

8.1.3.4 Lovozerites and related silicates

The cyclosilicates from this group are listed in Table 1 [91N1]. In addition, some other synthetic silicates having structures close to the above mentioned were included in this review. – The distribution of cations in lovozerites are listed in Table 2, and in Table 3 the atomic sites for representative silicates are tabulated. The space groups and lattice parameters are given in Table 4.

8.1.3.4.1 Crystal structure. Lattice parameters

Lovozerite family

The lovozerite family includes a large group of natural and synthetic silicates with common structural features [90T1]. The first structural investigations were made for natural lovozerite, $\text{H}_6\text{Na}_2\text{Zr}[\text{Si}_6\text{O}_{18}]$ [60I1] and synthetic silicates $\text{Na}_6\text{Cd}_3[\text{Si}_6\text{O}_{18}]$ and $\text{Na}_5(\text{Na},\text{Mn})_3\text{Mn}[\text{Si}_6\text{O}_{18}]$ [73O1]. Then, other silicates having related structures were reported [75C1, 01Y1]. In [90T1] has been shown that all crystal structures of the lovozerite group are made up of pseudocubic blocks with similar structures. A distinguishing feature of the lovozerite structure is that all cations occupy a part of positions in the sites of a body centered pseudocubic lattice with unit cell parameter $a = 3.75 \text{ \AA}$ [83F1, 85O1, 86O1]. In [60I1, 75C1] was reported that according to their analysis is more convenient to distinguish pseudocubic blocks with parameter $a = 7.5 \text{ \AA}$, composed of eight unit cells of the body centered lattice.

The pseudocubic block with $a = 7.5 \text{ \AA}$ contains one lovozerite ring $[\text{Si}_6\text{O}_{18}]$. Si atom center six of the eight small cubes with $a = 3.75 \text{ \AA}$ in such a way that of the four triad axes of the cube only one is left. This explain the fact that despite the circumstance that all the cations in the structure occupy positions at sites of body-centered-cubic (bcc) lattice, the highest symmetry of lovozerite-like structures is only trigonal, $\bar{R}3m$. Since the block with $a = 7.5 \text{ \AA}$ contains 16 sites of a bcc lattice and six of them are occupied by Si atoms, there are ten possible positions for the remaining cations: two at the centers of two free small cubes on the triad 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 edges of the block (A-positions) and three at the centers of the faces (B-positions) – Fig. 1a. The D position has in its environment six valence-saturated bridging oxygens of lovozerite ring $[\text{Si}_6\text{O}_{18}]$ and therefore it is always vacant [75C1, 90T1]. On this basis, the generalized formula of the block is $\text{A}_3\text{B}_3\text{C}_2\text{M}[\text{Si}_6\text{O}_{18}]$. The atomic environments of A, B, C and M sites depend on the modes of packing the blocks. All the structures of this family are formed from homotypic pseudocubic blocks with corrugated rings $[\text{Si}_6\text{O}_{18}]$ within them. In [90T1] all the theoretically possible variants of combination of such blocks with formation of a three-dimensional structure were considered. The generalized formula for the lovozerite structural type $\text{A}_3\text{B}_3\text{C}_2\text{M}[\text{Si}_6\text{O}_{18}]$ corresponds to nine cation positions. Considering that A, B and M are common to four, two and eight adjacent blocks, respectively, the formula of a block was rewritten $(1/4)\text{A}_{12}(1/2)\text{B}_6(1/8)\text{M}_8[\text{Si}_6\text{O}_{18}]$. Thus, nine cations (excluding Si) of the block are distributed over 28 positions taking account of the multiplicity of these positions.

