

STRUCTURE
OF INORGANIC COMPOUNDS

Refined Crystal Structure of Lovozerite
 $\text{Na}_2\text{CaZr}[\text{Si}_6\text{O}_{12}(\text{OH},\text{O})_6] \cdot \text{H}_2\text{O}$

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Abstract—The structure of Na,Ca,Zr-silicate lovozerite, $\text{Na}_2\text{CaZr}[\text{Si}_6\text{O}_{12}(\text{OH},\text{O})_6] \cdot \text{H}_2\text{O}$, from the Khibiny alkaline massif (the Kola Peninsula) was refined by single-crystal X-ray diffraction analysis (Syntex P1 diffractometer, $\lambda\text{MoK}\alpha$ radiation, $2\theta/\theta$ scanning technique). The refinement ($R_{hkl} = 0.077$, 1531 independent reflections; anisotropic thermal parameters) confirmed the trigonal system proposed for the mineral earlier (sp. gr. $R\bar{3}$; $a = 10.18(1) \text{ \AA}$, $c = 13.13(2) \text{ \AA}$, $Z = 3$) and revealed the presence of two additional positions (C and B) statistically occupied by Ca and Na atoms (and partly by Mn) and H_2O molecules, respectively. © 2001 MAIK “Nauka/Interperiodica”.

The crystal structure of the alkali zirconium silicate lovozerite was first solved in 1960 within the monoclinic space group $C2$ ($a = 10.48 \text{ \AA}$, $b = 10.20 \text{ \AA}$, $c = 7.33 \text{ \AA}$, $\beta = 92^\circ 30'$) [1]. Lovozerite can be considered as a parent mineral for a large group of natural and synthetic compounds, whose structures are based on a framework of six-membered silicon–oxygen (lovozerite-type) rings linked through isolated M -octahedra. The cavities of the framework are occupied by Na atoms and H_2O molecules. Later [2], lovozerite of composition $(\text{Na}_{2.5}\text{Ca}_{0.5}\text{Mg}_{0.2})_{3.2}(\text{Zr}_{0.7}\text{Fe}_{0.2}^{3+}\text{Ti}_{0.1})_{1.0}(\text{Si}_{5.8}\text{Al}_{0.2})_{6.0}\text{O}_{13.0}((\text{OH})_{5.2}\text{Cl}_{0.2})_{5.4}$ found in pegmatites from the Khibiny massif (the Kola Peninsula) was studied by the X-ray diffraction method. It was shown that the mineral belongs to the trigonal system ($a = 10.18 \text{ \AA}$, $c = 13.01 \text{ \AA}$) with the possible space groups $R\bar{3}2$, $R\bar{3}m$, and $R\bar{3}m$. The matrix of the transformation of the trigonal unit cell into the monoclinic one has also been reported: $(-1/3 \ -2/3 \ -2/3; 1 \ 0 \ 0; -1/3 \ -2/3 \ 1/3)$. The parameters of the monoclinic unit cell thus obtained ($a = 10.53 \text{ \AA}$, $b = 10.18 \text{ \AA}$, $c = 7.32 \text{ \AA}$, $\beta = 92^\circ 40'$) were virtually equal to those determined previously [1]. It should be noted that the lovozerite formula $\text{Na}_2\text{ZrSi}_6\text{O}_{15} \cdot 3\text{H}_2\text{O} \cdot 0.5\text{NaOH}$ proposed as the most probable in [1] is incorrect, because it takes no account of the presence of divalent cations, which, according to the data of chemical analysis, should be present in this mineral. This incorrectness is also evidenced by the results of all the more recent studies, which revealed that divalent cations occupy the position C in the lovozerite structural type. The crystallochemical analysis of lovozerite-like compounds [3, 4] demonstrated that their structures consist of identical pseudocubical ($a = 7.5 \text{ \AA}$) block units of the general formula $A_3B_3C_2M[\text{Si}_6\text{O}_{18}]$ (Fig. 1). The vertices of the blocks

are occupied by M cations ($M = \text{Zr}, \text{Ti}, \text{Mn}, \text{Fe}, \text{Ca}, \text{Sn}, \text{Cd}, \text{etc.}$) octahedrally coordinated by oxygen ions. The Si cations are located in the centers of six octants of each block. The centers of the remaining two octants (along one of the threefold axes of the prototype cell) are also occupied by octahedrally coordinated C cations ($C = \text{Ca}, \text{Mn}, \text{Na}, \text{etc.}$). The positions at the midpoints of the edges (A) and in the centers of the faces (B) of the above-mentioned blocks are filled predominantly with Na cations (more rarely, with Fe, Ti, Mn, Ca, Cd, or H). The diversity of the structures of the minerals of the lovozerite group is associated with the variations in the mode of filling of the above positions in the block and in the mode of junction of the adjacent blocks.

