carried out. In this case, the same original  $f$  curve corresponding to Si was assigned to all tetrahedral cations. In the results, it was found that, if the "white" tetrahedra are populated almost completely by silicon, then the "gray" tetrahedra are only ~60% populated. The latter value corresponds approximately to the average scattering capability of the two atoms,  $(\text{Si} + \text{B})/2$ . This result is in complete agreement with indications of the Patterson and Fourier syntheses. Thus, Model 1 can be rejected with confidence.

So far as the other three models were concerned, from the R factor all appeared to be equally probable. The closeness of the values of R for the centrosymmetric and acentric variants is easily explained by the fact that the positions of the overwhelming number of atoms in the cell of leucosphenite practically conforms to symmetry  $C_2/m$ . Consequently, the structure remains under conditions of clearly pronounced pseudosymmetry even in the presence of an ordered distribution of Si and B (Models 3 and 4). The formal criterion of making an estimate from the magnitude of the R factor becomes unreliable, and such arguments as "reasonableness" of interatomic distances and thermal parameters come into the foreground.

On the basis of this criterion, the centrosymmetric model with partial ordering of the Si and B atoms (Model 2) is clearly preferred. The atomic coordinates and isotropic thermal factors for this model are given in Table 2, and the interatomic distances are given in Table 4. The local balance of valences in the leucosphenite structure is given in

TABLE 1. R Factors for Different Structural Models of Leucosphenite

| No. | Model                         | Space group | Multiplicity of general position | Number of independent atoms | R, % |
|-----|-------------------------------|-------------|----------------------------------|-----------------------------|------|
| 1   | Complete disorder of Si and B | $C_2/m$     | 8                                | 16                          | 15.1 |
| 2   | Partial ordering              | $C_2/m$     | 8                                | 16                          | 13.5 |
| 3   | Complete ordering             | $C_m$       | 4                                | 28                          | 13.3 |
| 4   | Complete ordering             | $C_2$       | 4                                | 28                          | 13.5 |

TABLE 2. Coordinates and Thermal Parameters of Independent Atoms in the Leucosphenite Structure (space group C2/m)

| Atom            | x     | y     | z     | B    | Atom           | x     | y     | z      | B    |
|-----------------|-------|-------|-------|------|----------------|-------|-------|--------|------|
| Ba              | 0     | 0     | 0     | 2.15 | O <sub>2</sub> | 0.120 | 0.093 | 0.286  | 0.97 |
| Ti              | 0     | 0.086 | 0.500 | 0.69 | O <sub>3</sub> | 0.123 | 0.166 | 0.623  | 0.71 |
| Si <sub>1</sub> | 0.249 | 0.167 | 0.766 | 1.07 | O <sub>4</sub> | 0.456 | 0     | 0.287  | 1.43 |
| Si <sub>2</sub> | 0.222 | 0.152 | 0.190 | 1.17 | O <sub>5</sub> | 0.500 | 0.090 | 0      | 1.59 |
| (Si, B)         | 0.494 | 0.082 | 0.198 | 1.28 | O <sub>6</sub> | 0.181 | 0.246 | 0.216  | 1.15 |
| Na <sub>1</sub> | 0.500 | 0.222 | 0.500 | 1.62 | O <sub>7</sub> | 0.203 | 0.133 | -0.028 | 0.92 |
| Na <sub>2</sub> | 0.300 | 0     | 0.500 | 2.30 | O <sub>8</sub> | 0.630 | 0.110 | 0.305  | 0.88 |
| O <sub>1</sub>  | 0.096 | 0     | 0.625 | 0.71 | O <sub>9</sub> | 0.378 | 0.141 | 0.276  | 1.03 |

