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Abstract

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ON THE CRYSTAL STRUCTURE OF NIO-CALITE

The optical data on niocalite were first published in 1956 by Nickel ⁽¹⁾, who assigned this mineral to the monoclinic system. In paper ⁽²⁾ the unit-cell parameters were determined as $a = 10.82$; $b = 10.42$; $c = 7.38 \text{ \AA}$; $\beta = 109^\circ 40'$, and, from the extinctions among the reflections $h0l$ (reflections with $h = 2n$ are present), two possible space groups were recorded: $P2/a$ and Pa . This result is repeated in Strunz' s handbook ⁽³⁾. Kern et al. ⁽⁴⁾, on the basis of their X-ray data, assign niocalite to orthorhombic symmetry with cell parameters $A = 7.33$; $B = 10.43$; $C = 20.28 \text{ kX}$. In this setting there are extinctions among the reflections hkl , which indicate a Bravais-centered lattice B . The authors ⁽⁴⁾ tentatively assigned niocalite to the space group $B222$.

Light-yellow crystals of Canadian niocalite were kindly provided to us for study by A. G. Zhabin. In a careful X-ray study of single-crystal fragments of niocalite from one and the same locality, two modifications of the mineral were found: monoclinic ($I_{hkl} = I_{h\bar{k}l} \neq I_{\bar{h}kl} = I_{\bar{h}k\bar{l}}$) and orthorhombic ($I_{hkl} = I_{\bar{h}kl} = I_{h\bar{k}l} = I_{\bar{h}k\bar{l}}$). The structural analysis was carried out for the "radiographically monoclinic" crystal of niocalite*. The analysis showed that the question of the symmetry of the mineral is more complex than it might have seemed at first glance.

From an untreated niocalite specimen with a cross section of $0.2 \times 0.2 \text{ mm}^2$, reciprocal-lattice photographs (Mo radiation) were obtained in the photographic camera: $hk0-hk5$, $h0l-h3l$, and $0kl$. The unit-cell parameters were determined from rotation photographs in an RKV camera (standard K_2SO_4): $a = 10.79 \pm 0.02$; $b = 10.36 + 0.01$; $c = 7.30 \pm 0.01 \text{ \AA}$; $\beta = 110^\circ$. As in all minerals of the wöhlerite-cuspidine ⁽⁵⁻⁷⁾ and seidozerite-rinkite ⁽⁸⁻¹⁰⁾ groups, niocalite exhibits a pronounced pseudoperiod $c' = c/2$. Indexing of the "monoclinic" niocalite was carried out in the pseudo-orthorhombic setting, which corresponds to the setting of ⁽⁴⁾. In this case it turns out that the breaking of orthorhombic symmetry appears only in reflections with $l = 2n + 1$. The relationship between the cells of the pseudo-orthorhombic and monoclinic settings is as follows:

$$\mathbf{A} = \mathbf{c}; \quad \mathbf{B} = \mathbf{b}; \quad \mathbf{C} = 2\mathbf{a} + \mathbf{c}.$$

The intensities of all reflections were estimated visually on a blackening scale with a step of $\sqrt[4]{2}$. The linear absorption coefficient $\mu_l = G \sum p\mu_a$ (μ_a is the atomic absorption coefficient for $\lambda = 0.71 \text{ \AA}$ (¹¹), calculated for niocalite, is equal to 36 cm^{-1}). In determining the structure, no absorption correction was introduced.

As is known, a common feature of the structures of minerals of the wöhlerite-cuspidine group is the presence of symmetry 2_1 . In monoclinic niocalite, strictly speaking, symmetry elements with glide are absent, since there are no systematic extinctions among reflections of any type.

* The quotation marks emphasize a certain conditionality in assigning this symmetry to niocalite.