The ambiguity of the results of lovozerite investigation [1, 2] as well as the lack of the structural data for the trigonal modification of the mineral described in [2] gave impetus to the refinement of its crystal structure.

The lovozerite specimen was selected from a small veined rischorrite pegmatite stripped by the Apatitovyĭ Tsirk quarry at the Rasvumchorr mountain in the south of the Khibiny alkaline massif (the Kola Peninsula). The pegmatite is composed of potash feldspar, nepheline, black prismatic aegirine-diopside, green fibrous aegirine, alkaline amphibole, eudialyte, lamprophyllite, and lovozerite as the main minerals. Lomonsovite, magnesiumastrophyllite, pectolite, calborsite, rasvumite, hisingerite, etc. are present in minor amounts. Lovozerite replaces eudialyte crystals and is developed as a rim and, sometimes, as massive grained complete pseudomorphs up to 3–4 cm in diameter (isometric grains of sizes up to 1–1.5 mm) and has the sandy-yellow or the creamy color. Relics of the primary ultra-agpaitic paragenesis indicate that these pseudomorphs after eudialyte were originally composed of

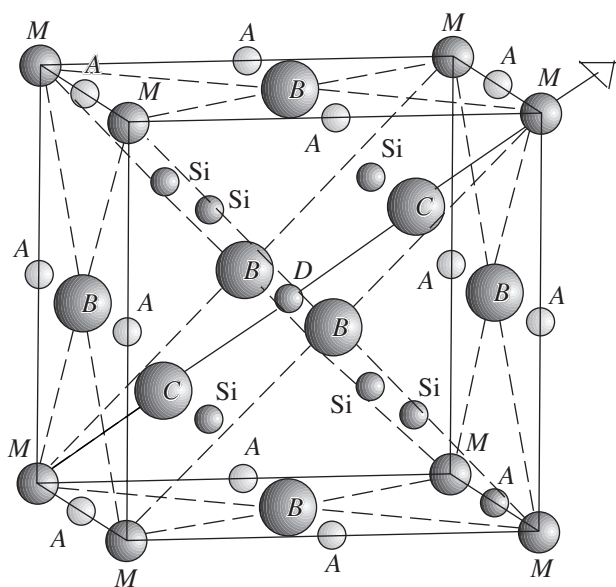


Fig. 1. Schematic arrangement of the atomic positions in the cubic "prototype unit cell" of the lovozerite structural type [4].

zirsinalite $\text{Na}_6\text{CaZrSi}_6\text{O}_{18}$. As the alkalinity of the medium decreased, this mineral lost some sodium, which was accompanied by hydration, and transformed into lovozerite stable under these conditions. The chemical composition of the lovozerite was studied by the electron probe analysis. Quantitatively, sodium and water contents were determined by the wet method. The average composition (wt %) is as follows: Na_2O , 7.7; K_2O , 0.6; CaO , 4.6; MgO , 0.1; MnO , 1.4; Fe_2O_3 , 2.0; SiO_2 , 58.7; TiO_2 , 0.5; ZrO_2 , 15.4; HfO_2 , 0.3; Nb_2O_5 , 0.1; H_2O^+ , 10.3; the sum is 101.7. The empirical formula (with respect to $\text{Si}_6(\text{O}, \text{OH})_{18}$): $(\text{Na}_{1.52}\text{K}_{0.08})_{\Sigma 1.60} \cdot (\text{Ca}_{0.50}\text{Mn}_{0.12}\text{Mg}_{0.02})_{\Sigma 0.64} (\text{Zr}_{0.77}\text{Fe}_{0.15}\text{Ti}_{0.04}\text{Hf}_{0.01})_{\Sigma 0.97} \cdot [\text{Si}_6\text{O}_{12.61}(\text{OH})_{5.39}]_{\Sigma 18} 0.82\text{H}_2\text{O}$.