TABLE 3. Local Balance of Valences in Leucosphenite Structure

| Anion          | Cation           |                         |                  |                  |                              |                              | $\Sigma \omega_i/n_i$ |
|----------------|------------------|-------------------------|------------------|------------------|------------------------------|------------------------------|-----------------------|
|                | Si <sup>4+</sup> | (Si, B) <sup>3,5+</sup> | Ti <sup>4+</sup> | Ba <sup>2+</sup> | Na <sub>1</sub> <sup>+</sup> | Na <sub>2</sub> <sup>+</sup> |                       |
| O <sub>1</sub> | —                | —                       | 2 × 2/3          | 1/5              | —                            | 1/7                          | 2-34/105              |
| O <sub>2</sub> | 1.0              | —                       | 2/3              | 1/5              | —                            | 1/7                          | 2+1/105               |
| O <sub>3</sub> | 1.0              | —                       | 2/3              | —                | 1/8                          | —                            | 2-5/24                |
| O <sub>4</sub> | 2 × 1.0          | —                       | —                | —                | 1/8                          | —                            | 2+1/8                 |
| O <sub>5</sub> | 2 × 1.0          | —                       | —                | 1/5              | —                            | —                            | 2+1/5                 |
| O <sub>6</sub> | 1.0              | 7/8                     | —                | —                | 1/8                          | 1/7                          | 2+1/7                 |
| O <sub>7</sub> | 1.0              | 7/8                     | —                | —                | 1/8                          | —                            | 2                     |
| O <sub>8</sub> | —                | 2 × 7/8                 | —                | —                | —                            | 2 × 1/7                      | 2+1/25                |
| O <sub>9</sub> | —                | 2 × 7/8                 | —                | —                | —                            | —                            | 2-1/4                 |

TABLE 4. Interatomic Distances (in Å) in the Leucosphenite Structure

|                                   |          |                                   |          |                                    |          |
|-----------------------------------|----------|-----------------------------------|----------|------------------------------------|----------|
| <b>Si<sub>1</sub> tetrahedron</b> |          | <b>Si<sub>2</sub> tetrahedron</b> |          | <b>(Si, B) tetrahedron</b>         |          |
| Si <sub>1</sub> —O <sub>3</sub>   | 1.56     | Si <sub>2</sub> —O <sub>2</sub>   | 1.60     | (Si, B)—O <sub>4</sub>             | 1.58     |
| Si <sub>1</sub> —O <sub>6</sub> * | 1.62     | Si <sub>2</sub> —O <sub>8</sub>   | 1.65     | (Si, B)—O <sub>5</sub>             | 1.44     |
| Si <sub>1</sub> —O <sub>7</sub>   | 1.68     | Si <sub>2</sub> —O <sub>7</sub>   | 1.60     | (Si, B)—O <sub>8</sub>             | 1.57     |
| Si <sub>1</sub> —O <sub>8</sub> * | 1.63     | Si <sub>2</sub> —O <sub>9</sub>   | 1.63     | (Si, B)—O <sub>9</sub>             | 1.63     |
| O <sub>3</sub> —O <sub>7</sub>    | 2.65     | O <sub>2</sub> —O <sub>6</sub>    | 2.70     | O <sub>4</sub> —O <sub>5</sub>     | 2.62     |
| O <sub>8</sub> —O <sub>8</sub> *  | 2.62     | O <sub>2</sub> —O <sub>7</sub>    | 2.54     | O <sub>4</sub> —O <sub>8</sub>     | 2.52     |
| O <sub>3</sub> —O <sub>6</sub> *  | 2.64     | O <sub>3</sub> —O <sub>9</sub>    | 2.65     | O <sub>1</sub> —O <sub>9</sub>     | 2.49     |
| O <sub>7</sub> —O <sub>6</sub> *  | 2.73     | O <sub>6</sub> —O <sub>7</sub>    | 2.61     | O <sub>5</sub> —O <sub>8</sub>     | 2.50     |
| O <sub>7</sub> —O <sub>8</sub> *  | 2.68     | O <sub>3</sub> —O <sub>9</sub>    | 2.63     | O <sub>5</sub> —O <sub>9</sub>     | 2.53     |
| O <sub>6</sub> *—O <sub>9</sub> * | 2.56     | O <sub>7</sub> —O <sub>9</sub>    | 2.70     | O <sub>8</sub> —O <sub>9</sub>     | 2.52     |
| <b>Ti octahedron</b>              |          | <b>Na<sub>1</sub> polyhedron</b>  |          | <b>Ba polyhedron</b>               |          |
| Ti—O <sub>1</sub>                 | 1.92 (2) | Na <sub>1</sub> —O <sub>3</sub> * | 2.38 (2) | Ba—O <sub>1</sub>                  | 2.91 (2) |
| Ti—O <sub>2</sub>                 | 2.00 (2) | Na <sub>1</sub> —O <sub>6</sub> * | 2.84 (2) | Ba—O <sub>2</sub>                  | 2.79 (4) |
| Ti—O <sub>3</sub>                 | 1.98 (2) | Na <sub>1</sub> —O <sub>8</sub>   | 2.71 (2) | Ba—O <sub>7</sub>                  | 3.01 (4) |
|                                   |          | Na <sub>1</sub> —O <sub>9</sub>   | 2.38 (2) |                                    |          |
| O <sub>1</sub> —O <sub>1</sub> *  | 2.53 (1) | <b>Na<sub>2</sub> polyhedron</b>  |          | <b>Cation-cation</b>               |          |
| O <sub>1</sub> —O <sub>2</sub>    | 2.74 (2) | Na <sub>2</sub> —O <sub>1</sub> * | 2.24 (1) | Ti—Ti                              | 2.90     |
| O <sub>1</sub> —O <sub>2</sub> *  | 2.92 (2) | Na <sub>2</sub> —O <sub>2</sub>   | 2.76 (2) | Si <sub>1</sub> —Si <sub>2</sub>   | 3.09     |
| O <sub>1</sub> —O <sub>3</sub>    | 2.81 (2) | Na <sub>2</sub> —O <sub>4</sub>   | 2.23 (1) | Si <sub>1</sub> —Si <sub>1</sub> * | 3.08     |
| O <sub>2</sub> —O <sub>3</sub> *  | 2.79 (2) | Na <sub>2</sub> —O <sub>4</sub> * | 2.76 (1) | Si <sub>1</sub> —(Si, B)           | 2.90     |
| O <sub>2</sub> —O <sub>3</sub>    | 2.72 (2) | Na <sub>2</sub> —O <sub>5</sub> * | 2.40 (2) | Si <sub>2</sub> —(Si, B)           | 2.91     |
| O <sub>3</sub> —O <sub>3</sub> *  | 2.91 (1) |                                   |          | (Si, B)—(Si, B)*                   | 2.76     |
|                                   |          |                                   |          | (Si, B)—(Si, B)*                   | 2.86     |

