

MICROTWINNING OF
 $\text{Na}_5(\text{Na}_{0.5+x}\text{Ca}_{0.5-x})_2(\text{Nd}_x\text{Ca}_{1-x})_2[\text{Si}_6\text{O}_{18}]$
 AND CRYSTAL CHEMISTRY OF SILICATES
 OF THE LOVOZERITE FAMILY

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The idea of the paper emerged after finishing an X-ray crystal structure investigation of a synthetic compound belonging to the lovozerite family. Crystals of $\text{Na}_5(\text{Na}_{0.5+x}\text{Ca}_{0.5-x})_2(\text{Nd}_x\text{Ca}_{1-x})_2[\text{Si}_6\text{O}_{18}]$ were obtained in the $\text{Na}_2\text{O}-\text{CaO}-\text{Nd}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ system under hydrothermal conditions. Unit cell parameters, measured by photographic method and refined on an autodiffractometer were as follows: $a = 14.926(5)$, $b = 15.003(4)$, $c = 7.446(5)$ Å, $\gamma = 91.79^\circ$, Laue class $2/m$.

We were unable to solve the structure with the aid of direct and Patterson methods in any of the possible symmetry space groups ($P2_1/a$, $P2_1/b$, $P2_1/n$). In analyzing the three-dimensional function of the interatomic vectors we distinguished intense peaks with radius vectors $q = u/2$; $v/2$ and $(u + v)/2$. This fact can be explained by the presence either of pseudo periods or twinning. Therefore to solve the structure we calculated the partial function of interatomic vectors, where as pseudotranslation vector we chose the vector $p = v/2$. Using this special method we concluded that the diffraction experiment was obtained from a twin and that the unit cell representing the diffraction pattern was twinned [1].

The unit cell of the monocrystalline components of the twin with parameters $a = 7.501(5)$, $b = 14.926(5)$, $c = 7.446(5)$ Å, $\gamma = 91.79(3)^\circ$ can be obtained from a twinned cell with the aid of the following matrices: $1/2 \ 0 \ 0 / 0 \ 1 \ 0 / 0 \ 0 \ 1$ and $0 \ 1/2 \ 0 / 1 \ 0 \ 0 / 0 \ 0 \ 1$.

With such twinning the twin index is $n = 2$, i.e. half of the reciprocal lattice points of each single crystal are simultaneously reciprocal lattice points of the other single crystal, while the second half is independent. Therefore in this case in the diffraction pattern there are superimposed reflections representing diffraction from both components of the twin; non-superimposed reflections representing diffraction only from one component of the twin, and empty points – “twinning extinction” (figure 1).

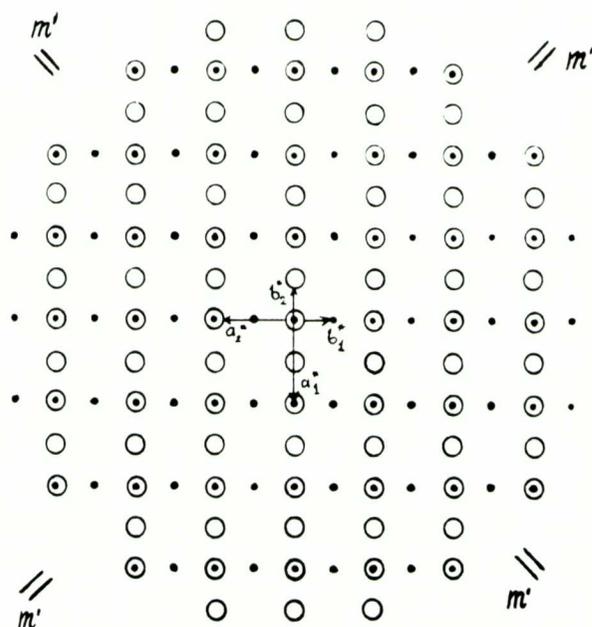


Fig. 1. Schematic image of the reciprocal space. Projection on plane perpendicular to c^* axis. Showing the reciprocal vectors of both components of the twin; dots and circles mark reflection of different components.

The model obtained for the structure (figure 2) with allowance for microtwinning was refined by means of the TWIN program [2].