The block vertices are occupied by octahedrally coordinated M cations ($\text{M} = \text{Zr}, \text{Ti}, \text{Mn}, \text{Fe}, \text{Ca}, \text{Sn}, \text{Cd}$ etc.). The centers of two free (not occupied by Si cations) octants located on one of the threefold axes of the protocell are also occupied by octahedrally coordinated C cations ($\text{C} = \text{Ca}, \text{Mn}, \text{Na}$, etc). The positions at the middle of the edges (A) and in the centers of the faces (B) are filled mainly with Na cations (sometimes with Fe, Ti, Mn, Nd, Ca, Cd or H). Different structures of lovozerite-like compounds were explained by different filling of the above positions in the block and at the junctions of the adjacent blocks. Projection of the lovozerite structure on the xy plane is given in Fig. 1b.

The silicates with lovozerite structure which contain one tetravalent cation are: $\text{Na}_8\text{Sn}[\text{Si}_6\text{O}_{18}]$ [80S1, 80Z1], $\text{Na}_6\text{MnTi}[\text{Si}_6\text{O}_{18}]$ (**kazakovite**) [79V1], $\text{Na}_6\text{CaZr}[\text{Si}_6\text{O}_{18}]$ (**cyrnsinalite**) [80P1] and $\text{H}_6\text{Na}_2\text{Zr}[\text{Si}_6\text{O}_{18}]$ (**monoclinic lovozerite**) [60I1]. In the structure of these compounds the tetravalent cations occupies only M sites – Table 2. Positions A, B and C are occupied mainly by monovalent cations. When the silicate contains divalent cations (kazakovite or cyrsinalite), then they statistically populate the C sites with probability 0.5. With this distribution of cations, all the parallel faces of the block become identical. This uniquely determines the possible type of relation for adjacent blocks in all directions - translational. In the structures of the first three silicates, the cation distribution does not interfere with the maximum possible symmetry of the block, $\bar{3}m$ – Table 2. As a consequence, the high symmetry structure of $\bar{R}3m$ -type results [90T1]. In monoclinic lovozerite, a special feature of the distribution of the Na and H atoms leads to a reduction in the symmetry of the block to 2 which

ultimately determines the symmetry A2(C2) and the translation lattice of this structure – Table 2. In cyrsinalite, the lattice period along the triad axis is doubled in comparison to kazakovite but having identical cation distribution. The doubling of the period is due to small rotations of $[\text{SiO}_4]$ tetrahedra and the lovozerite rings [80P1]. It was supposed that this is due to some ordering of the Ca, Mn and Fe atoms in the C positions [90T1]. The crystal structure of $\text{Na}_8\text{Sn}[\text{Si}_6\text{O}_{18}]$ was refined in the space group $R\bar{3}m$ [80S1] or A2/m [80Z1]. In both cases the distributions of cations in the blocks and the main crystal-chemical characteristics in the structure were identical. According to [90T1] the preference was given to the result of [80S1]. The matrix of transition from the monoclinic structure given by [80Z1] to rhombohedral cell reported by [80S1] is : 0, $\frac{1}{2}$, $\frac{1}{2}$; 0, $\frac{1}{2}$, $-\frac{1}{2}$; 1, 0, 0.

The structures of lovozerites containing less or no tetravalent cations, but an increased content of di- and trivalent cations will be now considered [90T1]. Replacing half of the Ti^{4+} ions by Fe^{3+} with simultaneous increase in the content of divalent cations (Ca), the **koashvite** silicate, $\text{Na}_6(\text{Ca},\text{Mn})(\text{Fe},\text{Ti})[\text{Si}_6\text{O}_{18}]$, is obtained [80C3, 90T1]. In the koashvite structure the distribution of cations in the block differs from that in kazakovite. Two of all 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-sites – Table 2. This distribution of cations in the block leads to a marked change in the structure. Since only one pair of parallel faces of the block remain equivalent, the translation may be realized only in this direction. The two other pairs of faces are translationally nonidentical. The faces adjoining an edge centered by (Fe,Ti) cations 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 blocks themselves (m), and the symmetry elements joining the blocks in associations, determine the symmetry of the structure [90T1] – Table 2.

