

### 8.1.4.9 Neptunite, hellandite, sörensenite, astrophyllite, epididymite, bavenite, lorenzenite and related silicates

#### 8.1.4.9.1 Crystal structures. Lattice parameters

In the section, the physical properties of silicates listed in Table 1 are presented. A more detailed description of the crystal structures is given for some representative silicates, from the above groups, in correlation with other physical properties. The atomic sites are listed in Table 2 while in Table 3 the lattice parameters and space groups are given.

#### Neptunite, $\text{KNa}_2\text{Li}(\text{Fe}, \text{Mg}, \text{Mn})_2\text{Ti}_2\text{Si}_8\text{O}_{24}$

The crystal structure of neptunite was studied [63B1, 63B3, 66B1, 66C2, 72L1 91K1, 97L1]. The silicate crystallizes in a monoclinic-type structure. In earlier studies the centric space group C2/c was attributed [66B1, 66C1]. The fundamental component of the structure was identified [66C1] as a three-dimensional tetrahedral  $\text{SiO}_4$  network in which infinite  $\text{SiO}_4$  chains running along [110] and  $[\bar{1}10]$  are connected along [001]. Interwoven within this framework is a similar network of edge-sharing  $[\text{Fe}, \text{Ti}]\text{O}_6$  octahedral chains along [110],  $[\bar{1}10]$  which are interconnected through shared corners along [001]. Since neptunite is piezoelectric, a property that cannot occur in a centric structure, the presence of an acentric space group Cc was suggested [66C2], but the authors were not able to carry out the refinement in this space group [91K1]. Nevertheless they assumed that ordering of octahedral Fe and Ti within a pseudocentric oxygen arrangement was responsible for the acentricity. The near K-edge Ti X-ray absorption was related to Ti coordination and bonding in neptunite [87W1]. An intense “pre-edge” absorption at 4969 eV was observed, which was believed to be characteristic of strong octahedral site distortion. However, these distortions were not observed in diffraction data, because refinement in a centric space group yields only average  $(\text{Fe}, \text{Ti})\text{O}_6$  geometries. Later on, [91K1] has shown that the crystal structure of neptunite has an acentric space group Cc, due to ordering of octahedrally coordinated metals (Ti, Fe, Mn, Mg). As above stated, in the neptunite structure Ti and (Fe, Mn, Mg) octahedra share edges to form chains that run along [110] and  $[\bar{1}10]$ . These chains are, in turn, linked through shared corners along [001]. The resulting octahedral framework is interwoven by a similar  $[\text{Si}_8\text{O}_{22}]$  tetrahedral framework [91K1]. Li, Na and K occupy 6-, 8- and 10-coordinated sites within this framework. A pyroxene-like fragment of the neptunite structure [66B1] is depicted in Fig. 1a which also shows the atom notations in agreement with Table 2. These pyroxene like units are symmetrically related – Fig. 1b – by a  $c$  glide plane to form the characteristic structure of neptunite. The metal-containing polyhedra show strong distortions at all temperatures. In particular, Ti exhibits a strong off-center displacement ( $\approx 0.25$  Å) within its octahedron, leading to four Ti-O distances of 2.0 Å, one of 2.2 Å and one at 1.7 Å. The displaced Ti position is in good agreement with a position that minimizes differences between ionic bond strengths and was interpreted as an energy minimum in an ionic potential model. By neutron diffraction, the distribution of 3d ions on different crystallographic sites has been shown, namely [91K1]: (1) Ti occupies the Ti1 site by an amount of 100 %. (2) On the Ti2 site, there is 10 % Fe (no Mg, Mn). (3) On the Fe1 and Fe2 sites, iron is substituted by unknown amounts of Mn, Mg and Ti. The degree of substitution is higher for Fe1 than for Fe2. We note that mangan-neptunite is characterized by a high content of Mn atoms.

The silicate  $\text{Na}_2\text{KMn}_2\text{LiV}_2\text{Si}_8\text{O}_{24}$  is isostructural with neptunite [02G1]. This crystallizes in space group Cc or C2/c.

#### Hellandite group of silicates

According to [65O1], for **hellandite** the chemical formula  $\text{Ca}_3(\text{Y}, \text{R})_4\text{B}_4\text{Si}_6\text{O}_{27} \cdot 3\text{H}_2\text{O}$  has been proposed. The structure of hellandite was later determined and reported to be monoclinic [77M1]. This consists of  $\text{B}_4\text{Si}_4\text{O}_{22}$  chains oriented parallel to [001] and cross-linked into a framework by corner-sharing M1 octahedra – Fig. 2 [77M1, 02O1]. This arrangement produces tunnels extending along [001] which are filled by three distinct eightfold-coordinated sites (M2, M3, M4) occupied by Ca, Y, R, actinides and also vacancies. A strong R ordering of the type  $\text{M2} \gg \text{M4} > \text{M3}$  was reported [77M1]. The proposed structural formula,  ${}_{\text{M2},3,4}[\text{Ca}_{5.5}\text{R}_{5.0}\square_{1.5}]^{\text{M1}}(\text{Al}_{1.1}\text{Fe}^{3+}_{0.9})(\text{OH})_4[\text{Si}_8\text{B}_8\text{O}_{40}(\text{OH})_4]$ , included significant vacancies at the (M2, M3, M4) sites and eight OH groups pfu. Several new occurrences of hellandites were reported [02O1]. In [70E1] a new mineral **tadzhikite** was described, with a similar XRD pattern as hellandite, but having different composition.