Thus crystals of $\text{Na}_5(\text{Na}_{0.5+x}\text{Ca}_{0.5-x})_2(\text{Nd}_x\text{Ca}_{1-x})_2[\text{Si}_6\text{O}_{18}]$ are twinned according to the TLQS [3], and the twin index is $n = 2$ (according to Friedel's classification, twinning by a reticular pseudomerohedry). The symmetry elements of twinning are the plane (120) and the axis [210], and the symmetry of the twin is $m'm'm$ (figure 3) [4].

The structure of the test compounds belongs to the family of lovozerite-like structures [5]. Lovozerite, discovered in 1935, became the ancestor of a large group of natural and synthetic compounds with common structural features (tables 1 and 2). Just like in all lovozerite-like structures, in ours we can distinguish pseudocubic blocks with period $a = 7.5 \text{ \AA}$. Each block contains one six-membered lovozerite ring $[\text{Si}_6\text{O}_{18}]$. The vertices, the centers of the edges and faces, and the centers of two of the eight octants of the block are the cation positions. Si-atoms center six of the eight small cubes with $a = 3.75 \text{ \AA}$ in such a way that only one of the four triad axes of the cube is left. This explains the fact that, despite the circumstance that all the cations in the structure occupy positions at sites of the body-

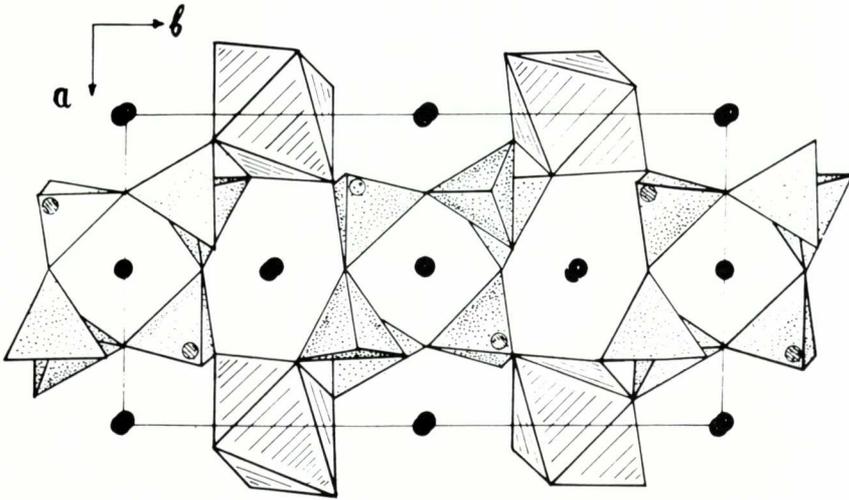


Fig. 2. Projection of structure on xy plane. The Na atoms are represented by black spheres, and the Na, Ca atoms by shaded ones. For clarity the Nd, Ca seven pointed polyhedra are simplified to octahedra.

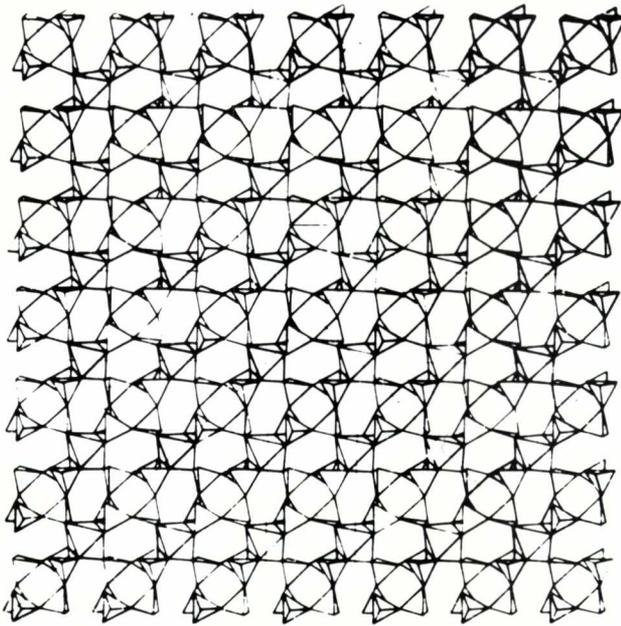


Fig. 3. Schematic image of twinning on (120) plane and along $[\bar{2}10]$ axis. We see the change in the law of joining of the lovozerite-like pseudocubic block on the twin joints.

Table 1. Distribution of Cations in Pseudocubic Lovozerite Block.

