

8.1.3.8 Hyalotekite, hilairite and phosinaite groups of silicates

The silicates from the above groups are listed in Table 1 [91N1]. In addition to hyalotekite (VIIC11) the crystal structure of hilairite (VIIC12) and phosinaite (VIIC13) families will be reviewed. The atomic sites and thermal parameters for representative silicates are listed in Table 2, while in Table 3 the crystal structures and lattice parameters are tabulated.

8.1.3.8.1 Crystal structure. Lattice parameters

Hyalotekite

The hyalotekite, cca $\text{Pb}_2\text{Ba}_2\text{Ca}_2[\text{B}_2(\text{Si}_{3/2}\text{Be}_{1/2})\text{Si}_8\text{O}_{28}]\text{F}$, crystallizes in a triclinic-type structure having space group $I\bar{1}$ [82M1]. The structure is based on an incomplete framework of corner-linked oxygen tetrahedra. The underlying structural principle is shown as a polyhedral diagram down [001] in Fig. 1. The structure has three principal linked components: ${}^0[\text{Si}_4\text{O}_{12}]$ four-membered rings, ${}^0[\text{B}_2(\text{Si}_{3/2}\text{Be}_{1/2})\text{O}_{12}]$ four-membered rings and $(\text{Ca}_2\text{Pb}_4\text{O}_{26}\text{F})$ clusters. The tetrahedra link to form an incomplete framework of composition ${}^3[\text{T}_6\text{O}_{14}]$ ($4\text{T}_6 = \text{Be}_4\text{B}_4\text{Si}_{19}$ in the unit cell) which remotely resembles that of feldspars. A dominant feature is the occurrence of ${}^0[\text{Si}_4\text{O}_{12}]$ four-membered rings, which are nearly in the $\{001\}$ plane, approximately positioned at $z \cong 1/4, 3/4$. Such a ring involves the Si2-, Si3-, Si4- and Si5- oxygen tetrahedra. Another four-membered tetrahedral ring occurs in the structure, approximately situated at $z \cong 0, 1/2$. Two opposing tetrahedra in the ring are oriented with the z -axis nearly coinciding with a pseudo \bar{y} -axis through a pair of tetrahedral edges. This tetrahedron is approximately $[\text{Si}_{3/4}\text{Be}_{1/4}]\text{O}_4$ in composition. The remaining non-equivalent tetrahedron is a $[\text{BO}_4]$ tetrahedron. For this ring, all oxygen vertices are linked to other tetrahedra in the structure. The formal composition of this ring would be ${}^0[\text{B}_2(\text{Si}_{3/4}\text{Be}_{1/2})\text{O}_{12}]$. The entire tetrahedral incomplete framework would have the composition ${}^3[\text{T}_6\text{O}_{14}]$ where $4\text{T}_6 = \text{Be}_4\text{B}_4\text{Si}_{19}$ which is the tetrahedral cation content of the unit cell. The two non-equivalent tetrahedral four-membered rings link through O5, O6, O9 and O10. The remaining atoms are (Pb,Ba), Ca and F. The Ca atoms are situated along the $00z$ line above and below F at the inversion center which joins to 2Ca and 4(Pb,Ba) atoms. The (Pb,Ba) atoms are located within the large distorted eight-membered rings much like the alkaline earth atoms in feldspar.

Concerning the ordering of cations over tetrahedral positions, it can be noted that the four-ring involving Si2–Si5 at $z \cong 1/4$ appears to possess a fully ordered occupancy of $[\text{SiO}_4]$ tetrahedra by Si^{4+} exclusively. In absence of further evidence for deciding the site population of Si, the site population of Si1 was preferred to be written $\text{Si}_{3/4}\text{Be}_{1/4}$ in agreement with chemical analysis [82M1]. The formula for the tetrahedral fraction can therefore be written $[\text{Si}_8(\text{Si}_{3/2}\text{Be}_{1/2})\text{B}_2\text{O}_{28}]$ with two such units in the unit-cell.