The  $\text{TiO}_2$  contents vary from 3.7 wt % in type-II tadjhikite to 6.5 wt % in type-I tadjhikite, and (apparently) no OH. Type-I tadjhikite was reported to be monoclinic and type II probably triclinic with the unit formula  $\text{Ca}_6(\text{Ce}, \text{Nd}, \text{La}, \square)_4(\text{Ti}, \text{Fe}, \text{Al})_2\text{Si}_8\text{B}_8\text{O}_{44}$ . In [77M1] was noted that unit cell parameters of tadjhikite could be transformed into those of hellandite by means of the matrix  $[101/010/00\bar{1}]$ , and concluded that the above silicates are isostructural. Later on, in [82C1] was confirmed that tadjhikite could be considered as an anhydrous (Ti, Ce)-rich end member of hellandite group. By refining the structure of unheated tadjhikite, positional disorder of R at the M2 site (four subsites) was found, which was related to the partly metamict state of the sample [98H1]. Bond-valence analysis suggested a significant amount of  $\text{H}_2\text{O}$  and the structural formula was proposed as  $^{\text{M}3}\text{Ca}_2^{\text{M}4}(\text{Ca}, \text{Y})_2^{\text{M}2}(\text{HR}^{3+}, \square)_2^{\text{M}1}(\text{Ti}^{4+}, \text{Fe}^{3+})[\text{B}_4\text{Si}_4\text{O}_{16}(\text{O}, \text{OH})_6]^{05}(\text{OH})_2$ . Some hellandites were studied later [99O1, 00O1]. According to the above reports, additional data were obtained [02O1]: (1) The Be and Li contents are significant. Structure refinement showed that they occur in tetrahedrally-coordinated site (T) that connects the borosilicate chains, to locally form a sheet of tetrahedra – Fig. 2. (2) The H content is always low and is lower in samples containing higher Be and Li contents. The H is bonded solely to the O5 O atom and protrudes into the tetrahedrally-coordinated cavity locally occupied by Be and Li. (3) No vacancies occur at the M sites when all chemical constituents have been correctly analysed. (4) R are ordered at the M2 and M4 sites and HR and actinides are strongly ordered at the M2 sites. We denote by LR and HR light and heavy rare-earths.

As mentioned above hellandite and tadjhikite are isostructural. However, the tetrahedral layer in hellandites contains an extra framework tetrahedral cavity which, at least under particular conditions, can host  $^{41}\text{Be}$  and/or  $^{41}\text{Li}$  [99O1]. No residual suitable site for H has been found in the difference Fourier map beyond the one near O5. The M1 octahedra are occupied mainly by Al and  $\text{Fe}^{3+}$ , but crystals rich in  $\text{Ti}^{4+}$  have been described. The M1 cations bond to the O5 anion. Therefore, high  $\text{Ti}^{4+}$  contents at M1 may also compensate for the lack of H at O5.

The occurrence of new members of the hellandite group was reported [02D1], as **ciprianiite** and **mottanaite**-(Ce). Both silicates are monoclinic having space group P2/a. The ideal structure of mottanaite-(Ce) is  $^{\text{M}3,4}\text{Ca}_4^{\text{M}2}(\text{R}^{3+}\text{Ca})^{\text{M}1}\text{Al}^{\text{T}}\text{Be}_2\text{Si}_4\text{B}_4\text{O}_{22}^{05}\text{O}_2$  where  $\text{R}^{3+} = \text{Y} + \text{R}$  and Ce dominates over R. The occupancy of the additional tetrahedral site is balanced by lower contents of trivalent cations at the M2, M3 and M4 sites with respect to hellandite. The low hydrogen contents in mottanaite was correlated with full occupancy at the T site. The ideal formula of ciprianiite is  $^{\text{M}3,4}\text{Ca}_4^{\text{M}2}[(\text{Th}, \text{U})\text{R}]^{\text{M}1}\text{Al}^{\text{T}}\square_2\text{Si}_4\text{B}_4\text{O}_{22}^{05}(\text{OH}, \text{F})_2$ . In this formula, the tetrahedrally coordinated T site is vacant. The heterovalent exchange, relating ciprianiite and hellandite is  $^{\text{M}3,4}\text{Ca}^{\text{M}2}(\text{Th}, \text{U})^{\text{M}3,4}\text{R}_1^{\text{M}2}\text{R}_{-1}$  [02O1].