Compound	A	B	C	M	symmetry of block
lovozerite T $H_3Na_3Zr[Si_6O_{18}]$	12Na	6H	2H	8Zr	$\bar{3}m$
kazakovite $Na_6MnTi[Si_6O_{18}]$	12Na	6Na	2(Mn, \square)	8Ti	$\bar{3}m$
$Na_6Sn[Si_6O_{18}]$	12Na	6Na	2Na	8Sn	$\bar{3}m$
cyrsinalite $Na_6CaZr[Si_6O_{18}]$	12Na	6Na	2(Ca, \square)	8Zr	$\bar{3}m$
lovozerite M $H_6Na_2Zr[Si_6O_{18}]$	8Na+4H	6H	2H	8Zr	2
$Na_6Sn[Si_6O_{18}]$	12Na	6Na	2Na	8Sn	$\bar{3}m$
koashvite $Na_6(Ca,Mn)(Fe,Ti)[Si_6O_{18}]$	11Na+(Fe,Ti)	6Na	2(Ca,Mn, \square)	6(Fe,Ti)+2Na	<i>m</i>
imandrite $Na_6Ca_{1.5}Fe[Si_6O_{18}]$	10Na+2Fe	6Na	2(Ca, \square)	4Fe+4Na	2/ <i>m</i>
$Na_5(Na,Mn)_3Mn[Si_6O_{18}]$	10(Na,Mn)+2Mn	6Na	2(Na,Mn)	4Mn+4(Na,Mn)	2/ <i>m</i>
$Na_6Mn_3[Si_6O_{18}]$	10Na+2Mn	6Na	2Mn	4Mn+4Na	2/ <i>m</i>
$Na_6Cd_3[Si_6O_{18}]$	8Na+4Cd	6Na	Cd+Na	8Cd	<i>m</i>
$Na_5(Na,Ca)_2(Nd,Ca)_2[Si_6O_{18}]$	8Na+4(Nd,Ca)	6Na	2(Ca,Na)	8(Nd,Ca)	2/ <i>m</i>
kombeite I $Na_6Ca_3[Si_6O_{18}]$	–	–	–	–	–
$Na_6Ca_3[Si_6O_{18}]$	12(Ca,Na)	6Na	2(Na,Ca)	8Ca	$\bar{3}m$
kombeite II $Na_4Ca_4[Si_6O_{18}]$	–	–	–	–	–
$Na_4Ca_4[Si_6O_{18}]$	8(Ca,Na)+4Ca	4Na+2 \square	2(Ca,Na)	8Ca	2

Table 2. Crystallographic characteristics of lovozerite-like structures.

Compound	<i>a</i>	<i>b</i>	<i>c</i>	γ	space group	references
lovozerite T $H_5Na_3Zr[Si_6O_{18}]$	10.174		13.053		$R\bar{3}m$	[5]
kazakovite $Na_6MnTi[Si_6O_{18}]$	10.174		13.053		$R\bar{3}m$	[9]
$Na_6Sn[Si_6O_{18}]$	10.189		13.186		$R\bar{3}m$	[7]
cyrsinalite $Na_6CaZr[Si_6O_{18}]$	10.290		26.310		$R\bar{3}c$	[10]
lovozerite M $H_6Na_2Zr[Si_6O_{18}]$	7.33	10.48	10.20	92.50°	<i>A2</i>	[11]
$Na_6Sn[Si_6O_{18}]$	7.340	10.576	10.183	92.90°	<i>A2/m</i>	[8]
koashvite $Na_6(Ca,Mn)(Fe,Ti)[Si_6O_{18}]$	10.169	20.899	7.335		<i>Pmnb</i>	[12]
imandrite $Na_6Ca_{1.5}Fe[Si_6O_{18}]$	10.331	10.546	7.426		<i>Pmnn</i>	[13]
$Na_5(Na,Mn)_3Mn[Si_6O_{18}]$	10.40	10.40	7.45		<i>Pm2_n</i>	[14]
$Na_6Mn_3[Si_6O_{18}]$	10.354	10.251	7.374		<i>Pmnn</i>	[15]
$Na_6Cd_3[Si_6O_{18}]$	10.40	10.40	7.45		<i>Pm2_n</i>	[16]
$Na_5(Na,Ca)_2(Nd,Ca)_2[Si_6O_{18}]$	7.50	14.926	7.446	91.79°	<i>P2₁/b</i>	[4]
kombeite I $Na_6Ca_3[Si_6O_{18}]$	10.429		13.149		$R\bar{3}m$	[19]
$Na_6Ca_3[Si_6O_{18}]$	10.500		13.184		$R\bar{3}m$	[17]
kombeite II $Na_4Ca_4[Si_6O_{18}]$	10.464		13.176		<i>P3₁21</i>	[19]
$Na_4Ca_4[Si_6O_{18}]$	10.464		13.168		<i>P3₁21</i>	[18]