When the tetravalent cations are replaced by trivalent (Fe) and divalent (Ca) ones, the **imandrite** silicate, $\text{Na}_6\text{Ca}_{1.5}\text{Fe}[\text{Si}_6\text{O}_{18}]$ is obtained [80C2]. In this case the distribution of cations in the block involves that two opposite (in diagonal direction) edges of the block are already centered by high-charged cations, while the adjacent vertices are occupied by Na atoms – Table 2. Thus, 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. In this case the type of joining of the blocks in one direction can be uniquely determined as translational, but in the other two by a 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 elements of the block 2/m, together with the symmetry elements of the relations, determine the symmetry and the lattice structure [90T1] – Table 2.

With further change of the cation composition (when replacing trivalent cations by divalent ones), two different structure types may be obtained, dependent on the ionic radius of the substituent atoms. When replacing Fe by Mn or Cd, the distribution of cations in the block is the same as in imandrite and the silicates $\text{Na}_5(\text{Na},\text{Mn})_3\text{Mn}[\text{Si}_6\text{O}_{18}]$ [73O1], $\text{Na}_6\text{Mn}_3[\text{Si}_6\text{O}_{18}]$ [76P1] and $\text{Na}_6\text{Cd}_3[\text{Si}_6\text{O}_{18}]$ [67S1] are isostructural with imandrite [90T1]. It is to be noted that the distribution of cations in the block of the structure of the Na,Cd silicate differs somewhat from all the other compounds – Table 2. Due to the lack of accuracy in determining the structure, it was finally supposed that the cation distribution in block is similar to that in imandrite [90T1].

The replacement of Fe by Ca atoms (larger than Mn or Cd) and the addition of Nd atoms, leads to a redistribution of the cations – Table 2. Nd atoms occupy 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 sites are occupied by Na atoms and the C sites are statistically filled by Na and Ca atoms [90T1]. 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 both lovozerite-type (three translations) and imandrite-type structures. In both cases the positions M and 1/3A, identically occupied by (Nd,Ca) atoms, would appear in different anion environments (octahedron and eight-pointed polyhedron). Two oxygen atoms of the eight-pointed polyhedron are bridging atoms of the lovozerite ring. It is for this reason that an intermediate variant of the structure organisation is preferred. In two directions, the blocks are related by a translation and in the third by a glide plane. The result of this conjunction of the blocks is described by the monoclinic unit cell of synthetic $\text{Na}_5(\text{Na},\text{Ca})_2(\text{Nd},\text{Ca})_2[\text{Si}_6\text{O}_{18}]$ silicate [89T1].

Complete replacement of trivalent cations by divalent Ca leads to compositions of the types $\text{Na}_6\text{Ca}_3[\text{Si}_6\text{O}_{18}]$ [83F1, 85O1] and $\text{Na}_4\text{Ca}_4[\text{Si}_6\text{O}_{18}]$ [83F1, 86O1, 87F1]. In $\text{Na}_6\text{Ca}_3[\text{Si}_6\text{O}_{18}]$ all the M positions are occupied by Ca, while the A and C sites are statistically occupied by Ca and Na atoms and the B sites by Na atoms. The

