

#### 8.1.4.6 Xonotlite group of silicates

The minerals from this group are listed in Table 1 [91N1]. In addition, a number of synthetic silicates having related structures were prepared and studied. These have the general formula  $A_nMSi_6O_{15} \cdot xH_2O$  with  $A = Na, K, Li, Cs$ ;  $M = Nd, Ce, Y, Zr, Ti, Sn$ , and  $n = 1$  to 3. A review on the crystal structures of the minerals and synthetic silicates from this group was given by [97H1]. The Si/O ratio of 2/5 in these compounds (silicate tetrahedra linked by sharing three atoms per tetrahedra, plus one unshared O atom) permits layer, double chain or double ring configurations. The factors that govern the stabilities of ring, chain and layered structures are not well established. In [97H1] was shown that in the layered structures the larger M cations (Nd, Ce) produce a greater degree of corrugation than do Zr and Ti cations. The more open structures of neodymium and cerium silicates contain large channels that may serve as pathway for fast alkali ion transport.

##### 8.1.4.6.1 Crystal structures. Lattice parameters

A description of the structures on the main silicates from the group is presented. Then, we follow [97H1] in analyzing comparatively the crystal structures of some  $A_nMSi_6O_{15} \cdot xH_2O$  silicates. The atom positions in some representative structures are given in Table 2, while in Table 3 the space groups and lattice parameters are listed.

##### Xonotlite

The crystal structure of xonotlite and its polytypism was analyzed by [79K1, 01H1]. In the description of xonotlite polytypism we follow mainly the paper of [01H1], an excellent review on the matter. Xonotlite is a fibrous hydrate silicate of calcium, whose chemical composition  $Ca_6Si_6O_{17}(OH)_2$  is closely related to that of wollastonite. Upon dehydration, xonotlite is in fact transformed into wollastonite, the *b*-axis of which being parallel to the fibre axis *b* of xonotlite [56D1]. Some studies on both natural and synthetic xonotlites show higher water content than assumed by the above formula [71G1, 98N1]. For xonotlite both monoclinic [56M1] and triclinic [79K1] structures were evidenced. The structure of the triclinic variant is in principle similar to that of the monoclinic type. The xonotlite polytypism was discussed based on a monoclinic subcell [79 K1]. Xonotlites are used in technics as on steam cured cements [97T1], for immobilization of radioactive waste, Cs absorption from hydrous solutions [85M1] as well as in many other applications [01H1].

The single-crystal diffraction pattern of xonotlite [54T1, 79K1] showed sharp reflections, diffuse reflections and streaks. Considering only the sharp reflections a subcell was defined. Taking the streaks into account a cell with doubled *b*-axis resulted. Sharp reflections were found for  $k = 2n$ , whereas the diffuse ones and streaks were observed for  $k = 2n+1$ . The streaks run both parallel to *a*\* and *c*\*, indicating one-dimensional disorder in two directions [66G1, 80C1]. Short spikes perpendicular to the above mentioned streaks, observed by electron microscopy study, have been interpreted in terms of two-dimensional disorder [64D1]. In [55M1, 56M1, 81E1] a structure model was proposed for xonotlite which consists of calcium polyhedral layers and infinite  $SiO_4$  double chains. Based on this structure model, six polytypes, four ordered and two dimensionally disordered, were suggested. Five of these polytypes were evidenced by electron diffraction on natural samples [66G1, 80C1]. The first complete structural determination of an ordered polytype has been carried out by [79K1]. Common to all polytypes is a polyhedral layer of one calcium atom in octahedral- and two calcium atoms in sevenfold coordination – Fig. 1 [01H1]. The calcium atoms in sevenfold coordination have six close neighbours in form of a trigonal prism plus a seventh oxygen attached at one prism face. The octahedra are edge sharing to form an infinite chain along the *b*-axis (chain A). A corresponding chain of edge-sharing polyhedra along the *b*-axis is built by the calcium atoms in sevenfold coordination (chains B, B'). All chains are joined together, by edge sharing, to form a layer parallel to (001) with BAB' arrangement of chains. Chains B and B' are related to each other by a twofold axis parallel to *b* and a mirror plane perpendicular to it. The arrangement of only Ca-oxygen polyhedra can be described in a cell having C2/m symmetry [79K1, 01H1]. The Ca polyhedral layers are linked by  $[Si_6O_{17}]$  double chains. Each  $[Si_6O_{17}]$  double chain – Fig. 2 – consists of a wollastonite-like pair of  $[Si_3O_9]$  "dreiereinfachketten" of corner-linked  $SiO_4$  tetrahedra. The single chain has a periodicity of three tetrahedra, two of them being joined to give a  $[Si_2O_7]$  pair alternating with a single tetrahedron which connects the paired tetrahedra and therefore is labeled bridging tetrahedron. In xonotlite, two  $[Si_3O_9]$  "dreiereinfachketten" are joined to form a  $[Si_6O_{17}]$  "dreierdoppelkette" by sharing apical oxygen atoms of two bridging tetrahedra. The two single chains are related to each other by an inversion center, a twofold axis, and a mirror plane perpendicular to the

twofold axis. Thus the symmetry of the double chain is  $2/m$  [01H1]. The OH group is located at the free apices of calcium octahedra where no bridging  $\text{SiO}_4$  tetrahedra are attached.