In [02O1] a general formula for hellandite group minerals was proposed,  $\text{X}_4\text{Y}_2\text{ZT}_2[\text{B}_4\text{Si}_4\text{O}_{22}]\text{W}_2$ , where X = Na, Ca, Y,  $\text{LR}^{3+}$  at the eightfold-coordinated M3 and M4 sites, Y = Ca, Y,  $\text{HR}^{3+}$ ,  $\text{Th}^{4+}$ ,  $\text{U}^{4+}$  at the eightfold-coordinated M2 site, Z = Al,  $\text{Mn}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Ti}^{4+}$  at the octahedral M1 site, T =  $\square$ , Li, Be at a tetrahedrally-coordinated site (new) and W = OH, F,  $\text{O}^{2-}$  at the O5 site. Eight possible root end-member compositions were proposed. The hellandite end-members known so far are: hellandite-(Y), hellandite-(Ce), tadjhikite-(Ce), mottanaite-(Ce) and ciprianiite. The root name tadjhikite must be used for samples with  $\text{Ti}^{4+} > 0.5$  apfu, with no reference to the OH content. In Table 2 are given the lattice sites for hellandite [77M1]. As above mentioned, later on [02D1], a tetrahedral site was introduced which for mottanaite has the coordinates  $x = 0.0393(5)$ ,  $y = 0.5424(20)$  and  $z = 0.8668(10)$  which missed from Table 2b.

### Sörensenite, $\text{Na}_4\text{Be}_2\text{Sn}(\text{Si}_3\text{O}_9)_2 \cdot 2\text{H}_2\text{O}$

The structure of sörensenite was reported to be monoclinic having space group C2/c [65S1, 74M1, 76M1]. The description of the structure given by [90S1] will be followed. The structure, as viewed looking along the unique monoclinic axis – Fig. 3a – can be envisaged as thick (100) slabs composed of tetrahedrally coordinated Si and Be atoms interlayered with slabs of isolated octahedrally coordinated  $\text{Sn}^{4+}$  atoms [76M1, 90S1]. The above arrangement produces a number of open cavities containing the Na atoms (one of which is shown in Fig. 3a) and water molecules. The structure is of relatively low density with coordination polyhedra connected by vertex sharing, except for one edge shared between two Be tetrahedra and the edge sharing of the large, irregularly-coordinated  $\text{NaO}_7$  polyhedra. The  $\text{Sn}^{4+}$  ion occupies a position on an inversion center and is surrounded by an octahedron of oxygen atoms. Besides Si atoms, Sn's second nearest neighbours include Na atoms and H atoms forming long, weak hydrogen bonds to four of the six oxygen ligands – Fig. 3c. There are three independent Si atoms in the ratio 1:1:1 forming single chains of corner-sharing tetrahedra which run along the *b*-axis – Fig. 3b. These chains are similar in both repeat period (three) and general shape to those found in wollastonite. The  $\text{SiO}_4$

tetrahedra are fairly regular. All share corners with an  $\text{SnO}_6$  group and two other  $\text{SiO}_4$  groups, but the  $\text{Si}_2$  polyhedron is connected to two  $\text{BeO}_4$  groups, while  $\text{Si}_1$  and  $\text{Si}_3$  are connected to only one.  $\text{Si}_1$  and  $\text{Si}_3$  also have four Na neighbours (as well as a remote H neighbour), while  $\text{Si}_2$  has only three Na neighbours and no long H contact. There are thus two topologically different types of  $\text{SiO}_4$  tetrahedra. In order to connect to the  $\text{SnO}_6$  and  $\text{Be}_2\text{O}_6$  groups, the  $\text{SiO}_4$  chains are somewhat contorted. There are two independent, tetrahedrally coordinated  $\text{BeO}_4$  groups which are joined together by sharing a tetrahedral edge – Fig. 3b. The resulting  $\text{Be}_2\text{O}_6$  group lies on a twofold axis. Related, at least in part, to this edge sharing, the individual  $\text{BeO}_4$  tetrahedra are quite distorted. The bonds to atoms in the shared edge are about 5 % longer than to atoms on the unshared edge and the shared edge is the shortest edge of the group. The net effect is to stretch the  $\text{Be}_2\text{O}_6$  group along the Be-Be axis, making it possible for these two edge-shared tetrahedra to span the same distance as two same-sized, but corner-shared  $\text{SiO}_4$  tetrahedra – Fig. 3b. There are also two different Na atoms, each occupying an irregular cavity in the structure. The  $\text{NaO}_7$  groups show a broad range of distances. The  $\text{Na}_2$  polyhedron is more distorted than the  $\text{Na}_1$  one. One of the ten independent oxygen atoms in the structure, O7 – Table 2 – is not connected to any Si atom but rather is bonded to the two different hydrogen atoms present, forming a water molecule. This  $\text{H}_2\text{O}$  molecule is so positioned to simultaneously complete the coordination polyhedra around an  $\text{Na}_1$  and an  $\text{Na}_2$  atom while forming two long, weak hydrogen bonds to the other oxygens. The configuration around the water molecule is shown in Fig. 3c. There are no short Sn-H contacts, several intermediate length Si-H contacts (to two of the three Si atoms) and a range of Na-H distances, some of which are relatively short. The shortest H-Na distance is to  $\text{Na}_1$ , the less distorted Na coordination polyhedron.