composition of this type is evidenced in one variety of silicate **combeite** [83F1] and in synthetic silicate $\text{Na}_6\text{Ca}_3[\text{Si}_6\text{O}_{18}]$ [85O1]. The above distribution makes all the parallel faces identical in pairs and the symmetry of the block is $\bar{3}m$. In the upshot there is the only possible translational relation between the blocks, determining the symmetry $R\bar{3}m$ [90T1]. Increasing the number of divalent cations, another variety of **combeite**, $\text{Na}_4\text{Ca}_4[\text{Si}_6\text{O}_{18}]$ is obtained [83F1, 87F1] as well as their synthetic analog [86O1]. In the structures of these phases, Ca beside the M positions occupies the $(1/3)$ A positions. Two vacancies then arise in the B positions. The distribution of the atoms – Table 2 – reduces the symmetry of the block to 2 and none of the pairs of parallel faces are identical. We note that first structural study on combeite was realized by [57S1]. Later on, it has been shown, that the silicate crystallizes in two forms: low temperature and high temperature. The structures were refined in space group $R\bar{3}m$ (high-temperature form) and $P3_2$ (low-temperature form) [83F1]. The results of chemical analysis were different from those obtained as result of structural study. In [85O1, 86O1] these drawbacks were analyzed and the space group $P3_221$ was proposed for the low-temperature form. The data from [83F1] were later reanalyzed [87F1]. The authors showed that both forms of combeite consist of six-rings of SiO_4 tetrahedra which are circular in the high-temperature form ($R\bar{3}m$) and elliptically distorted in the low temperature form ($P3_221$) [87F1]. We note that the results of refinement in space group $P3_221$ [86O1] – Table 3b – are very close to those of [87F1] in space group $P3_221$.

Litvinskite, $(\text{Na}, \text{H}_2\text{O}, \square)_3(\square, \text{Na}, \text{Mn}^{2+})\text{Zr}[\text{Si}_6\text{O}_{12}(\text{OH})_3(\text{OH}, \text{O})_3]$

The litvinskite structure – Fig 1c – consists of the framework of six-membered lovozerite-type rings of tetrahedra $[\text{Si}_6\text{O}_{12}(\text{OH})_3(\text{OH}, \text{O})_3]$ sharing oxygen vertices with isolated M-octahedra ($M = \text{Zr}, \text{Ti}, \text{Mn}, \text{Fe}, \text{Ca}, \text{Sn}, \text{Cd}$, etc). The M octahedra are located at the vertices and in the centers of the basal faces of the unit cell and are occupied predominantly by Zr^{4+} cations [01Y1]. Free vertices of the Si tetrahedra are occupied by the $(\text{OH})^-$ groups, whereas C-octahedra, statistically filled with Na^+ , Mn^{2+} , Ca^{2+} and Fe^{2+} cations, share the oxygen faces with M-octahedra and are also involved in the framework. The remaining three vertices of each C-octahedron are occupied by the O^{2-} ions and $(\text{OH})^-$ groups. The number of the O^{2-} ions replaced by the $(\text{OH})^-$ groups correlates with the degree of filling of the C position. The Na cations occupy the cavities of the framework and two crystallographically nonequivalent positions: A1 at the mid-points of the c -axis of the unit cell between the M-octahedra, related by a translation, and the position A2 in the channels of the hexagonal section along the $[001]$ direction. The water molecules and a small fraction of K and Na cations can be located in the channel cavities [01Y1]. The litvinskite structure differs from the lovozerite one, the former having an additional cation position to A, namely C occupied by $(\text{Na}, \text{Ca}, \text{Mn}^{2+}, \text{Fe}^{2+})$. Thus, the space group $C2$ (A2) of lovozerite is changed into the space group Cm of litvinskite. The C position in litvinskite structure, filled with Na^+ , Mn^{2+} , Ca^{2+} and Fe^{2+} cations is also typical for kazakovite [79V1] or cyrsinalite (zirsinalite) [80P1]. However, a high Na content in these silicates result in a symmetry and structure different from that of litvinskite.

$\text{Na}_4\text{CaSi}_3\text{O}_9$, $\text{Na}_4\text{SrSi}_3\text{O}_9$, $\text{K}_4\text{CaSi}_3\text{O}_9$