EXPERIMENTAL

X-ray diffraction data were collected from a single crystal of dimensions $0.15 \times 0.15 \times 0.25$ mm. The parameters and the symmetry of the trigonal unit cell ($a = 10.18 \text{ \AA}$, $c = 13.13 \text{ \AA}$) were refined on an automated single-crystal Syntex $P\bar{1}$ diffractometer. The X-ray data were collected on the same diffractometer. The details of the X-ray diffraction study are given in Table 1. The systematic absences of the hkl reflections not satisfying the condition $-h + k + l = 3n$, and the non-equivalence of the pairs of the hkl and $kh\bar{l}$ reflections indicate the rhombohedral Bravais lattice and two possible space groups— $R3$ and $R\bar{3}$. All the subsequent calculations were carried out with the use of the AREN program package [5]. At the first stage, the monoclinic system proposed in [1] was tested by refining the lovo-

zerite structure in the monoclinic C -centered unit cell with the parameters $a = 10.54 \text{ \AA}$, $b = 10.18 \text{ \AA}$, $c = 7.33 \text{ \AA}$, $\beta = 92^\circ 79'$. The matrix of the transformation from the R - to the C -centered cell was as follows: $-1/3 \ -2/3 \ -2/3; 1 \ 0 \ 0; -1/3 \ -2/3 \ 1/3$. The atomic coordinates reported in [1] were used as the starting model. The refinement of the model by the least-squares method within the possible space groups $C2/m$, $C2$, and Cm gave inadequate results due to the considerable scatter in the interatomic distances in the Si-tetrahedra and the high reliability factors (0.17, 0.15, and 0.12, respectively). Hence, the subsequent calculations were carried out within the acentric space group $R3$. The starting model was refined isotropically by the least-squares method to $R_{hkl} = 0.12$. The difference electron density synthesis revealed two additional maxima with the coordinates $x_1 \approx 0.25$, $y_1 \approx 0$, $z_1 \approx 0.75$ and $x_2 \approx 0.01$, $y_2 \approx 0.5$, $z_2 \approx 0.1$ (coincided with the C and B positions, respectively) of the pseudocubic block typical of the lovozerite structural type (Fig. 1). It was assumed that the C position is occupied by Ca, Na, and Mn cations, whereas the B position is occupied by H_2O molecules. The distribution of the cations over all independent crystallographic positions was determined by refining the occupancies and then the atomic scattering curves were chosen with due regard for the data of chemical analysis, the determination of the effective ionic radii of the cations, the thermal parameters of the atoms, and the average cation–oxygen distances. The refinement of the model by the least-squares method with allowance for mixed filling of some cationic positions gave the minimum final reliability factors $R_{hkl} = 0.104$ and 0.077 in the isotropic and anisotropic approximations, respectively. The distribution of the cations is indicated in Table 2.

The detailed crystallochemical formula of lovozerite is $(\text{Na}_{2.2}\text{K}_{0.1})(\text{Ca}_{0.4}\text{Na}_{0.2}\text{Mn}_{0.1})(\text{Zr}_{0.8}\text{Fe}_{0.1}\text{Ti}_{0.03}\text{Hf}_{0.03}) \cdot [\text{Si}_6\text{O}_{12}(\text{OH})_3(\text{OH}_{0.6}\text{O}_{0.4})_3] \cdot 0.9\text{H}_2\text{O}$. The idealized formula is $(\text{Na}, \square)_3(\text{Ca}, \text{Na}, \square)\text{Zr}[\text{Si}_6\text{O}_{12}(\text{OH})_3(\text{OH}, \text{O})_3] \cdot \text{H}_2\text{O}$. The anionic portion of the structure was separated into the O^{2-} ions and $(\text{OH})^-$ groups based on the results of calculations of the local valence balance according to Pyatenko [6]. The high values of the atomic thermal parameters and a rather high R_{aniso} factor (0.077) are explained by an insufficiently high quality of the single crystal used and, consequently, insufficiently high quality of the experimental data and the presence of vacancies. The final coordinates of the basis atoms and the equivalent thermal parameters are given in Table 2.