Due to the fact that the  $[\text{Si}_6\text{O}_{17}]$  “dreierdoppelkette” has the same length as two calcium polyhedra, each double chain of  $\text{SiO}_4$  tetrahedra can be attached to calcium octahedra at two different positions – Fig 3. This is the reason for the appearance of the various polytypes [01H1]. To compare the above polytypes, a small unit, common to polytype structures [55M1, 56M1, 79K1], was introduced, having monoclinic symmetry and has been named cell of **hypothetical protoxonotlite** [79K1] – Table 3. Polytype structures may be analyzed as a different arrangement of this protoxonotlite cell. The protoxonotlite cell is not a crystallographically correct unit since it does not comply with the requirement of the three-dimensional periodic translation, but it is necessary that along [100] adjacent cells are shifted by  $+b/4$  or  $-b/4$ . Neither the calcium ribbon, nor the next double chain of  $\text{SiO}_4$  tetrahedra can be correctly placed without  $\pm b/4$  shift. In addition, along [001] adjacent protoxonotlite cells are either juxtaposed or shifted by  $b/2$ . Only along [010] the protoxonotlite cell is always repeated by a normal translation [01H1]. According to this approach, the first difference between the monoclinic [55M1, 56M1] and triclinic [79K1] polytypes is the repetition of protoxonotlite cells along [100]. In the monoclinic structure, the protoxonotlite cells are alternately shifted by  $+b/4$  and  $-b/4$  whereas in the triclinic polytype they are arranged by a continuous step of  $b/4$  (or  $-b/4$ ). A second difference occurs parallel to the  $c$ -axis. In the monoclinic polytype the tetrahedral double chains are juxtaposed whereas in the triclinic polytype adjacent protoxonotlite cells are shifted by  $b/2$ . This structure description suggests that xonotlite may exhibit one-dimensional disorder parallel to the  $a$  and  $c$ -directions and hence polytypes distinct in stacking along both directions.

The [66G1] notation for the monoclinic polytype reported by [55M1, 56M1] was named P121, whereas the triclinic polytype [79K1] was named F222. Later on, for notation of polytypes, a modified Gard [66G1] system was approved [84G1], where the first letter indicates the symmetry of the cell (monoclinic M). Three lower-case letters, accompanied by numbers, if necessary, follow the symmetry symbol to indicate the periodicity along the three axes. An additional symbol, d, is added for disordered structure, as a subscript to the letter involved.

As above mentioned, in the xonotlite structure variable stacking occurs in two directions. In the  $a$ -direction, adjacent protoxonotlite cells are shifted either by  $+b/4$  or  $-b/4$ , leading to the two possibilities of either continuous shift by  $+b/4$  (or  $-b/4$ ) or alternating shift by  $+b/4$  and  $-b/4$ . In the  $c$ -direction adjacent protoxonotlite cells are either juxtaposed or shifted by  $+b/2$ . Combining the different stacking mechanisms in both directions, the four simplest ordered polytypes results – Fig 4. The term “simplest polytypes” means that more sophisticated combinations such as  $(+b/4, -b/4, -b/4)$  or  $(+b/4, +b/4, -b/4, -b/4)$  ..... for protoxonotlite cells adjacent along  $a$ , or combinations as (no shift, shift  $b/2$ ,) or (shift of  $b/2$ , shift of  $b/2$ , no shift)..... for protoxonotlite cells adjacent along  $c$ , were not considered. These ordered polytypes are [01H1]: M2a2bc (C221): continuous shift of the protoxonotlite cell by  $+b/4$  for stacking in  $a$ -direction and juxtaposed cells along [001]; M2a2b2c (F222): continuous shift of protoxonotlite cells by  $+b/4$  for stacking in  $a$ -direction and shift of  $+b/2$  for stacking in  $c$ -direction (this arrangement leads to the triclinic polytype [79K1]); Ma2bc (P121): alternate shift of protoxonotlite cells by  $+b/4$  and  $-b/4$  for stacking in  $a$ -direction and juxtaposed cells along [001] (this arrangement leads to the monoclinic polytype as proposed by [55M1, 56M1]); Ma2b2c (A122): alternate shift of protoxonotlite cells by  $+b/4$  and  $-b/4$  for stacking in  $a$ -direction and shift by  $+b/2$  for stacking in  $c$ -direction. For M2a2bc and M2a2b2c, a continuous shift of protoxonotlite cells by  $-b/4$  for stacking in  $a$ -direction is just as possible as the shift by  $+b/4$  introduced above [01H1]. Domains with only  $-b/4$  and domains with only  $+b/4$  shifts are in a twin relationship. The composition plane between the two twin components is (100) and a twofold rotation about  $b$  is the twin operation. If both twin sectors are evident on diffraction photographs these polytypes were called M2a2bc-twin and M2a2b2c-twin [01H1].