#### Sverigeite, $\text{NaBe}_2(\text{Mn,Mg})_2\text{SnSi}_3\text{O}_{12}(\text{OH})$

The sverigeite crystallizes in an orthorhombic-type structure having space group Imma [89R1]. In the above paper the essential correctness of the formula given by [84D1] was confirmed and in addition the existence of some structural entities was revealed. Thus, the structure of sverigeite may be described in terms of three architectural elements: (1) straight octahedral chains of edge-sharing  $\text{SnO}_6$  octahedra and planar  $\text{NaO}_4$  groups (incomplete octahedra) running parallel to [001]; (2) sinuous tetrahedral chains consisting of vertex-sharing beryllsilicate  $\text{Be}_2\text{SiO}_8(\text{OH})$  3-rings and  $\text{Be}_2\text{Si}_2\text{O}_{11}(\text{OH})$  4-rings running parallel to [100] and (3) discrete  $\text{M}_2\text{O}_{10}$  groups of edge-sharing  $\text{MO}_6$  octahedra, which serve to link adjacent octahedral chains in the [100] and [010] directions. Additional linkage between octahedral chains along [010] is provided by  $\text{SiO}_4$  groups from the tetrahedral chains. The silicate tetrahedra do not share vertices with one another. However, each silicate tetrahedron does share two vertices with adjacent beryllate, ( $\text{BeO}_4$ ), tetrahedra to form the tetrahedral chains, and sverigeite may therefore approximately be termed a single-chain beryllsilicate [89R1]. Na displays a most unusual fourfold rectangular-planar coordination which may be regarded as a distorted octahedron with two vacant axial ligand sites.

#### Astrophyllite

The astrophyllite group of minerals (AGM) are alkali titano-, niobo- and zircono-silicates which have the general formula  $\text{A}_2\text{BC}_7\text{D}_2\text{T}_8\text{O}_{26}(\text{OH})_4\text{X}_{0...1}$  where  $\text{A} = [^{10-13}]\text{K, Rb, Cs, Na, H}_3\text{O, H}_2\text{O or } \square$ ;  $\text{B} = [^{10}]\text{Na or Ca}$ ;  $\text{C} = [^6]\text{Mn, Fe}^{2+}, \text{Fe}^{3+}, \text{Na, Mg or Zn}$ ;  $\text{D} = [^6]\text{Ti, Nb or Zr}$ ;  $\text{T} = \text{Si or Al}$ ;  $\text{X} = \text{F, OH, O or } \square$  [00P1]. The group is divided into the astrophyllite subgroup ( $\text{Fe} > \text{Mn}$ ) and the kupletskite subgroup ( $\text{Mn} > \text{Fe}$ ) – Table 1. The silicates from both subgroups crystallize either in a triclinic structure (space group  $\text{P}\bar{1}$ ) or a monoclinic cell (space group  $\text{C2/c}$ ) [03P1, 03P2]. The astrophyllite subgroup includes **astrophyllite** [63P1, 64P1, 67W1, 76Z1, 82L1, 98S1, 00Y1], **magnesium astrophyllite** [63P1, 74H1], **niobophyllite** [64N1], **hydroastrophyllite** [74H1, 75F1], **zircophyllite** and **Fe-dominant analog** of zircophyllite [03P1, 03P2]. The kupletskite subgroup includes **kupletskite** [98C2, 01P1], **niobokupletskite** [00P1] and **cesium kupletskite** [71E1]. According to [91N1] in astrophyllite group **jinchajiangite** is also included [82H1].

The refinement of the crystal structure of mica-like triclinic astrophyllite [00Y1] shows that this consists of three-layer HOH (TOT) sheets parallel to the (001) plane. The central sheet layer, O, is formed by Fe octahedra. The peripheral layers are built of ribbon-like silicon-oxygen radicals  $[\text{Si}_4\text{O}_{12}]^{8-}$  located along the shortest (5.4 Å) unit cell parameter and linked via Ti-octahedra – Fig. 4. Three-layer sheets linked by Ti octahedra sharing the (OH, F)-apices and large K and Na cations in the intersheet cavities form a three-dimensional framework of the structure. In the monoclinic-type lattice the T layers lying on both sides of the O layer are bound by the twofold

rotation axes lying in the plane of the O layer [63P1, 98S1]. A more detailed comparative analysis of the triclinic- and monoclinic-type structure will be made in case of kupletskites.