RESULTS AND DISCUSSION

On the whole, the refinement of the lovozerite structure confirmed the initial model [1], based on the framework of six-membered rings of the $[\text{Si}_6\text{O}_{12}(\text{OH})_3(\text{OH}, \text{O})_3]$ tetrahedra (the average Si–O distances in the Si(1)- and Si(2)-tetrahedra are 1.55 and 1.60 \AA , respectively) sharing the oxygen vertices with isolated M -octahedra (the M –O distances vary from 2.0

Table 1. Principal details of X-ray diffraction study of lovozerite

Characteristic	Value
Crystal dimensions, mm	0.15 × 0.15 × 0.20
Automated single-crystal diffractometer	Syntex $P\bar{1}$
Radiation	Mo K_{α}
Monochromator	Graphite
Sp. gr.	$R3$
Unit-cell parameters	$a = 10.18(1) \text{ \AA}$ $c = 13.13(2) \text{ \AA}$ $V = 1180(3) \text{ \AA}^3$
Number of formula units, Z	3
Scanning technique	$2\theta/\theta$
Maximum $\sin\theta/\lambda$	1.064
Scan rate	4–24 deg/min
Number of measured reflections with $I > 1.96 \delta(I)$ within the reciprocal-space hemisphere	1531
Number of independent reflections	753
Program package	AREN
Reliability factors R_{hkl} :	
isotropic refinement	0.104
anisotropic refinement	0.077
Weighting scheme used in the least-squares procedure	$w = 1/(A + F + BF^2)$ $A = 2F_{\min}$ $B = 2/F_{\max}$

Table 2. Coordinates of the basis atoms and individual thermal parameters in the lovozerite structure

Atom (position)	Position multiplicity	Position occupancy	x/a	y/b	z/c	$B_{\text{eq}}, \text{ \AA}^2$
(A)	9	0.73Na + 0.03K	0.341(3)	0.172(2)	0.166(2)	4.3(3)
(B)	9	0.3H ₂ O	0.002(8)	0.462(6)	0.006(4)	4.4(3)
(C)	3	0.35Ca + 0.20Na + 0.08Mn	0	0	0.742	6.2(2)
(M)	3	0.80Zr + 0.14Fe + 0.03Ti + 0.03Hf	0	0	0	2.9(2)
Si(1)	9	Si	0.4829(8)	0.5172(8)	0.2208(6)	3.3(2)
Si(2)	9	Si	0.1835(5)	0.3696(6)	0.0952(5)	2.2(1)
O(1)	9	O	0.447(3)	0.224(3)	−0.003(2)	7.3(6)
O(2)	9	(OH, O)	0.555(3)	0.424(3)	0.248(2)	6.5(5)
O(3)	9	(OH)	0.208(2)	0.104(2)	0.325(1)	3.1(3)
O(4)	9	O	0.336(3)	0.433(4)	0.159(2)	8.8(9)
O(5)	9	O	0.101(2)	0.184(2)	0.091(1)	3.1(3)
O(6)	9	O	0.601(2)	0.667(2)	0.161(1)	4.9(4)