There is a structural distortion due to Pb^{2+} . Hyalotekite's aristotype belongs to a space group with higher symmetry than found in the actual structure; that is $I2/m \rightarrow I\bar{1}$. If the large cations and their coordinating anions were extracted, the picture changes drastically. Fig. 1b shows the $\text{Pb}_1\text{Pb}_2\text{O}_{20}\text{F}$ cluster which is composed of four fused PbO_7F polyhedra. They are roughly equivalent and would be identical in space group $I2/m$. Each polyhedron shares two faces with two other polyhedra and the common F vertex is also corner-linked to the fourth polyhedron [82M1]. Thus, F links to four $\text{Pb}^{2+}(\text{Ba}^{2+})$ cations and also to two Ca^{2+} cations above and below. In this structure, four triangular faces are shared, two with adjacent Pb^{2+} cations and two with adjacent Ca^{2+} cations. The feature about the PbO_7F group is that all bonds to the face-sharing vertices are the shortest for their polyhedra – Fig. 1b – while the remaining three Pb–O bonds on the opposite side of the F atom are the longest for their polyhedra. This was attributed to the lone pair-bond effect, with the $6s^2$ lone pair located opposite the tightly bond F^- anion. Pb^{2+} and Ba^{2+} are split in hyalotekite, separated by about 0.4...0.5 Å. Consequently two sets (Pb1,Ba1) and (Pb2,Ba2) are associated spatially in pairs. The most severe polyhedral distortion occurs for Pb^{2+} . Since Pb^{2+} and Ba^{2+} are separated by $\cong 0.5$ Å, there is a possible segregation from the parent $I2/m$ structure due to the $6s^2$ lone pairs effect on Pb^{2+} . Thus, the structure has space group $I\bar{1}$. The atomic sites in $I\bar{1}$ -comparatively to $I2/m$ -refinement are given in Table 2a [82M1].

Hilairite-type silicates

The **hilairite**, $\text{Na}_2\text{ZrSi}_3\text{O}_9 \cdot 3\text{H}_2\text{O}$, crystallizes in a rhombohedral structure having space group R32 [74C1, 8111]. The same crystal structure was reported for the **calcium analog of hilairite**, $\text{CaZrSi}_3\text{O}_9 \cdot 3\text{H}_2\text{O}$ [88B1], the **rare-earth (R) analog of hilairite** [92R1] and for **komkovite**, $\text{BaZrSi}_3\text{O}_9 \cdot 3\text{H}_2\text{O}$ [90V1, 91S1]. In hilairite the Zr atoms are octahedrally coordinated and there is a tetrahedral coordination of the silicon. The hilairite structure consists of a mixed framework of spiral chains $[\text{Si}_3\text{O}_9]$ joined through vertices of the Zr tetrahedra. The cavities in the framework contain Na^+ and H_2O – Fig. 2a. The basis of the komkovite structure is a mixed $(\text{ZrSi}_3\text{O}_9)^{2-}$ framework of $[\text{ZrO}_6]^{8-}$ octahedral and helical $[\text{Si}_3\text{O}_9]^{6-}$ chain – Figs. 2a,b. There are six Si tetrahedra for the period $a \cong 15.80 \text{ \AA}$, as found in hilairite. While in hilairite the identity period of the chain is equal to three tetrahedra which corresponds to $c' = c/2$, in komkovite, a slight deformation of the chain, caused mainly by a change in the coordinate x of the bridge O4 atom, results in a true identity period of six tetrahedra – Figs. 2c,d [91S1]. In idealized form, for convenience of comparison of the hilairite family silicates, this chain was considered with a period of three tetrahedra, i.e. $[\text{Si}_3\text{O}_9]_\infty$ [91S1]. The komkovite structure can be considered as a derivative of the hilairite structure with two monovalent Na^+ ions replaced by one divalent Ba^{2+} ion, which occupy the Na1 position in the hilairite structure – Table 2c. In komkovite the Ba^{2+} cations are located in large Zr–Si–O cavities in the framework. The Ba and Zr polyhedra are at $1/2$ translation along the threefold axes. The pseudoperiod $c' = c/2$ of komkovite structure is disrupted by the location of the water molecules and part of the O atoms. The position of the water molecule changes in komkovite as compared to hilairite. The large Ba atom whose coordination sphere the H_2O molecule enters, shifts the water molecule to a position roughly corresponding to the Na2 site in hilairite. H_2O molecules in komkovite form helical chains around the 3_2 axes in contrast to the Si–O chains along the 3_1 axes. The H_2O molecules in komkovite occupy $\sim 80 \%$ of their positions. In hilairite Na2 atoms also occupy only 70% of their positions.