The astrophyllite group of minerals is an intermediate member of a polysomatic [96F1] or homologous [99C1] series. A comparison of minerals of the above series shows that they have: (1) a HOH structure, where H is a heterogeneous sheet similar to the TOT structure in phyllosilicates and O octahedral, (2) an  $a$ -axial length of approximately 5.4 Å, corresponding to the  $a$ -value observed in mica (see subvol III/27i5) and (3)  $d_{001} \approx 10.9$  Å. The homologous series can be expressed by indicating the number of diorthosilicate groups separating rows of D octahedra:  $n = 1$  in perraultite [98Y1],  $n = 2$  in AGM,  $n = 3$  in nafertisite [96F1] and  $\infty$  in mica [99C1] (subvol III/27i5). The AGM structure can be subdivided into two main composite sheets stacked along [001] in a 2:1 ratio [01P1]. The first is an O-sheet, extending from  $z = 0.40 \dots 0.60$  in triclinic species and from  $z = -0.05$  to  $0.05$  in monoclinic kupletskite, consisting of a closest-packed sheet of  $\text{MnO}_6$ ,  $\text{FeO}_6$ ,  $\text{MgO}_6$  or  $\text{NaO}_6$  octahedra. There are four crystallographically distinct O-sheet octahedra (M1-M4). The O-sheet is sandwiched between two H-sheets, extending from  $z = -0.15$  to  $-0.05$ . The H-sheet consists of open-branched zweier [100] single chains of  $[\text{Si}_4\text{O}_{12}]^{8-}$  [85L1, 01P1], which are in turn cross linked by corner-sharing  $\text{DO}_6$  octahedra or  $\text{DO}_5$  polyhedra as in magnesium astrophyllite [98S1] where  $D = \text{Nb, Ti, Zr}$ . The resultant Si/D ratio is 4/1. Individual  $\text{DO}_6$  octahedra are linked across the interlayer space via a common apical anion,  $\phi(16)$ , where  $\phi$  is an unspecified anion. The interlayer of triclinic AGM contains two crystallographically distinct cation sites, A and B, whereas kupletskite Ma2b2c contains three crystallographically distinct cation sites A1, A2 and B – Table 2. The variation in stacking sequence of individual HOH layers is responsible for the polytypism observed between monoclinic and triclinic kupletskite [01P1].

Polytypism in astrophyllite group has been proposed by a number of workers and recognized in electron diffraction studies [76V1, 76Z1, 85D1, 99C1]. The basis for the derivation of 14 modular polytypic AGM structures [76Z1, 85D1] was that of the “building layers” or “modules” each consisting of a combination of two neighbouring H sheets linked via a common apical anion and an independent O-sheet. In such an approach, a centered orthogonal cell defined by two octahedra wide ( $a$ ) and seven octahedra long ( $b$ ) is used. The base of each of seven O-sheet octahedra is regarded as a regular triangular network of anions, resulting in seven possible attachment points for the adjacent H-H layer [01P1]. The mutual disposition of the H-H units over apical positions (HHO units) results in four geometrically different HHOHH units and 14 possible polytypes with either triclinic, monoclinic or orthorhombic symmetry [76Z1]. Four of these 14 derived structures are based on the same triclinic subcell. Only three of these arrangements have been found in nature: monoclinic magnesium astrophyllite [63P1, 98S1], triclinic AGM [67W1, 98C1, 00P1] and kupletskite Ma2b2c [01P1]. Possible crystallographic mechanisms for the formation of astrophyllite polytypes include cation ordering, changes in packing of coordinating anions, variations in orientations of the O-sheet octahedra with respect to the adjacent H-sheets [96J1] or by complete translation of the HOH layer by combinations of symmetry elements, not evidenced in the triclinic structure. Since the minerals of the astrophyllite group are defined as layered silicates composed of HOH layers that are similar to the TOT layers in mica, the AGM polytype pair can be described as variations in the stacking of HOH layers. As example, in triclinic and monoclinic kupletskite the structural make up of the HOH layers differs only in the designation of the single, albeit split, A site in triclinic species as A1 and A2 in the monoclinic species – Table 2. In all other aspects, individual HOH layers are structurally identical. In a triclinic structure – Fig. 5a, adjacent HOH layers are related to each other by a center of symmetry. Stacking can be described as HOH/+HOH/+HOH or +++, with a layer stacking period of one. A displacement of  $\approx 5$  Å along  $b$  exists between adjacent layers, resulting in an offset of the adjacent layers such that the apices of the  $\text{D}\phi_6$  octahedra do not define an orthogonal arrangement. In monoclinic kupletskite – Fig. 5b, adjacent HOH layers are related by a twofold axis parallel to  $b$ , resulting in a stacking period along  $c$  of two differently oriented HOH layers, defined as +HOH and –HOH. The resulting stacking sequence with a two-layer period can be described as +HOH/–HOH/+HOH or +–+–. This polytypic form is equivalent to that reported by [76Z1]. A more orthogonal configuration is achieved such that  $\text{D-}\phi_6(16)\text{-D}$  polyhedral pairs lie in planes perpendicular to (001)[01P1]. Thus,  $a_{\text{mon}} = a_{\text{tricl}}$ ,  $b_{\text{mon}} = 2(b \sin \gamma)_{\text{tricl}}$  and  $c_{\text{mon}}$  spans two HOH layers.

### Kupletskite, cesium-kupletskite

Kupletskite is the manganese analogue of astrophyllite [56S1]. Cesium-kupletskite, is the Cs-analogue of kupletskite and crystallizes in a triclinic-type structure [71E1].

**Niobophyllite,  $K_2Na(Fe^{2+},Mn)_7(Nb,Ti)_2Si_8O_{26}(OH)_4(F,O)$** 

Niobophyllite is the niobium analogue of astrophyllite. The silicate crystallizes in a triclinic-type structure having space group P1 or  $P\bar{1}$  [64N1].

**Jinshajiangite,  $Na_5Ba_4(Fe,Mn)_{15}Ti_8Si_{15}O_{64}(F,OH)_6$** 

Jinshajiangite crystallizes in a monoclinic structure having space group C2/m, Cm or C2 [82H1].