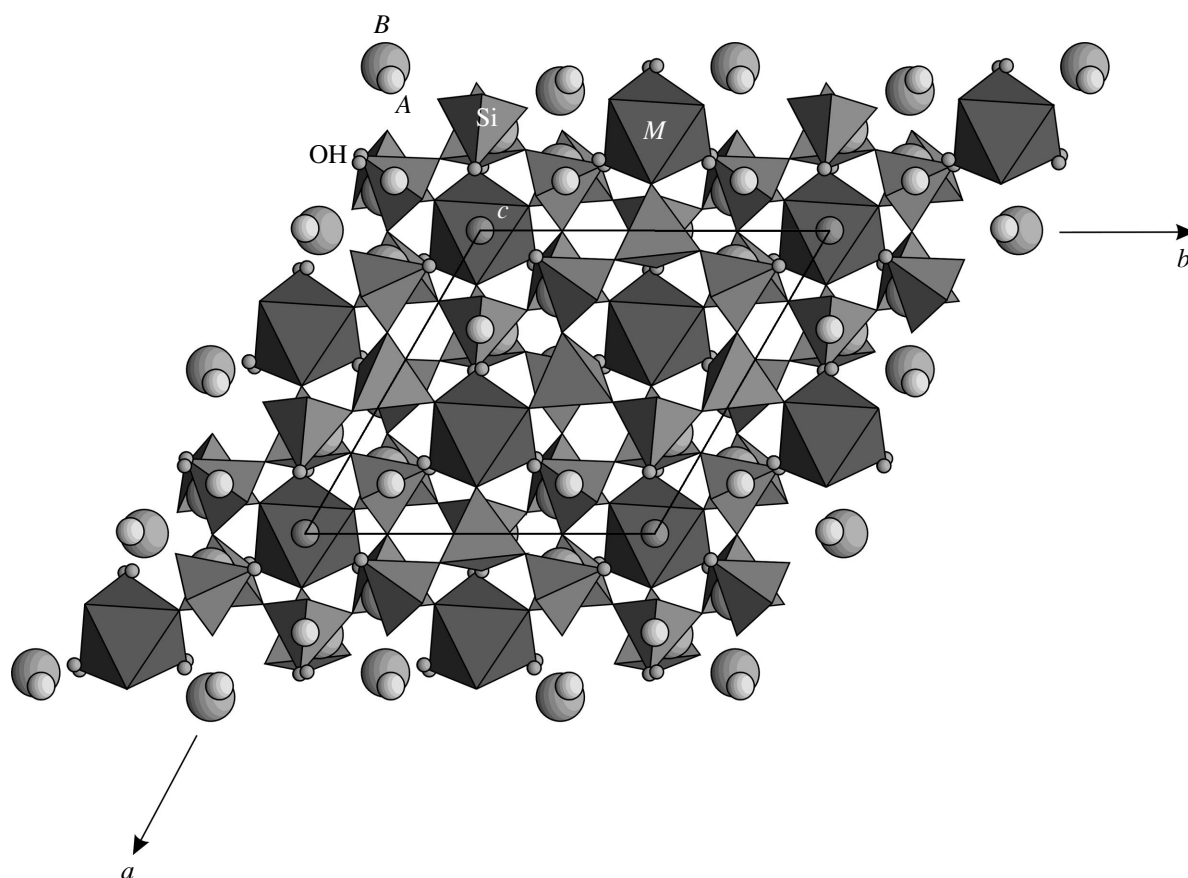


Fig. 2. Crystal structure of lovozerite projected onto the xy plane.

to 2.11 Å; the average is 2.06 Å) (Fig. 2). The M cations (predominantly Zr) in the model of lovozerite proposed earlier [1] and in the refined structure are located in the lattice sites of the pseudotrigonal (monoclinic) and trigonal unit cells, respectively. In the monoclinic cell, the M positions are located in the centers of the basal faces of the C cell. The matrix of the transformation from the C unit cell to the double-centered hexagonal R cell is $1/2 -1/2 1; 0 1 0; -1 0 1$. The refined lovozerite structure differs from the earlier model primarily in that in the former, the cationic C position is statistically (by ~60%) filled with Ca, Na, and Mn atoms (the C -O distances vary from 2.19 to 2.89 Å; the average is 2.54 Å). The C -octahedra share the oxygen faces with the M -octahedra and also contribute to strengthening of the crystal structure.

It should be noted that the C position was also found in the structure of a new representative of the lovozerite group, Na,Zr-silicate litvinskite $(\text{Na}, \text{H}_2\text{O}, \square)_3 (\square, \text{Na}, \text{Mn}^{2+})\text{Zr}[\text{Si}_6\text{O}_{12}(\text{OH})_3(\text{OH}, \text{O})_3]$ ($a = 10.589$ Å, $b = 10.217$ Å, $c = 7.355$ Å, $\beta = 92.91^\circ$, sp. gr. Cm , $Z = 2$) [7, 8] discovered in ultra-agpaitic pegmatites from the Lovozero massif (the Kola Peninsula). However, these positions in two minerals are filled differently. Thus, the C position in lovozerite is occupied predominantly