centered cubic lattice, the maximum symmetry of the lovozerite-like structures is only trigonal, $R\bar{3}m$ [5].

Since these blocks contain 16 sites of a body-centered cubic lattice and six of them are occupied by silicon atoms, there are ten possible positions for the remaining cations: two at the centers of two free small cubes on the three-fold axis (C-position), one at the vertices of the block (M-position), one at the center of the block (D-position), three at the centers of the edges of the block (A-positions), and three at the centers of the faces (B-positions) (figure 4). Note that the D-position has in its environment six valence-saturated bridging oxygen of the lovozerite ring $[\text{Si}_6\text{O}_{18}]$, and therefore it is always vacant. On this basis, the generalized formula of the block acquires the form $A_3B_3C_2M[\text{Si}_6\text{O}_{18}]$.

The atomic environment of the positions A , B , C and M depends on the modes of packing of these blocks in space. Let us consider all the possible variants of the joining of the blocks together, irrespective of the cation distributions in them. In the organization of the packing of the blocks in space, they can be joined together by any symmetry element or by trivial and nontrivial translations. For the blocks to be joined by any particular method, the following three conditions must be satisfied: 1) The cation positions of adjacent faces of neighboring blocks must coincide with one

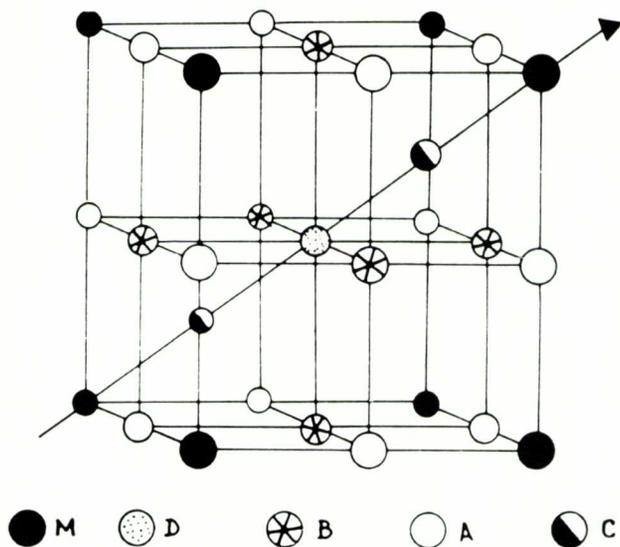


Fig. 4. Scheme of pseudocubic lovozerite block. Of the 16 cation positions six are not shown (at the centers of six octants of a cube), being always occupied by Si atoms of a silicon-oxygen ring.

another; 2) there must not be anomalously short contacts between the oxygen atoms of the lovozerite rings of adjacent blocks; 3) each cation position must be surrounded by a perfect Pauling polyhedron of anions.

The conclusion of the possible structural models is drawn by successive substitution of different symmetry elements for a compound of one or two pairs of lovozerite blocks. The resulting models are analyzed from the viewpoint of the possibility of their existence. We considered in detail the coordination polyhedra formed about the cation positions. Special attention was paid to the requirements imposed by the conditions of local valence balance of any particular cation position, taking account of the dimensions of the formed polyhedra and the number of their vertices.

Allowing for the three above conditions, the number of possible variants of the relations of adjacent blocks was small (figure 5): a) translation over one face; b) center of inversion lying at the center of the face of the block; c) three-fold screw axis, parallel to the triad axis of the block but not coinciding with it, with translation component equal to the space diagonal of the block; d) slip plane passing through three Si atoms and the C position parallel to a face of the block; e) dyad screw axis passing parallel to the edges of the block through *A* and *B* positions with a translational component equal to the parameter of the block. Note that a single block is not characterized in the general case of translation.