\*Asterisks denote atoms inferred from symmetry operations of the basal atoms.

Table 3. From the information given, it follows that both types of parameters agree well with normal standards for the silicates. At the same time, the series of interatomic distances and individual B factors appear to be beyond the limits of the norm in the acentric models. Thus, the length of individual Si—O bonds is shortened to 1.51 Å in Model 3 (Cm) and to 1.46 Å in Model 4 (C2). Some of the

Na—O bonds are also too short (2.07, 2.18, and 2.19 Å). On the other hand, the B—O bonds both in this and other cases are far longer than standard and approach the Si—O bonds in length. In Model 3, of the four independent B—O bonds in the tetrahedron, three fall within the limits 1.56–1.60 Å, and in Model 4 fall within the range 1.60–1.67 Å. And each quaternary bond is correspondingly short-

ened to 1.39 and 1.37 Å. Consequently, regardless of the fact that information as to an ordered distribution of Si and B was contributed on the basis of refinement of the acentric models, a tendency toward equalization of distances in the Si and B tetrahedra is present. This circumstance rules out "pure" B atoms, i.e., it points to the absence of strict ordering of the  $\text{Si}^{4+}$  and  $\text{B}^{3+}$  cations.

Analysis of the thermal parameters of the structure leads to this same conclusion. In both acentric variants, considerable oscillation in the magnitudes of the B factors for chemically identical atoms takes place. Thus, the thermal corrections for Si lie within the limits  $-0.75$  to  $-1.59$  for the group Cm and within the limits  $-0.44$  to  $-1.94$  for group C2. The analogous parameters for the O atoms oscillate from  $+0.20$  to  $-2.64$  and from  $-0.04$  to  $-2.70$ , respectively. The thermal constant for  $\text{B}^{3+}$  was found to be positive,  $+0.55$  and  $+0.65$ , in both cases, which also indicates the  $f$  curve of B assigned to the respective atoms to be too low.