by Ca and Na cations by about 60%, whereas this position in litvinskite is occupied by 33% and predominantly by Na and Mn cations. Similar to litvinskite, this position in lovozerite is the only one that does not obey the center of inversion, i.e., violating the centrosymmetric structure. The Na cations in the lovozerite structure are located in the framework cavities and statistically occupy (by ~80%) the A position (in the monoclinic space group, this position is split into two independent positions). The A -O distances in the eight-vertex A -polyhedra vary from 2.38 to 2.87 Å (the average is 2.61 Å). In the study of the litvinskite structure [8], the possibility of the higher (trigonal) symmetry of the mineral has been examined; however, the results of the structure refinement within the trigonal unit cell turned out to be inadequate.

In the refined lovozerite structure, there is an additional B position statistically (by ~30%) filled with H_2O molecules. This position was not detected either in the initial lovozerite model [1] or in litvinskite [8].

The comparison of the refined lovozerite structure with the structure of zirsinalite having the similar composition $\text{Na}_6(\text{Ca}_{0.5}\square_{0.5})_2\text{Zr}[\text{Si}_6\text{O}_{18}]$ ($a = 10.29$ Å, $c = 26.31$ Å, sp. gr. $R\bar{3}c$, $Z = 6$) [9] after the transformation of the atomic coordinates of the latter [9] from the trig-

onal R unit cell to the double-centered hexagonal cell showed that these structures are virtually identical (the matrix of the transformation from the hexagonal R cell of zirsinalite to the analogous unit cell of lovozerite is $0 -1 0; 1 1 0; 0 0 1/2$). The only difference reduces to that the A position in the cubic prototype cell of the lovozerite structure (Fig. 1) is occupied by Na atoms and the B position is statistically (by $\sim 30\%$) occupied by H_2O molecules, whereas both these positions (A and B) in the zirsinalite structure characterized by the substantially higher Na content are filled with Na atoms alone. The Ca atoms in the zirsinalite structure statistically (by $\sim 50\%$) occupy both C positions with retention of the center of symmetry, whereas only one of two C positions in the lovozerite structure is occupied by Ca (Na, Mn) atoms (also statistically, by 60%), which excludes the presence of centers of inversion in the latter structure. In addition, doubling of the unit-cell parameter c of zirsinalite ($c = 26.31 \text{ \AA}$) in comparison with that of lovozerite ($c = 13.01 \text{ \AA}$) is explained by the presence of the coordinate planes c and the center of inversion in the holohedral sp. gr. $R\bar{3}c$ of zirsinalite, which are absent in the sp. gr. $R3$ of lovozerite. The structural similarity of lovozerite and zirsinalite is determined genetically. According to Khomyakov, lovozerite cannot be crystallized alone and, thus, can arise only as homoaxial pseudomorph after zirsinalite [10]. No facts inconsistent with this hypothesis have been found. Hence, the process of lovozerite generation from zirsinalite reduces to the loss of more than one-half of sodium atoms, with the deficiency of the positive charge being compensated by the replacement of the corresponding number of oxygen atoms by the OH groups. This process is also accompanied by incorporation of water molecules into one of the empty cavities. The number of cations located in the framework cavities drastically decreases upon the transformation of zirsinalite into lovozerite, which manifests itself in the density ($2.9\text{--}3.0 \text{ g/cm}^3$ for zirsinalite and $2.4\text{--}2.7 \text{ g/cm}^3$ for lovozerite) and in the refractive indices ($1.605\text{--}1.610$ and $1.53\text{--}1.57$ for zirsinalite and lovozerite, respectively). However, neither the cationic composition nor the configuration of the $\{Zr[Si_6(O, OH)_{18}]\}$ framework are changed in the transition from zirsinalite to lovozerite, which provides the close structural rela-

tionship between the prototype phase (zirsinalite) and the newly formed mineral (lovozerite).

To summarize, the refinement of the lovozerite structure confirmed the trigonal symmetry of the mineral proposed earlier by Kapustin *et al.* [2] and revealed the presence of two additional (C and B) positions statistically occupied by Ca and Na (and partly by Mn) cations and H_2O molecules, respectively. Thus, the idealized formula of lovozerite should be written as $Na_2CaZr[Si_6O_{12}(OH, O)_6] \cdot H_2O$.

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