The above three conditions are necessary but not sufficient to effect a bond between adjacent blocks. So as to realize a bond of one particular type, it is necessary that the coincident (after joining of the blocks) cation positions should be populated by identical atoms. Consequently, the distribution of cations in a block completely determines the possible type of combination of the blocks.

With realization of any mode of combination of adjacent blocks, like or unlike cation positions may coincide, but they must be populated by identical cations. To get a translational relation, it is necessary that at least two parallel faces of the block shall be identical. For relation of a center of inversion there must be at least one face containing the center, and the cation occupation of the opposite face must be different. Otherwise, simultaneously with the relation by the center of inversion there arises a translational relation. Thus to a relation of each type there is inherent a characteristic distribution of cations [6].

Let us consider compounds with a lovozerite-like structure, containing one tetravalent cation: $\text{Na}_8\text{Sn}[\text{Si}_6\text{O}_{18}]$ [7,8], $\text{Na}_6\text{MnTi}[\text{Si}_6\text{O}_{18}]$ (kazakovite) [9], $\text{Na}_6\text{CaZr}[\text{Si}_6\text{O}_{18}]$ (cyrsinalite) [10] and $\text{H}_6\text{Na}_2\text{Zr}[\text{Si}_6\text{O}_{18}]$ (monoclinic lovozerite) [11]. In the structures of all these compounds the tetravalent cation occupies only the *M* position (table 1). Positions *A*, *B* and *C* are occupied mainly by univalent cations.