$\text{Na}_4\text{SrSi}_3\text{O}_9$ crystallizes in a monoclinic $C2$ -type structure [91D1]. The structure is built from a zig-zag Si_3O_9 chain parallel to $[001]$, a “dreier” single chain in the classification of [85L1], but with a conformation quite different from the familiar “dreier chain” of calcium silicate such as wollastonite (see chap. 8.1.4.3, subvolume 2714). $\text{Na}_4\text{CaSi}_3\text{O}_9$ crystallizes in a cubic $\text{Pa}3$ -type structure similar to $\text{K}_4\text{SrGe}_3\text{O}_9$ [75G1]. The crystal structure contains rings of 12-corner sharing SiO_4 tetrahedra normal to the threefold axes [84F1]. The crystal structures of $\text{K}_4\text{CaSi}_3\text{O}_9$ [75G1] and $\text{K}_4\text{BaSi}_3\text{O}_9$ [77B1] were reported to be cubic. The Na_2SiO_3 – SrSiO_3 phase diagram was analysed by [74M1].

$\text{Na}_5(\text{Na}_{0.5+x}\text{Ca}_{0.5-x})_2(\text{Nd}_x\text{Ca}_{1-x})_2[\text{Si}_6\text{O}_{18}]$

The structure of this silicate, with $x = 0.158$ was refined as monoclinic, having space group $P2_1/b$ [89T1]. The compound belongs to the family of lovozerite-like structures. Pseudocubic blocks with period $a = 7.5 \text{ \AA}$ can be distinguished. 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 cation positions. The vertices and centers of four parallel edges of the blocks are occupied by Nd and Ca atoms. The Na and Ca atoms occupy

positions within the block on the space diagonal, and the centers of all the other edges and faces are occupied by Na atoms.

Tisinalite, $\text{H}_3\text{Na}_3(\text{Mn,Ca,Fe})\text{TiSi}_6(\text{O,OH})_{18}\cdot 2\text{H}_2\text{O}$

Tisinalite crystallizes in the trigonal space group $R\bar{3}m$ [80K1].

Shafranovskite, $(\text{Na,K})_6(\text{Mn,Fe})_3\text{Si}_9\text{O}_{24}\cdot 6\text{H}_2\text{O}$

Shafranovskite has space group $P31m$ or $Pmm1$ [82K2].

Zakharovite, $\text{Na}_4\text{Mn}_5\text{Si}_{10}\text{O}_{24}(\text{OH})_6\cdot 6\text{H}_2\text{O}$

Zakharovite is trigonal having space group $P31m$ or $P3m1$ [82K1].

Traskite, $\text{Ba}_{12}\text{Fe}_2\text{Ti}_6\text{Si}_{12}\text{O}_{54}\text{Cl}_3\cdot 7\text{H}_2\text{O}$

The chemical composition of traskite reported in [65A2] was later revised [65A1]. Traskite crystallizes in a hexagonal-type structure having space group $P6/mmm$, $P6mm$, $P622$, $P\bar{6}m2$ or $P\bar{6}2m$ [65A2]. In [76M1] the presence of space group $P\bar{6}m2$ was assumed. The basis of the structure is formed by a tubular construction of barium polyhedra. Three stages of this structure (in projection along the c -axis) are shown by means of similar Ba ten-vertex polyhedra at each level – Fig. 2a,b,c [76M1]. The stage at $z = 0$ – Fig. 2a – contains Ba_3 polyhedra; each of which may be visualised in the form of a tetragonal prism with two caps (hemioctahedra) on neighbouring faces. The polyhedra, paired along a common edge, create ditrigonal rings around the $\bar{6}$ axes in the center of the cell, the core of these rings being a trigonal Ca prism connected to the Ba framework, along the c -direction, by standing diortho-groups – Fig. 2d. The stage at $z = 0.25$ – Fig. 2b – is complicated by tetrahedral prisms with centered opposite faces. The cavities of this stage are filled with octahedra of three kinds. The most skeletal layer is at the level $z = 0.5$ – Fig. 2c. The large polyhedra of this layer (almost regular pentagonal prisms) are coupled to one another along the vertical edges and form cavities (around $\bar{6}$ axis) in which rings with the composition $[\text{Si}_{12}\text{O}_{36}]$ are situated – Fig. 2d [76M1]. The tubular barium framework of traskite is cemented by a discontinuous silicon-oxygen coupling: the larger spaces around the origin of coordinates by $[\text{Si}_{12}\text{O}_{36}]$ rings, the smaller ones around the threefold axes by $[\text{Si}_2\text{O}_7]$ groups – Fig. 2d. The atomic coordinates are given in Table 3. In traskite the position A was reported to be occupied by Fe and Ti, position B by Fe and Mn, position C by Ca and Sr and position D by Ti, Fe, Mg, Al [76M1]. Thus, the Ti, Fe, Mn, Ca, Mg cations occupy cavities of the broad three-dimensional framework which the barium polyhedra create.