The only possibility from the crystal-chemical point of view of a screw axis 2_1 (along the b axis) is refuted by the presence of three, although very weak, reflections: 030, 050, 0130. The absence of systematic extinctions among reflections of any type within the Laue class $C_{2h} = 2/m$ (with the b axis along the special direction) leads to the diffraction group $2/mP - - / - -$, i.e., to three possible space groups: $C_s^1 = Pm$, $C_{2h}^1 = P2/m$, and $C_2^1 = P2$. The first two of these groups can be discarded on the basis of an analysis of the Patterson projections, in which no concentration of peaks along the b axis is observed, which excludes the plane m . The question of the group $P2$ was considered separately. After careful comparison

Table 1

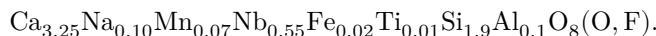
Approximate values of the coordinates of the basis atoms of niocalite within the symmetry $P2_1$

Atoms	x/a	y/b	z/c	Atoms	x/a	y/b	z/c
(Nb, Ca) ₁	0.18	0.11	0.34	O' ₂	0.41	0.47	0.18
(Nb, Ca) ₂	0.32	0.88	0.16	O ₃	0.08	0.53	0.88
Ca ₃	0.18	0.12	0.84	O' ₃	0.42	0.46	0.71
Ca ₄	0.32	0.88	0.65	O ₄	0.01	0.28	0.70
Ca ₅	0.43	0.59	0.47	O' ₄	0.50	0.23	0.26
Ca ₆	0.43	0.59	0.97	O ₅	0.00	0.28	0.23
Ca ₇	0.07	0.41	0.53	O' ₅	0.50	0.23	0.80
Ca ₈	0.07	0.40	0.04	O ₆	0.24	0.25	0.59
Si ₁	0.38	0.30	0.73	O' ₆	0.24	0.26	0.16
Si ₂	0.38	0.30	0.15	O ₇	0.25	0.77	0.91
Si ₃	0.12	0.69	0.35	O' ₇	0.26	0.77	0.36
Si ₄	0.14	0.74	0.79	O ₈	0.14	0.01	0.08
O ₁	0.36	0.27	0.92	O' ₈	0.35	0.02	0.44

Atoms	x/a	y/b	z/c	Atoms	x/a	y/b	z/c
O ₁ '	0.16	0.78	0.57	O ₉	0.14	0.00	0.54
O ₂	0.08	0.55	0.28	O ₉ '	0.36	0.00	0.92

of the Patterson projections of niocalite with the corresponding Patterson projections of wöhlerite, we were able to assert with sufficient confidence that the structural motif of niocalite is close to the motifs of wöhlerite and låvenite. Taking into account that the structures of wöhlerite and låvenite cannot be reconciled with a 2-fold rotation axis of symmetry, it was natural to reject the group $P2$ for monoclinic niocalite as well. The conclusion that there is no rotation axis in the structure of niocalite was confirmed by analyses of the Patterson projections. It should be emphasized that there is no elementary solution to the question of the symmetry of niocalite. This question was resolved only after the structural model of niocalite had been established.

According to the chemical analysis of Canadian niocalite ⁽²⁾, the unit cell indicated above contains 4 units of the composition:



In work ⁽¹⁾, from the same chemical analysis, the formula $\text{Ca}_4\text{NbSi}_2\text{O}_{10}(\text{O}, \text{F})$ was erroneously obtained; it is repeated in ^(2,3). According to our recalculation of analysis ⁽²⁾, the unit cell of niocalite contains 24 cations instead of the 28 indicated in ⁽¹⁾.

The interpretation of the Patterson projections $p(xy)$ and $p(yz)$ was carried out within the pseudosymmetry of niocalite $P2_1$. From the minimization functions $M_4(xy)$ and $M_3(yz)$, the coordinates of all cations were extracted. The structure was refined by a procedure of alternating calculations of F_{calc} and electron-density projections. In doing so, 189 independent and nonzero $hk0$ reflections and 104 $0kl$ reflections were used. Naturally, obtaining exact values of 90 coordinate parameters using only 293 reflections from equatorial layer lines is difficult, especially if one takes into account the overlap of atoms in the projections. At present we are continuing the refinement of the niocalite structure from three-dimensional data. Coor-

coordinates of the basis atoms of niocalite, estimated from the projections, are given in Table 1.