The temperature of the endothermic effect decreases from 220°C in hilairite [74C1] to 140°C in komkovite [90V1]. This may be explained by the fact that the zeolitic properties of water manifest themselves better when the bonds between cations and H_2O molecules are weakened (the corresponding interaction distances increase) and strictly (H_2O) chains are formed in the channels structure.

In the natural rare-earth (R) analog of hilairite⁶⁾ [92R1], the highly charged cations are situated in two positions M1 and M2 on the threefold axes – Table 2b. The M1 position is occupied by $(\text{Zr}_{0.7}\text{Nb}_{0.1}\text{Ti}_{0.2})$ whereas the larger Y and R cations were located in M2 ($\text{Y}_{0.8}\text{R}_{0.2}$). The alkali cations also occupy two positions in the R-hilairite structure with an octahedron for Na1 on the threefold axis and a seven-vertex polyhedron for Na2 on a twofold axis. In the larger polyhedron, a part of the Na atoms is replaced by K ($\text{Na}_2 = \text{Na}_{2.4}\text{K}_{0.6}$). The cavities in the framework as in hilairite contain Na^+ and H_2O . The octahedral positions of the flexible framework and its voids accommodate definite variations in chemical composition.

A structural difference of R-hilairite is that one of the two Zr-positions is occupied by Y(R) and Zr is 30% replaced by Ti and Nb in the other. The nonequivalency of “Zr” positions is the main reason for the pseudoperiodicity along the c -axis. A second distinctive feature compared to hilairite and komkovite is the large alkali content in it. Whereas in the Ba, Zr- and Ca,Zr-silicates the number of Ba(Ca) atoms is equal to the number of M-cations, in hilairite $\text{Na}/\text{Zr} = 2$ and in R-hilairite $\text{Na}/\text{M} = 2.5$. As a result, the Na1 and Na2 sites in R-hilairite structure are fully populated. This increases the strength of its framework. Besides the Na(K) ion, H-bonds formed by protons of waters in both types of Na-polyhedra also strengthen the framework [92R1].

A comparison of the cell constants of the silicates from the hilairite family shows that the lengthening of a from 10.526 \AA in Ca- and Ba- hilairites to 10.556 \AA and 10.825 \AA in hilairite and R-hilairite correlates with the degree of population of the Na2 site. In the komkovite structure (and apparently the Ca analog), this position is vacant; in hilairite, partially populated and in R-hilairite, fully so. The main reason for the sudden increase of the a parameter in R-hilairite is the replacement of one of the two dense Zr-octahedra by the less dense Y-octahedron. With respect to the c parameter, such a correlation is obviously smoothed owing to slight deformations of the Si-chains [92R1].

The three-dimensional mixed radical $(\text{ZrSi}_3\text{O}_9)^{2-}$ in the komkovite structure belongs to the group of framework anion radicals (OT_3X_9) in compounds with a typical formula $\text{A}_2(\text{OT}_3\text{X}_9)$ [84S1]. The tetrahedral anion radical consists of closed rings and infinite chains. In benitoite, and wadeite (section 8.1.3.1), different types of frameworks are built as three-membered rings $[\text{Si}_3\text{O}_9]$ and octahedral $[\text{OX}_6]$. Bazirite is isostructural to benitoite, and catapleiite is isostructural to wadeite (section 8.1.3.1) [91S1]. Gaidonnayite is a polymorphic variety of $\text{Na}_2(\text{ZrSi}_3\text{O}_9) \cdot 2\text{H}_2\text{O}$ and in this case the anion radical is represented by peculiar zig-zag $[\text{Si}_3\text{O}_9]$ chains

which are arranged in two intersecting directions. In the morphotropic series wadeite-catapleiite-gaidonnayite-hilairite, where the cations fillings are monovalent, the $[\text{Si}_3\text{O}_9]$ chains break and helical $[\text{Si}_3\text{O}_9]$ chains form in a hilairite-type framework [91S1]. The same behaviour was observed in the bazirite-komkovite series as well as in the catapleiite-hilairite ones. Under hydration, both types of wadeite and bazirite (benitiote) structures, tend to a framework with the topology of hilairite [91S1].