In this manner, analysis of the results of refinement leads to the conclusion of statistical relationships between Si and B in the leucosphenite structure. This is a somewhat unexpected conclusion in the light of known facts about the crystal chemistry of borosilicates. At the present time more than ten silicate structures with high B content have been worked out (danburite, tourmaline, stilwellite, dumortierite, grandidierite, datolite, axinite, etc.), and a disordered distribution of the elements was not indicated in any of them. This contradiction naturally has caused the authors to arrive at the results of analysis of leucosphenite with familiar caution.

In a previous communication [1], based on data which still have not been refined, a structure model of leucosphenite was described which had an ordered distribution of Si and B and was based on space group Cm. Analysis of this model has shown that the structure examined actually allows these shifts of atoms, which, in complete accord with the principle of ordering, results in satisfactory interatomic distances at all lattice points of the model, including the self-consistent B tetrahedra. In other words, purely geometrical obstacles do not exist for this model. However, their mock removal improves agreement between experiment and calculation, and the R factor rises from 13.3 to 16%. Some of the thermal parameters also remain far from normal values.

With the aim of additional verification of the results of refinement, two calculations were car-

ried out in which the structure was intentionally placed under conditions known to be unfavorable for a statistical distribution of B and Si. The first of these tests was presented as the refinement of the multiplicities of all six independent positions occupied by tetrahedral cations in the acentric group Cm (least squares method). In this case, a single  $f$  curve, which corresponded to that for  $\text{Si}^{4+}$ , was used for all cations. The positional parameters of the structure were refined at the first stage of calculation, and only then were the multiplicities refined. The cycle was repeated twice. The results confirmed that four of the six fourfold complexes ("white" tetrahedra) are occupied by Si atoms. The multiplicities are 4.29–3.93. So far as the other two positions ("gray" tetrahedra) are concerned, their corresponding multiplicities (3.15 and 1.92) correspond to  $f$  curves starting at 7.9 and 4.8 for  $\sin \theta / \lambda = 0$ . Thus, the scattering power of the cations in both positions examined proved to be lower than the scattering power of  $\text{Si}^{4+}$  (10 for  $\sin \theta / \lambda = 0$ ), but higher than the scattering power of  $\text{B}^{3+}$  (2 for  $\sin \theta / \lambda = 0$ ). The corresponding  $f$  curves are symmetric with respect to the mean  $f$  curve  $(\text{Si}^{4+} + \text{B}^{3+})/2$  (6 for  $\sin \theta / \lambda = 0$ ). Regardless of some ambiguity in results of this test (a noticeable difference in the multiplicities of the two latter positions), they nevertheless also provide evidence against the complete ordering of Si and B.<sup>1</sup>

The second test was a three-dimensional differential electron density synthesis. Calculation also was carried out for the acentric group Cm from coordinates previously refined for this group by the least squares method. The cations populating the "gray" tetrahedra were not included in the total at all, and the contributions of the bridge O atoms between the respective tetrahedra were subtracted. In the results it was established that the electron density peaks corresponding to the cations not given in the synthesis have practically the same amplitude. This indicates their similar scattering powers and, consequently, their analogous chemical nature. Thus, the electron density distribution does not give an indication as to the ordering of Si and B, either.

Summing up what has been presented, the conclusion can be drawn that within the limits of ac-

<sup>1</sup>An analogous result was also obtained from two-dimensional diffractometric data containing 127  $0kl$  reflections ( $0 \leq \sin \theta / \lambda \leq 1.10$ ). For greater objectivity, the respective calculations were carried out on the basis of the group with lowest symmetry, P1. The final value was  $R = 4.7\%$ .