(Na,Ba,Mn) fluorosilicate

The crystal structure of natural (Na,Ba,Mn) fluorosilicate, $\text{NaBa}_3(\text{Mn}^{2+},\text{Mn}^{3+})_4[\text{Si}_4\text{O}_{10}(\text{OH})_2][\text{Si}_2\text{O}_7]\text{O}_2\text{F}\cdot \text{H}_2\text{O}$ was studied [92Y1]. This crystallizes in a $Pnma$ -type structure. The basis of the structure is formed by two different silicon-oxygen radicals: four membered rings $[\text{Si}_4\text{O}_{10}(\text{OH})_2]$ and diortho groups $[\text{Si}_2\text{O}_7]$. Similar combinations of annular and isolated groups of tetrahedral anions are characteristic for **traskite** [76M1] (see above). The fourfold rings of Si tetrahedra are characteristic of Ba silicates and were found in baotite [70N1], verplanckite [73K2], labuntsovite [73G1], joaquinite [75D1] or taramellite [71F1].

Lourenswalsite $(\text{K,Ba})_2\text{Ti}_4(\text{Si,Al})_6\text{O}_{14}(\text{OH})_{12}$

Lourenswalsite crystallizes in a hexagonal-type lattice [87A1].

Tienshanite

Tienshanite, $\text{KNa}_9\text{Ba}_6\text{Ca}_2\text{Mn}_6\text{Ti}_6\text{B}_{12}\text{Si}_{36}\text{O}_{123}(\text{OH})_2$, crystallizes in a hexagonal-type structure, having probably space group $P6/m$ [67D1].

Jonesite

The crystal structure of jonesite, $\text{Ba}_2(\text{K},\text{Na})[\text{Ti}_2(\text{Si}_5\text{Al})\text{O}_{18}(\text{H}_2\text{O})](\text{H}_2\text{O})_n$, was shown initially to be orthorhombic having space group B22₁2 (C222₁ in standard setting) [77W1]. Inspection of strong spots in the Weissenberg photographs indicated a smaller pseudo cell with axes $a' = a/2 = 6.68 \text{ \AA}$, $b' = b = 25.95 \text{ \AA}$ and $c' = c/2 = 5.31 \text{ \AA}$ [77W1]. Later on [04K1], the structure was reported as monoclinic having space group P2₁/m. The structure is based upon porous double layer of distorted TiO_6 octahedra ($\emptyset = \text{O}, \text{H}_2\text{O}$) and TO_4 ($\text{T} = \text{Si}, \text{Al}$) tetrahedra parallel to (010). The layers consist of two sheets of corner-sharing TiO_6 octahedra and Si_2O_7 groups each – Fig. 3. The two adjacent sheets are linked along **b** by T_4O_{12} tetrahedral rings that are disordered over two positions. The double layer has an open structure characterized by eight-membered tetrahedral rings with apertures (free diameters) of 3.37×3.37 and $3.33 \times 3.33 \text{ \AA}^2$ for two symmetrically non-equivalent rings. K^+ cations and H_2O molecules are located in the pores of the double layers. Ba^{2+} cations are between the double layers and provide their linkage into three-dimensional structure. Jonesite is a titanosilicate with porous double layer structure [04K1].