**Eudidymite,  $Na_2Be_2Si_6O_{15}\cdot H_2O$** 

A structural scheme for eudidymite was proposed, based on  $[Si_3O_8]_\infty$  chains [47I1]. The inaccuracy of the above model was partially solved by [62P1], but the chemical formula given by them contained more oxygen than that shown by chemical analyses and the structure could not be refined by using their atomic coordinates. The structure was solved by [72F1] which give the composition  $Na_2Be_2Si_6O_{15}\cdot H_2O$ . The silicate crystallizes in a monoclinic-type structure having space group C2/c. The structure is based on double sheets of corner-sharing  $SiO_4$  tetrahedra of composition  $[Si_6O_{15}]_\infty$ . The sheets are parallel to (001) and are thus responsible for the {001} cleavage. The sheets are cross-linked by edge-sharing  $B_2O_6$  groups to form a complete three-dimensional framework structure, characterized by low optical birefringence. There are two crystallographically independent  $SiO_4$  groups – Fig. 6..

**Epididymite,  $NaBeSi_3O_7(OH)$** 

Epididymite is the orthorhombic dimorph of the monoclinic eudidymite [70R1]. The structure was investigated initially by [60P1] and further reanalyzed [70R1]. According to [70R1] the main structural feature of epididymite is the  $[Si_6O_{15}]_\infty$  double chain silicate tetrahedra paralleling the *c*-axis – Fig. 6. Each half-unit is quite similar to the single chain found in pectolite and wollastonite though different in that each is doubled by a mirror plane. The repeat distance of 7.33 Å in epididymite (three tetrahedra along *c*) may be compared with 7.02 Å in pectolite and 7.70 Å in wollastonite. The silicate chains are joined by two edge-sharing Be tetrahedra. The  $Be_2O_6$  group shares corners with each of the three silicon tetrahedra, thereby connecting all four independent  $[Si_6O_{15}]_\infty$  chains of the unit cell. The Na atoms have an irregular sevenfold coordination.

The polymorphic transformation between eudidymite and epididymite is of reconstructive type involving breakage of bonds and reorganization of cation and anion groups [72F1]. The extremely high dehydration temperature is construed to be the temperature at which the Be-O bonds yield, thus allowing the trapped water molecules to escape.

 **$K_2Be_2Si_6O_{15}$** 

The crystal structure of  $K_2Be_2Si_6O_{15}$  was studied by [76N1]. The silicate crystallizes in space group Cmc2<sub>1</sub>. In the structure the corrugated  $[Si_6O_{15}]_\infty$  layers extend parallel to the (101) plane, and twice intersect the cell along the *b*-axis. The layers are connected together by two-ring  $B_2O_6$  complexes in which two Be tetrahedra are coupled along a common horizontal (short) edge. Similar complexes, as already mentioned, were observed in the structures of epididymite [70R1], eudidymite [72F1], sörensenite [74M1]. The interlayer gaps accommodate two-ring groups of K-polyhedra. The seven-vertex K-polyhedra – trigonal prisms with an hemioctahedral cap, are connected in pairs, but now along a vertical edge. Pyroxene-like chains extend along the elongated direction of the crystal (*z*-axis). As in the structure of epididymite, the initial elementary motif is a wollastonite chain with  $Si_{2+1}O_9$  link – Fig. 7a. Similar with epididymite – Fig. 7b – the pairing of the parallel chains in  $K_2Be_2Si_6O_{15}$  takes place by reflection in a plane, but whereas in epididymite the doubling plane is parallel to the axis of the chain and passes through all the middle O atoms of the transverse diortho groups, in  $K_2Be_2Si_6O_{15}$  only the O atoms from the two longitudinal diortho groups lie in the same plane, and hence the condensation of the two chains results in the formation of  $[Si_6O_{16}]_\infty$  strips – Fig. 7c – and not  $[Si_6O_{15}]_\infty$  as in epididymite. This is the principal analogy in motif between  $K_2Be_2Si_6O_{15}$  and epididymite  $Na_2Be_2Si_6O_{15}\cdot H_2O$ , but the  $[Si_6O_{16}]_\infty$  strips in the structure of  $K_2Be_2Si_6O_{15}$  are also connected by the vertices of unpaired tetrahedra with inverted neighbours – Fig. 7c – with the formation (as in eudidymite) of two-story corrugated layers having the formula  $[Si_{12}O_{30}]_\infty$ . However, the similarity between  $K_2Be_2Si_6O_{15}$  and eudidymite is not so far-reaching, because of the difference in

construction principle. In the eudidymite layer, it is convenient to take the batisite (Chap. 8.1.4.7)  $\text{Si}_4\text{O}_{12}$  chains – Fig. 7d – drawn out along the  $\mathbf{b}$  (7.4 Å) edge of the cell. These chains are coupled by additional diortho groups. In the structure of eudidymite, the wollastonite chains are revealed less clearly than in the structures of epididymite and  $\text{K}_2\text{Be}_2\text{Si}_6\text{O}_{15}$  and now exhibit not a parallel, but almost perpendicular extension along the  $[110]$  and  $[1\bar{1}0]$ , i.e.  $d_{a+b} = 7.3$  Å.