The structure of the hilairite was also analysed in terms of the OD (order-disorder) theory [88I1]. They evidenced 5 OD structures with disordered Na sublattices in the class of alkali M(octahedra)-T(tetrahedra) silicates: lovozerite, rare-earth pentasilicate, NASICOM, catapleiite and hilairite. The five OD structures according to the type of bond of the M and T polyhedra into three-dimensional MT frameworks were classified in two groups. The first group (catapleiite, hilairite, NASICOM) has a three-dimensional MT framework of types MT_3O_9 and $\text{M}_2\text{T}_3\text{O}_{12}$ (with bridging O vertices of the types M–O–T and T–O–T). The second group (lovozerite, R-pentasilicates) has three-dimensional MT structures MT_6O_{18} and MT_4O_{12} in which part of the vertices of the T-polyhedra are of the terminal type T–O.

Phosinaites-type silicates

The phosinaite family includes **orthorhombic phosinaite** $\text{Na}_{11}(\text{Na,Ca})_2\text{Ca}_2\text{Ce}(\text{SiO}_3)_4(\text{PO}_4)_4$, its monoclinic analog **clinophosinaite** $\text{Na}_3\text{Ca}[\text{SiO}_3](\text{PO}_4)$ and **nagelschmidtite**, $\text{Ca}_7(\text{SiO}_4)_2(\text{PO}_4)_2$.

Phosinaite crystallizes in an orthorhombic-type lattice having space group $\text{P}2_12_12$ [81K2]. The yz projection of the structure is shown in Fig. 3a. In the structure of **phosinaite** as well as in **clinophosinaite** [80K1], the cation and anion frameworks play identical structure roles. The cation part of the structure is concentrated in geometrically similar sheets perpendicular to $[100]$ – Figs. 3b,c [81K2]. The sheets at the level $x \equiv 0$ and $x \equiv 0.5$ are formed from wavy (rocking) chains of mixed composition made up to Ce, Ca and Na polyhedra which are connected by two different pairs of Na polyhedra, Na 1-2 and Na 4-5. In each chain a “stirrup” can be distinguished formed by eight-pointed Ce polyhedra lying between Ca octahedra and (Ca,Na) seven-pointed polyhedra ($\text{Ca/Na} = 1/1$). The “stirrups” are linked by Na3 octahedra and Na6 five-pointed polyhedra. The same “stirrups” belonging to adjacent cation sheets along the x -axis, are joined via an edge of the Ca polyhedra forming wavy diagonal bands. Of the four types of Na polyhedra fixing the wavy chains, the Na1, Na2 and Na4 polyhedra are distorted octahedra, and the Na5 polyhedron is an eight-pointed prism with broken quadrangular bases. The similarity of the both sheets forming the cation composition of the framework in phosinaite is a distinguishing feature in comparison with the cation motif in the structure of clinophosinaite, in which the sheets of the first type ($x = 0$) are made up of wavy chains of Ca polyhedra connected by a pair of Na polyhedra, while those of the second type ($x \equiv 0.5$) are composed of Na polyhedra only [81K2].

The presence of Ce in phosinaite reduces its contents of Ca and Na in comparison with clinophosinaite, corresponding to isomorphic replacement: $\text{Na}^+ + \text{Ca}^{2+} \rightarrow \text{Ce}^{3+}$. Apparently Ce has an ordering influence on the whole structure. The two statistically distributed P2 tetrahedra in clinophosianite [80K1] are replaced by a precisely fixed P2 tetrahedron in phosinaite. The tubular columns in the anion framework consist of three levels of four-membered rings of two different types. The silicon-oxygen rings $[\text{Si}_4\text{O}_{12}]$ alternate with two levels of mixed rings formed by P tetrahedra and Na polyhedra (Na7 octahedra and Na8 five-pointed polyhedra). The P tetrahedron acts as a “pair former” for the Na polyhedra with minimal charge and large radius of the central cations. Thus, in the phosinaite structure there are nevertheless similar functions performed by the P orthotetrahedra and the Si tetrahedra in the rings.

Nagelschmidtite

X-ray studies suggest that a natural sample is a mixture of polymorphs, α - and β -modifications [77G1, 78F1].

8.1.3.8.2 Optical properties

The refractive indices of some silicates from the above mentioned groups are listed in Table 4.