Petarasite, $\text{Na}_5\text{Zr}_2\text{Si}_6\text{O}_{18}(\text{Cl},\text{OH})\cdot 2\text{H}_2\text{O}$

Petarasite crystallizes in a monoclinic-type structure having space group P2₁/m [80C1, 80G1]. The atomic sites are listed in Table 3b. The crystal structure of petarasite is an open three-dimensional framework with the composition $\text{Zr}_2\text{Si}_6\text{O}_{18}$ consisting of corner-shared six-membered silicate rings and ZrO_6 octahedra – Fig. 4. Elliptical channels ($3.5 \times 5.5 \text{ \AA}^2$), defined by mixed six-membered rings, consisting of pairs of SiO_4 tetrahedra linked by Zr octahedra, run parallel to the **b** and **c**-axes. Other channels limited by silicate rings run parallel to **c**. Two sodium atoms (Na1 and Na2) and the water molecules (W1 and W2) are located in channels parallel to **b** whereas the third sodium atom (Na3) and the Cl^- and $(\text{OH})^-$ ions are located in channels parallel to **c** [80G1]. The average Si–O and Zr–O bond distances are 1.615 \AA and 2.091 \AA , respectively. All three sodium atoms are seven-coordinated. The Cl^- and $(\text{OH})^-$ ions are solely bonded to the sodium atoms and are partially disordered. Structurally, petarasite is related to lovozerite [60I1], kazakovite [79V1] and synthetic phase $\text{Na}_6\text{Cd}_3[\text{Si}_6\text{O}_{18}]$ [67S1]. As mentioned already, all these phases are characterized by an open-sharing zircono- (or titano-) silicate framework with open channels that house the sodium atoms and, as in petarasite, water molecules and chlorine. In all cases, the diameter of the open channel is defined by mixed six-membered rings of alternating $[\text{Si}_2\text{O}_7]$ groups and $\text{Zr}(\text{Ti})$ octahedra [80G1].

Ashcroftine

The ashcroftine, $\text{K}_{10}\text{Na}_{10}(\text{Y},\text{Ca})_{24}(\text{Si}_{56}\text{O}_{140})(\text{OH})_4(\text{CO}_3)_{16}\cdot 16\text{H}_2\text{O}$ average structure is tetragonal [69M1, 87M1]. The structure is based on at least 39 atoms in the asymmetric unit. Of these 27 are ordered and make up the $[\text{K}_8\text{Na}_2\text{Y}_{24}(\text{OH})_4(\text{CO}_3)_{16}\text{Si}_{48}\text{O}_{128}\cdot 10\text{H}_2\text{O}]^{18-}$ fraction. The underlying polyanion is a giant $[\text{Si}_{48}\text{O}_{128}]$ ball whose connection define a polyhedron (balosilicate). It has the point symmetry $(4/m2/m2/m)$, a near subgroup of $(4/m \bar{3} 2/m)$ found for the related truncated cuboctahedron. Breaks in the ball admit an extensive circumjacent disorder region and together define the ${}^\infty[\text{Si}_{56}\text{O}_{140}]$ tubular inosilicate with channels and bulges oriented parallel to [001]. All terminal oxygens point outside, away from the central channel. The ordered carbonate fraction defines, among other things, ordered $[\text{Na}(\text{CO}_3)_4]$ clusters. The entire ordered region is called **curd** – Fig. 5a. The curd is centered at $(0 \ 0 \ 1/2)$, $(1/2 \ 1/2 \ 0)$ for the silicate fraction, and $(1/2 \ 0 \ 1/4)$, $(1/2 \ 0 \ 3/4)$, $(0 \ 1/2 \ 3/4)$ and $(0 \ 1/2 \ 1/4)$ – which exactly specify the centroids of Na1 – for the carbonate fraction. It includes Si1 to Si3, O1 to O10; Na1; C1, O11, O12; and C2, O13, O14 and OW2. The stoichiometry in the cell is $2[\text{Si}_{48}\text{O}_{128}]$ and $[\text{Na}_{14}(\text{CO}_3)_{32}]$. All 20 nonequivalent atoms are ordered and their sites fully populated – Table 3e. The curd is shown in Fig. 5a as a spoke diagram. The ordered silicate $\text{Si}_{48}\text{O}_{128}$ fraction has dimensionality 0. The stoichiometry is $16\text{Si}_3\text{O}_8$. It can be mapped on the surface of a ball, that is, it conserves a volume, by merely connecting the Si cations together. Such arrangement, as above mentioned, was called **balosilicate**. The large balls are encrusted with a border region, or **limbus** – Fig. 5c. The disordered region of 12 atoms (pathological atoms) in the asymmetric unit (**whey**) consists of partly occupied $\text{T}(\text{D}) = (\text{Si},\text{B}),\text{Si}; \text{Na}(\text{D}), \text{K}(\text{D})$ and ϕ ($\phi = \text{O}^{2-}, \text{OH}^-, \text{H}_2\text{O}$) sites – Table 3. The atoms were suffixed by D to indicate their disordered nature. In the whey the tetrahedrally coordinated cations were symbolized by T and the ligand by ϕ . Fig. 5b attempts to feature a combination of polyhedral and spoke representations of the crystal structure, the central $[\text{Si}_{48}\text{O}_{128}]$ unit and its