curacy of the experiment the leucosphenite structure is characterized by a disordered distribution of Si and B atoms in only one-third of all tetrahedra. In accordance with this, the most probable space group for leucosphenite must be considered to be the centrosymmetric group  $C2/m$ , and not  $Cm$  as indicated in [1]. The structural formula suggested earlier for the mineral,  $Na_8Ba_2Ti_4O_4[B_4Si_{20}O_{56}]$ , should be interpreted as  $Na_8Ba_2Ti_4O_4[Si_{16}(Si, B)_8O_{56}]$ . Here the parentheses emphasize the isomorphous substitution of B for Si in only one of the three eightfold positions occupied by tetrahedral cations. Regardless of the fact that the number of Si and B atoms in this position is the same in the specimens studied, the integral Si:B ratio for leucosphenite should not be looked upon as obligatory in principle.<sup>2</sup>

The leucosphenite structure type is characterized by a layer arrangement of atoms associated with a pseudohexagonal motif. The features of the silicon-oxygen radical  $[Si_{16}(Si, B)_8O_{56}]_{\infty}$  have been described earlier in [1]. Everything said there with respect to its "geometrical" genesis remains in force. Only the qualitative composition of the tetrahedral cations at the various lattice points of the radical has been changed. According to the new interpretation, all the tetrahedra of the four-member ring are populated by Si and B atoms, not in an ordered fashion but according to a statistical law. We suggest that if one more four-member ring of tetrahedra is placed in the center of Fig. 1B, then we will get a doubled mica layer with the characteristic six-member rings. The two-level tetrahedral net of leucosphenite affords rich material isolating in it (cutting out) different kinds of one-dimensional radicals (bands, chains, etc.). Infinite bands of the quaternary rings mentioned above stand out most clearly in it (see Fig. 1B). These bands pass parallel to the  $[110]$  and  $[\bar{1}10]$  diagonals of the cell and, intersecting at an angle of about  $60^\circ$ , they form the pseudohexagonal motif in which arise the extended fourteen-member loops of rhombic cross section. Along the axes of the bands, the purely "silicon" rings alternate with "borosilicon" (Si, B) bands, and rings of mixed type arise at their junctions. The first type of rings display point symmetry  $C_i$ , the second type have symmetry  $C_{2h}$ , and the last type have the lowest symmetry,  $C_1$ . We also note the presence of free vertices only for the "white" tetrahedra, which are populated by "pure" silicon. The bands examined have a staircase nature which is unlike the zigzag bands of the orthoclase type, which is the closest so far as structure is concerned.

Within the limits of the silicon-oxygen radical, the interatomic distances well reflect the geometrical differences between the purely silicon and the borosilicon tetrahedra. Thus, the length of the Si-O bonds varies within the limits 1.56-1.67 Å (mean 1.62 Å), and the (Si, B)-O bond lengths vary within the limits 1.44-1.64 Å (mean 1.56 Å). The lengths of the edges of the corresponding tetrahedra are 2.54-2.73 and 2.49-2.62 Å (mean 2.64 and 2.53 Å). The cation-cation distances decrease in the following order: Si-Si 3.08 Å, Si-(Si, B) 2.90 Å, and (Si, B)-(Si, B) 2.76 and 2.86 Å. Definite regularities are also observed both in the O-Si-O and Si-O-Si valence angles. The purely silicon tetrahedra are more regular and are characterized by O-Si-O angles of  $104^\circ10'$ - $113^\circ45'$ . The range of variation of the corresponding angles in the (Si, B) tetrahedra is wider:  $101^\circ51'$ - $120^\circ40'$ . The valence angles for the O bridge atoms have the following values: Si-O-Si  $140^\circ50'$ , Si-O-(Si, B)  $126^\circ35'$  and  $129^\circ20'$ , (Si, B)-O-(Si, B)  $122^\circ20'$  for cations located in one level, and  $169^\circ15'$  for cations in neighboring levels.