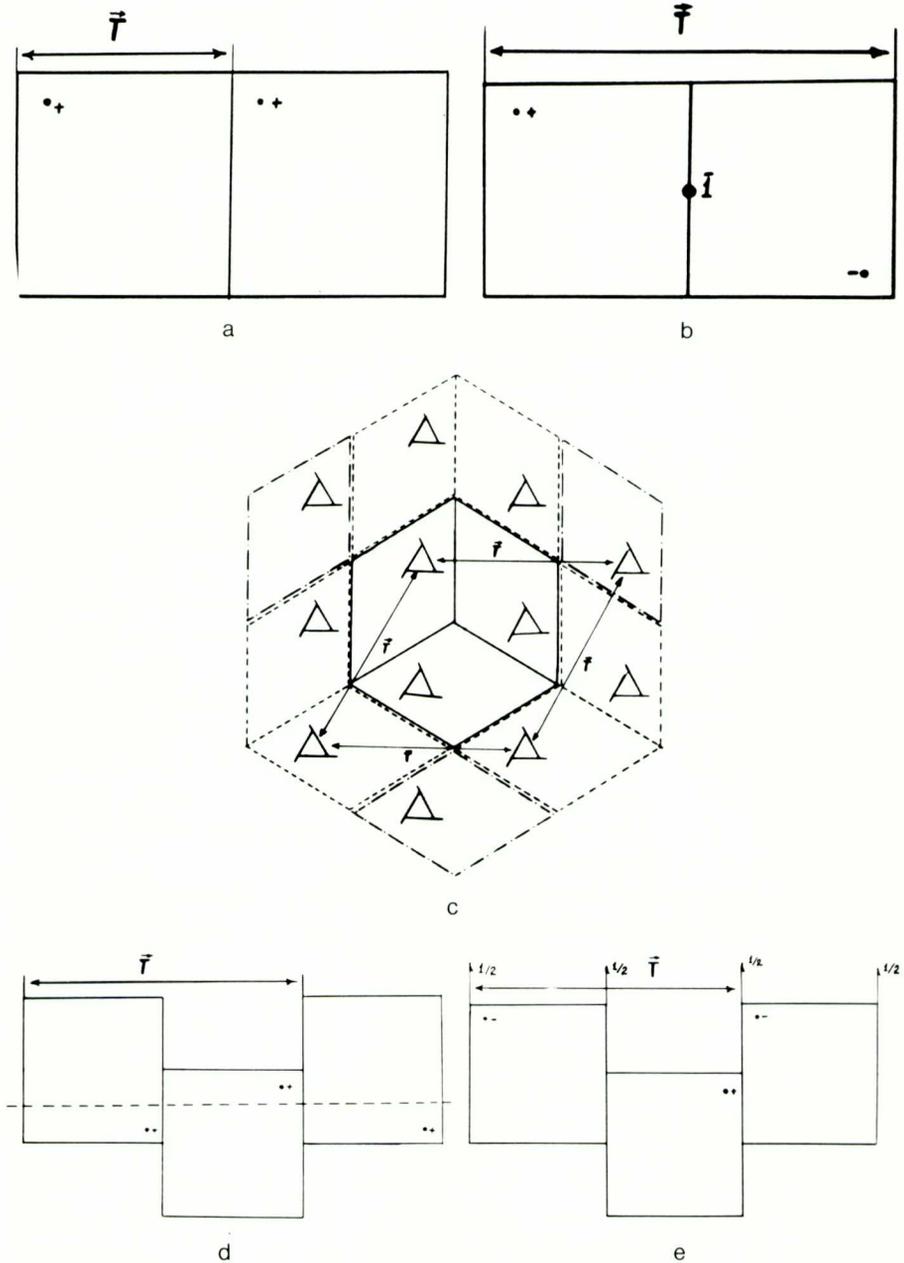


Fig. 5. Schematic image of different modes of relation of pseudocubic blocks. a) Translation; b) center of inversion; c) screw triad axis (projection onto perpendicular plane); d) slip plane; e) screw dyad axis.

With this distribution of cations, all the parallel faces of the block become identical. This uniquely determines the possible type of relation of adjacent blocks in all directions – translational. In the structures of the first three compounds the cation distribution does not interfere with the maximum possible symmetry of the block, $3\bar{m}$. A consequence of this is the high symmetry of the structures $\bar{R}3m$.

Let us now consider structures containing less or no tetravalent cations, but an increased content of di- and trivalent cations. In the koashvite [12] two of all the M positions on one edge are occupied by Na atoms, and the high charge cations (Fe, Ti) are displaced to the A position at the center of this edge. As before, the divalent cations occupy two C -positions. This redistribution of the cations in the block, at first sight negligible, leads to marked changes in the structure as a whole. Since only one pair of parallel faces of the block remains equivalent, the translational relation is effected only in this direction. The two other pairs of faces are translationally nonidentical. The faces adjoining an edge centered by cations (Fe, Ti) contain dyad screw axes parallel to this edge. The two faces opposite to them have centrosymmetrical cation distribution ($\bar{1}$ at the center of the faces). Thus the type of relations of the blocks is uniquely determined in all directions. The symmetry elements of the block themselves (m) and the symmetry elements joining the blocks in associations determine the symmetry of the structure as a whole.

With complete replacement of the tetravalent cations by trivalent (Fe) and divalent (Ca) ones, we get the composition of imandrite [13].

The novelty of the distribution of cations in the block is that two opposite (in the diagonal direction) edges of the block are already centered by high-charge cations, while the adjacent vertices are occupied by Na atoms. Then the symmetry of the block is increased from m to $2/m$. One pair of parallel faces remains identical, but the other two are related by glide planes. Hence we can uniquely determine the type of joining of the blocks, in one direction translationally, but in the other two directions by glide plane passing at $1/4$ the height of the block parallel to one of the faces, with a translational component along the edge. The symmetry element of the block $2/m$, together with the symmetry elements with the relations, determine the symmetry and the lattice of the structure as a whole.

With further change in the cation composition (with replacement of the trivalent cations by divalent ones), depending on the ionic radius of the substituent atoms, we get two different structural groups.

In the case of replacement of Fe by Mn or Cd, the distribution of cations in the block in comparison with imandrite undergoes no changes and former compounds $\text{Na}_5(\text{Na}, \text{Mn})_3[\text{Si}_6\text{O}_{18}]$, $\text{Na}_6\text{Mn}_3[\text{Si}_6\text{O}_{18}]$ and $\text{Na}_6\text{Cd}_3[\text{Si}_6\text{O}_{18}]$ [14, 15, 16] remain isostructural with imandrite. With replace-

ment of Fe by Ca atoms (larger than Mn and Cd), with addition of Nd atoms there follows a fundamentally novel redistribution of the cations. Neodymium atoms (isomorphic with calcium) occupy all the *M* positions and four of the 12 *A* positions on the parallel edges of the block. The remaining *A* positions and all the *B* positions are occupied by Na atoms, and the *C* positions are statistically filled by Na and Ca atoms.