enveloping **limbus** of Y1–O, Y2–O, K1–O, K2–O, Na2D–O and Na3D–O bonds (the last two atom positions in the **whye**). Also in the **whye** are T1D, which is shown here, and T2D that seal the dashed rupture together. Through additional units such as $[\text{TD}_2 \phi(\text{D}) \phi(\text{D})_2\text{O}_4]$ or $[\text{T}_2\text{O}_7]$ groups, the balls are bridged together along [001]. For this reason, the tetrahedral fraction can be considered tubular with enormous bulges in it. The tubular portion then is ${}^1_\infty[\text{T}_{56}\text{O}_{140}]$, T connoting tetrahedrally coordinated cations such as Si^{4+} or B^{3+} . Two independent carbonate groups and Na1 complete the curd. The border or edge between the ordered curd and the disordered **whye** includes the remaining ordered cations Y1, Y2, K1 and K2. They define a laurel wreath around the central $[\text{Si}_{48}\text{O}_{128}]$ curd.

8.1.3.4.2 Optical properties

Traskite

Optical absorption spectra were analysed for traskite which have both Fe^{2+} and Ti^{4+} as major elements [76M1]. The $E \perp c$ spectrum is shown in Fig. 6 [88M1]. The silicate is nearly colorless in $E \parallel c$. The absorption lines at 850 and 950 cm^{-1} can be assigned to Fe^{2+} transitions. The remaining feature at 440 nm was assigned to $\text{Fe}^{2+} - \text{Ti}^{4+}$ charge transfer.

A short description of the Raman spectrum of (Na,Ba,Mn) fluorosilicate was given by [92Y1].

Petarasite

The general features of the infrared spectrum is shown in Fig. 7 [80C1]. The fairly strong band at 770 cm^{-1} is within the range of 740...830 cm^{-1} for the infrared ring-breathing band, characteristic of ring silicates [61P1]. The absorption bands at 3630 and 3520 cm^{-1} (O–H stretching) and 1682 and 1600 cm^{-1} (H–O–H-bending) confirm the presence of H_2O . The broad band centered at about 3300 cm^{-1} is characteristic of symmetrical and antisymmetrical stretching vibrations of adsorbed water, whereas the lower frequency indicates the formation of moderately strong hydrogen bonds. The IR absorption spectra of the heated sample show that the removal of the molecular water is essentially complete at 450°C [80C1].

Litvinskite

For optical properties see [00P1].

For refractive indices of some lovozerites and related silicates see Table 5.