The similarity of the structural motifs of niocalite and cuspidine, låvenite, and wöhlerite makes it possible to assume that the principal reason violating the strict subordination of monoclinic niocalite to the space group $P2_1$ is the arrangement of cations in the structure, and not deviations in the coordinates of the atoms. The question of the symmetry of niocalite is reduced to determining the arrangement of approximately two Nb atoms over 16 cation positions in the

Fig. 1. Idealized projection of the niocalite structure on the $x0y$ plane. The numbers indicate the z -coordinates of the cations in thousandths of the c axis

Figure 1: Fig. 1. Idealized projection of the niocalite structure on the $x0y$ plane. The numbers indicate the z -coordinates of the cations in thousandths of the c axis

unit cell of niocalite. Calculation of a series of R -factors for various variants of the Nb distribution indicated that one may even suspect a triclinic

Fig. 1. Idealized projection of the niocalite structure on the $x0y$ plane. The numbers indicate the z -coordinates of the cations in thousandths of the c axis

scheme of Nb distribution in the unit cell. This scheme is visible in Fig. 1. The triclinic violation of symmetry is very small. If one adds to the occupied Ca_1 position an isomorphous impurity of Nb, the symmetry of niocalite will be strictly described by the group $P2_1$. The atomic coordinates given in Table 1 were calculated using effective values of atomic factors, which averaged the triclinic occupation of the positions related by the symmetry of the $P2_1$ group.

In geometry, the structural motif of niocalite is indeed close to the structure of cuspidine⁽⁵⁾, l avenite⁽⁶⁾, and wohlerite⁽⁹⁾, i.e., monoclinic niocalite is characterized by quadruple infinite ribbons along the c axis, made up of octahedra. The occupation of these octahedra by cations is shown in Fig. 1, in which the non-centrosymmetric character of the distribution of cations among the octahedra is clearly apparent. In niocalite, the octahedra occupied by cations of high valence (Nb) are joined to one another either in the middle of the quadruple infinite ribbon, or in the first and second columns of this ribbon. This character of the linkage of octahedra in niocalite distinguishes its structure from l avenite and wohlerite, in which such octahedra are separated into the outer columns (in l avenite) or alternate with octahedra occupied by large cations (in wohlerite).

It should be noted that the closeness of the chemical formulas of cuspidine $Ca_4[Si_2O_7]F_2$ and niocalite $Ca_{3.5}Nb_{0.5}Si_2O_{72}$ does not ensure the identity of their structures. The replacement of only 12.5 at.% Ca by Nb lowers

had a symmetry ranging from the monoclinic merohedry of cuspidine to the triclinic symmetry of niocalite. Most of the details of the structure of the latter obey the group $P2_1$, while certain features, as in other structures of the cuspidine group, possess rhombic pseudosymmetry.

As is seen from Fig. 1, on which the z -coordinates of the cations are indicated, three diorthogroups out of four are stretched over pure Ca octahedra, while the last is joined by one of its edges to the polyhedron (Nb, Ca) of the trigonal prism described. An analogous situation had already been noted earlier in the structure of velarite⁽⁷⁾. The shortening of one of the edges of the trigonal prism does not contradict the basic principles of the crystal chemistry of silicates with large cations⁽¹²⁾.

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REFERENCES

- ¹ E. H. Nickel, *Am. Min.*, **41**, 785 (1956).
- ² J. F. Rowland, E. H. Nickel, J. A. Maxwell, *Canad. Min. Metal. Bull.*, **547**, 667 (1957).
- ³ H. Strunz, *Mineralogical Tables*, Moscow, 1962.
- ⁴ R. Kern, A. Rimsky, J. C. Monier, *C. R.*, **243**, 2063 (1957).
- ⁵ R. F. Smirnova, I. M. Rumanova, N. V. Belov, *Zap. Vsesoyuzn. mineralog. obshch.*, vol. 87, 2, 159 (1955).
- ⁶ V. I. Simonov, N. V. Belov, *DAN*, **130**, No. 6 (1960).
- ⁷ R. P. Shibaeva, N. V. Belov, *DAN*, **146**, No. 4 (1962).
- ⁸ V. I. Simonov, N. V. Belov, *Kristallografiya*, **4**, No. 2 (1959).
- ⁹ R. P. Shibaeva, V. I. Simonov, N. V. Belov, *Kristallografiya*, **8**, No. 4 (1963).
- ¹⁰ Li Da-yu, V. I. Simonov, N. V. Belov, *DAN*, **162**, No. 6 (1965).
- ¹¹ *International Tables for X-ray Crystallography*, 1962.
- ¹² N. V. Belov, *Crystal Chemistry of Silicates with Large Cations*, Moscow, 1961.

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