This cation distribution makes all the parallel faces identical in pairs. Moreover, two pairs of faces are related by glide planes. As a result, the pseudocubic blocks in one direction can be related only by translations, and in two other directions both by translations and by glide planes. There appears the possibility of formation of structures both of the lovozerite type (three translations) and of the imandrite type. But in both cases, the positions *M* and $1/3 A$, identically occupied by (Nd, Ca) atoms, would appear in different coordination environments by anions (octahedron and eight-pointed polyhedron), which would lead to some deviation of the local balance of valence forces. Two oxygen atoms of the eight-pointed polyhedron are bridging atoms of the lovozerite ring. It is for this reason that some intermediate variant of the organization of the structure turns out to be preferable. In two directions the blocks are related by a translation, and in the third one – by a glide plane. The result of this conjunction of the blocks is described by monoclinic unit cell of the synthetic compound $\text{Na}_5(\text{Na}, \text{Ca})_2(\text{Nd}, \text{Ca})_2[\text{Si}_6\text{O}_{18}]$ [4]. This cation distribution in a block makes it possible for the blocks in two directions to be linked in two different ways. It is natural to expect that in the real structure these two ways will very probably be realized simultaneously, and this also leads to microtwinning of the crystals.

Complete replacement of the trivalent cations by divalent Ca leads to compositions of the types $\text{Na}_6\text{Ca}_3[\text{Si}_3\text{O}_{18}]$ and $\text{Na}_4\text{Ca}_4[\text{Si}_6\text{O}_{18}]$ [17, 18, 19]. The first type composition is realized in one variety of mineral kombeite and in the synthetic compound. In this composition all the *M* positions are occupied by Ca atoms while the *A* and *C* positions are statistically occupied by Ca and Na atoms, and the *B* positions by Na atoms. As a result, all the parallel faces are identical in pairs, and the symmetry of the block is increased to the maximum $\bar{3}m$. In the upshot the only possible translational relation between the blocks is realized, determining the symmetry $R\bar{3}m$ and the translational lattice of the structure as a whole.

Increasing the fraction of divalent cations to $\text{Na}_4\text{Ca}_4[\text{Si}_6\text{O}_{18}]$, we get another variety of kombeite and its synthetic analog [18, 19]. In the structures of these phases, calcium, besides the *M* position, occupies the $1/3 A$ positions. Two vacancies then arise in the *B* positions. This distribution reduces the symmetry of the block to 2, and none of the pairs of parallel faces is identical. But now it appears that if three faces intersecting at the

point of emergence of the triad axis of the block remain unaltered, and the other three are rotated through 120° about the triad axis, then all the three pairs of parallel faces become identical. This procedure can be described as rotation and displacement of the block by a screw axis $3_1(3_2)$, passing parallel to the triad axis of the block but not coinciding with it (fig. 5). Note that several variants of the distribution of four Ca cations in *A* positions are in principle possible, but only one of them realized in the structure of $\text{Na}_4\text{Ca}_4[\text{Si}_6\text{O}_{18}]$, permits the organization of a three-dimensional construction of pseudocubic blocks.

Thus we again emphasize that the distribution of cations in the block completely determines the symmetry and structural type of all the lovozerite-like phases.

ABSTRACT

Crystals of $\text{Na}_5(\text{Na}_{0.5+x}\text{Ca}_{0.5-x})_2(\text{Nd}_x\text{Ca}_{1-x})_2[\text{Si}_6\text{O}_{18}]$ have been studied by X-ray diffraction technique. These crystals are twinned according to TLQS, and the twin index is $n = 2$ (according to Friedel classification, this is twinning by reticular pseudomerohedry). The unit cell of the monocrystalline components of the twin has the following parameters: $a = 7.501(5)$, $b = 14.926(5)$, $c = 7.446(5)$ Å, $\gamma = 91.79(3)^\circ$, sp.gr. $P2_1/b$. The symmetry elements of twinning are the plane (120) and the axis [210], the symmetry of the twin being $m'm'm$.

The structure of the test compounds belongs to the family of lovozerite-like structures. Lovozerite became the ancestor of a large group (comprising more than 15 members) of natural and synthetic compounds with common structural features. In all these structures we can distinguish pseudocubic blocks with the period $a = 7.5$ Å. Each block contains one six-membered lovozerite ring $[\text{Si}_6\text{O}_{18}]$. A correlation between the cationic occupation of possible sites within a pseudocubic block and the formed structural arrangement is analyzed.

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