#### **Bavenite, $\text{Ca}_4(\text{Al,Be})_4\text{Si}_9\text{O}_{26}(\text{OH})_2$**

The bavenite crystallizes in an orthorhombic-type structure [63B2, 66C1]. Bavenite displays a framework-like structure in which the dominant motif is a fourfold chain of linked tetrahedra running parallel to  $\mathbf{b}$ . These are formed by four pyroxene-like chains connected circularly between themselves. Two different fourfold chains are connected along  $\mathbf{c}$  through two beryllium tetrahedra as bridges, forming a system, S1, of six-membered rings, running zigzag along  $\mathbf{b}$ . Moreover two different fourfold chains are connected along  $\mathbf{a}$  through two tetrahedra as bridges, forming a system of rings, S2, of alternately four and eight tetrahedra running parallel to  $\mathbf{b}$ . Each one of these systems is cut in the middle by a mirror plane parallel to  $\mathbf{b}$ . The mirror planes are perpendicular and cross. The S1 and S2 systems of rings are connected through rings of six non-equivalent tetrahedra. The calcium atoms occupy the channels formed by them along  $\mathbf{b}$ . Four Ca polyhedra are interconnected, related by the mirror planes. No connections exist between Ca polyhedra along  $\mathbf{b}$ . In this crystal structure there are no empty channels.

#### **Lorenzenite (Ramsayite), $\text{Na}_2\text{Ti}_2\text{O}_3(\text{Si}_2\text{O}_6)$**

The crystal structure of lorenzenite was studied by many groups [41K1, 49B1, 55S1, 69C1, 87S1]. Various space groups for the orthorhombic lattice were reported – Table 3. The Pbcn seems to be the correct one [87S1]. The structure consists of pyroxene-type  $[\text{Si}_2\text{O}_6]_\infty$  chains running approximately in the direction of the  $\mathbf{b}$ -axis and having O5 as the bridging oxygen atom. O4 of the silicate chain is bonded to one Ti only, whereas O3 of the chain connects two neighbouring Ti atoms. The  $\text{TiO}_6$  octahedra lie in two adjacent layers alternating in each layer with chains of  $\text{NaO}_7$  polyhedra. This arrangement generates a close-packing system of unique type (ramsayite type). The  $\text{TiO}_6$  polyhedron is a considerably distorted octahedron with six non-equivalent Ti-O bond lengths and with Ti lying off-center.

#### **$\text{Na}_2\text{O}\cdot\text{Zr}[\text{SiO}_4]$**

The  $\text{Na}_2\text{O}\cdot\text{Zr}[\text{SiO}_4]$  silicate crystallizes in a monoclinic-type structure having space group  $\text{P2}_1/\text{c}$  [70T1]. The main elements of the structure are chains of Zr octahedra extending along the  $\mathbf{b}$ -axis, which are linked via common vertices:  $[\text{ZrO}_5]_\infty$ . These columns are of “baroque” type, i.e. almost exactly along  $2_1$  screw axes lie vertical oxygen edges of the Zr octahedra, while the Zr atoms lie on opposite sides of the oxygen axes, with two Zr octahedra per repeat distance  $\mathbf{b}$ . The cell contains four Zr columns, which form two crystallographically independent pairs, one along  $2_1$  axes with  $x = 0$  and the other along  $2_1$  with  $x = 1/2$ . There is an obvious difference in orientation for the planes containing the Zr octahedra alternating in height in the two types of columns. The axes of these columns lie almost exactly at the nodes of pseudohexagonal net with a cell side  $a/2 = c/2$ . Along the pseudo-threefold axes of this net lie the  $[\text{Si}_4\text{O}_4]$  orthotetrahedra between three Zr columns. A Si tetrahedron has one O vertex in common with two of these columns, and two O vertices in common with the other one. A Zr column is linked to six adjacent ones by two Si tetrahedra. According to [70T1], this structure is of the type seen in lorenzenite: a structure dominated by medium-sized cations of high charge ( $\text{Ti}^{4+}$ ,  $\text{Zr}^{4+}$ ) which determine the architecture, leaving the large loose cations to fill the three-dimensional framework.

#### **Natisite, $\text{Na}_2\text{TiOSiO}_4$**

Natisite crystallizes in a tetragonal structure having space group  $\text{P4/nmm}$  [75M1, 78N1]. The structure contains layers of  $\text{SiO}_4$  tetrahedra and  $\text{TiO}_5$  square pyramids joined by sharing corners and separated by layers of  $\text{Na}^+$  ions. Na has only four nearest-neighbour O atoms at the corners of a rectangle with two other atoms further away completing an irregular octahedron [78N1].

**Li<sub>2</sub>TiOSiO<sub>4</sub>, Li<sub>2</sub>VOSiO<sub>4</sub>**

Li<sub>2</sub>VOSiO<sub>4</sub> crystallizes in a tetragonal structure of space group P4/nmm [98R1]. The compound is isostructural with Li<sub>2</sub>TiOSiO<sub>4</sub> [94Z1] and Na<sub>2</sub>TiOSiO<sub>4</sub> [78N1].