The translationally identical two-level nets of leucosphenite are separated by the cation layer shown in Fig. 1A. In this motif of Ti octahedra and Na polyhedra, "windows" are clearly looked through on which are superimposed diortho groups of the higher- and lower-lying tetrahedral nets. In the same layer, the pairs of Ti octahedra joined along a common edge and already described in [1] attract attention. The edge is substantially shortened (to 2.53 Å) in comparison with the other edges of the octahedra (2.78-2.92 Å). The Ti-O bond length lies within the normal limits 1.92-2.00 Å, although the octahedra themselves are noticeably distorted. The O-Ti-O valence angles lie within the interval  $82^\circ10'$ - $96^\circ25'$ . Two kinds of Na polyhedra border the Ti octahedra directly along the edges. Unlike the variant described in [1], the coordination numbers of Na are 7 and 8; however, a distorted octahedron can be isolated in the base of each Na polyhedron. The Na-O distances lie within the wide limits from 2.24 to 2.84 Å.

The bonding between the cation and anion layers of leucosphenite is easily represented if Fig. 1B is superimposed on Fig. 1A. The largest cations,  $Ba^{2+}$  (not shown on the figures), are located in spacious hollows of the silicon-oxygen radical - in

<sup>2</sup>Here it is appropriate to give the chemical formula worked out for leucosphenite from Middle Asia (second discovery in the USSR):  $Na_{6.8}K_{0.5}Mg_{0.4}Ca_{0.2}Sr_{0.1}Ba_{1.8}Ti_{3.4}Fe_{0.2}Nb_{0.1}Si_{20.1}B_{3.6}Al_{0.3}O_{60}$ .

the center of fourteen-member loops – and thus are found to be inside the anion layer. Playing the role of a missing four-member ring, the ten-vertex Ba completes four two-level six-member rings, each consisting of 10 tetrahedra (five vertical diortho groups) and the Ba polyhedron itself. Channels of pseudo-hexagonal cross section pass through the center of the last rings in the direction of the z axis. In these channels, Na atoms are located between the "doubled" six-member rings in a manner similar to that of the alkali cation in the milarite, osumilite, and armenite structures. However, this difference exists: The two-level rings in these latter minerals have strictly hexagonal symmetry, and are not bonded directly to each other in the layers.

Pairs of Ti octahedra are located above the ten-vertex Ba, forming infinite columns with it (Fig. 2). The Ti octahedra are bonded only to Si tetrahedra through its free vertices, which limits the size of the hollows occupied by the Ba atoms. This placement of the highly charged titanium above the "missing" ring of the two-level net is explained by the considerable valence unsaturation of the free vertices of the Si tetrahedra. In this manner, the insular groupings of two Ti octahedra play the role of extraordinary couplers between neighboring anion layers of the structure. As a result, as has been noted in [1], the contrast between intralayer and

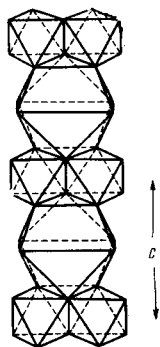


Fig. 2. Columns of Ti octahedra and Ba polyhedra in the leucosphenite structure.

interlayer bonding forces is substantially decreased, and the complete cleavage of leucosphenite along the [001] direction is not accompanied by similarity to mica, as is characteristic for such titanosilicates as astrophyllite and bathertsite.

The leucosphenite structure as a whole can be looked upon as being built up from trigonal packets containing the strands of cations of moderate radius ( $\text{Ti}^{4+}$ ,  $\text{Na}^{1+}$ ), which are typical of layer silicates and the Ba chainmail structures. Unlike the micaceous packets, where the free vertices (tips) of the Si tetrahedra are turned inward toward the strands, the tetrahedra of neighboring leucosphenite packets not only face each other but are also combined into diortho groups by a common vertex. As a result, the chainmail structures of adjacent trigonal packets are combined into two-level nets. As a result of this, leucosphenite has extra interpacket space, and the coarse  $\text{Ba}^{2+}$  cations are "corraled" into the hollows of the anion layer (in the chainmail structures).

Summing up, it can be emphasized that the crystalline construction of leucosphenite represents a characteristic structure type with a new silicon – oxygen radical – an infinite two-level layer,  $[\text{Si}_{16} \cdot (\text{Si}, \text{B})_8\text{O}_{56}]_{\infty}$ . With a high degree of probability it can be confirmed that the Si and B atoms in this radical have only partial ordering and display the properties of elements which are isomorphously replaced by each other.

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