**8.1.4.9.2 Nuclear gamma resonance (NGR) data****Neptunite**

The <sup>57</sup>Fe NGR study on neptunite evidenced that iron is in a divalent state [67B1]. In [91K1] neptunite was studied by the <sup>57</sup>Fe NGR method at 77, 293 and 400 K. The analysis of the spectra indicated all iron to be present as octahedral Fe<sup>2+</sup>. Although two distinct Fe sites were found in the structure, the spectra at 77 K and 293 K displayed only one quadrupole doublet. Two iron sites were only resolved in the 400 K spectrum. It was suggested that the temperature dependence of octahedral edge distortions is responsible for the separation of the doublets. The well resolved high-temperature spectrum revealed a lack of correspondence between observed and calculated intensities. This feature was ascribed to a possible third Fe site. Then, the <sup>57</sup>Fe NGR study was performed on neptunite single crystal [97L1]. Some <sup>57</sup>Fe NGR spectra are shown in Fig. 8. The refined parameters are listed in Table 4. The analysis revealed that only the model considering 2Fe<sup>2+</sup> and 1Fe<sup>3+</sup> doublets give agreement with experimental data. This assignment agrees with neutron diffraction study [91K1]. A small amount of iron occupies the Ti2 site. We note that this amount is lacking on the Fe1 site. The iron on the Ti2 site is in trivalent state, in agreement with optical data [88M1]. The observed charge transfer (Sec. 8.1.4.9.4) Fe<sup>2+</sup>-Ti<sup>4+</sup> obviously occurs over an intermediate step Fe<sup>3+</sup>-Ti<sup>3+</sup> according to the data of [97L1], which could be explained by a model which involves that nearly 50% of the iron occupies the Fe2 site, 46% is located on the Fe1 site and 4% exchange with titanium ions in Ti2 site. These data obtained by <sup>57</sup>Fe NGR method are also in agreement with residual electron densities as obtained from X-ray diffraction. The angle  $\beta$  between the main component of EFG,  $V_{zz}$  and  $\mathbf{b}$  is close to the calculated value of  $\beta$  for the Fe1 site from electron density map. The directions  $\beta$  of the EFG principal axes with respect to  $\mathbf{b}$  are given in Table 4. The calculated value of  $V_{zz}$  from electron densities ( $0.621 \cdot 10^{18}$  V/cm<sup>2</sup>) is of the same order of magnitude as obtained from <sup>57</sup>Fe NGR data ( $0.901 \cdot 10^{18}$  V/cm<sup>2</sup>) [97L1].

**8.1.4.9.3 Nuclear magnetic resonance (NMR) data****Sörensenite**

In agreement with the crystallographic finding of one Sn site per cell with Sn<sup>4+</sup> in almost regular octahedral surrounding – section 8.1.4.9.1 – the <sup>119</sup>Sn MAS NMR spectrum shows one fairly sharp resonance at – 706 ppm [90S1]. This resonance is accompanied in the MAS NMR spectrum by two spinning sidebands. From the indirect observation of the <sup>1</sup>H spin reservoir via the <sup>119</sup>Sn nucleus, it can be seen that the H<sub>2</sub>O moiety in sörensenite does not form a strong hydrogen bond to O-Sn.

From the <sup>23</sup>Na MAS spectrum, the number of sodium sites present was not really obvious due to insufficient spectral resolution – Table 5. The <sup>29</sup>Si MAS NMR spectrum shows three resonances with 1:1:1 intensity ratio, attributed to Si1, Si2 and Si3 sites – Fig. 9 [90S1]. The <sup>9</sup>Be MAS NMR spectrum shows one fairly broad and asymmetric resonance for the  $\pm 1/2$  transition centered at –2.5 ppm (shift uncorrected for quadrupolar interaction).

For <sup>1</sup>H NMR spectra in **eudidymite** see [67S1].

**8.1.4.9.4 Optical properties****Neptunite**

The polarized absorption spectra of neptunite, KNa<sub>2</sub>LiFe<sub>2</sub>Ti<sub>2</sub>Si<sub>8</sub>O<sub>24</sub>, at 296 K, are given in Fig. 10 [88M1]. There is believed to be a Fe<sup>2+</sup>-Ti<sup>4+</sup> charge transfer, Fe and Ti occurring in two edge-sharing octahedral chains along [110] and  $[\bar{1}10]$  [66B1, 66C1]. These chains are interconnected through shared corners. The nearest cations within the chains are 3.14...3.28 Å apart and the interaction vectors have substantial components in all optical directions. An ordered arrangement within the chains such that Fe<sup>2+</sup> alternate with Ti<sup>4+</sup> was proposed to account

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for piezoelectricity in neptunite. The 415 nm transition in the spectrum, in the visible region, was assigned to  $\text{Fe}^{2+}$ - $\text{Ti}^{4+}$  charge transfer. The width at half-height of this transition is  $\sim 9000 \text{ cm}^{-1}$  [88M1].

For IR study of **eudidymite** see [67S1].

Some refractive indices are listed in Table 6.