In [66G1] the two disordered polytypes  $P \infty 21$  and  $A \infty 22$  were proposed, which become in the modified notation  $\text{Ma}_d2bc$  and  $\text{Ma}_d2b2c$ . In direct space these disordered polytypes are closely related to M2a2bc-twin and M2a2b2c-twin with the difference that in the disordered polytypes the domains are so small that in the diffraction pattern streaks were observed parallel to  $a^*$ . Streaks parallel to  $c^*$  were recorded by [80C1] but were not observed by [66G1]. In the direct space these polytypes describe disorder where protoxonotlite cells are either juxtaposed along [001] or shifted by  $b/2$ . Even disorder in two directions may be expected which would lead to the  $\text{Ma}_d2b2c_d$  polytype.

In [01H1], the refined structure of the M2a2b2c polytype [79K1] was taken as basic structure to calculate the structures of the three other simplest polytypes: Ma2bc (space group  $P2_1/a$ ) Ma2b2c (space group  $A2/a$ ) and M2a2bc (space group  $P\bar{1}$ ) – Table 3. Unique reflection arrangements in the reciprocal lattice, characteristic of each polytype were defined to identify xonotlite polytypes on X-ray single crystal patterns. Precession- and

Weissenberg-patterns of a natural xonotlite indicated the predominance of the (100) twinned M2a2b2c polytype, followed by the Ma2b2c polytype, and very low concentrations of the Ma2bc polytype. The M2a2bc polytype could not be identified. Diffuse streaks parallel to  $a^*$  and less intensives ones parallel to  $c^*$  on single crystal patterns suggest the presence of additional disordered polytypes [01H1].

The OD character of xonotlites was analyzed [01H1] – see also Chap. 8.1.4.5. Xonotlites, as mentioned already, display one-dimensional disorder in two directions (along  $a$  and  $c$ ). Only the disorder along  $a$  conforms with the OD theory. For stacking disorder along  $c$ , the two possible arrangements display pairs of adjacent layers which are geometrically not equivalent, thus the vicinity condition for OD-structures is not fulfilled [64D1, 97D1]. For this reason two OD-groupoid families, distinct by (1) simple– (for the Ma2bc and M2a2bc polytypes) and (2) doubled – periodicity (for the Ma2b2c and the M2a2b2c polytypes) parallel to  $c$  were defined. The corresponding OD-layers are similar to that in wollastonite [97M1]. They are defined by the translation periods  $b$ ,  $c$  and a third basis vector  $a_0$ , which is not a translation vector.

Xonotlites may be synthesized hydrothermally at 200...350°C and elevated pressures during some days [77K2, 91S1, 97T1, 97Y1, 99S1]. Xonotlite is believed to form topotactically out of tobermorite [59T1, 77K2]. The crystallinity of synthetic xonotlite is of rather poor quality [01H1].

The compositions of xonotlites may be changed by various substitutions. The maximum aluminium content which substitutes  $Si^{4+}$  is 5%. The Al-substituted samples have lattice parameters significantly different from Al free samples [77K2].  $Ca^{2+}$  can be almost completely substituted by  $Co^{2+}$  or  $Ni^{2+}$  [85K1] and partially can be replaced by  $Mg^{2+}$  [91S1]. Low concentrations of  $Na^+$ ,  $K^+$ ,  $Mn^{2+}$  and  $Fe^{3+}$  were found in several xonotlites [99D1].

#### **Armstrongite, $CaZrSi_6O_{15} \cdot 2.5H_2O$ ; dalyite $K_2ZrSi_6O_{15}$**

Armstrongite crystallizes in a monoclinic-type structure having space group C2 [78K1]. In the crystal structure, the distorted Zr and Ca octahedra (alternating like the Zr and Na octahedra in elpidite [65N1]) form isolated columns along the  $b$ -axis (elongation axis of the crystal). The pseudoperiod of the column in armstrongite (7.08 Å) is somewhat less than the period of the column in elpidite (7.13 Å) and differs markedly from the period of the purely Ca column in xonotlite (7.34 Å), wollastonite (7.32 Å) and tobermorite (7.30 Å). The structure of armstrongite is closest to that of **dalyite** [65F1]. The tetrahedral layer in dalyite is a strongly distorted armstrongite one. The difference between the structures of these silicates is most pronounced in the manner in which the silicate layer is joined to the Zr octahedra. In both structures the base of the Zr octahedron facing the tetrahedral layer has one vertex in common with the tetrahedron of the six-membered ring of the same “tobermorite” band. The other two vertices of the base are joined to the vertices of the tetrahedra of the parallel “tobermorite” band, but in case of armstrongite these are the tetrahedra of the two neighbouring four-membered rings [78K1]. - See also the section on  $A_nMSi_6O_{15}$  silicates.

#### **Elpidite, $Na_2ZrSi_6O_{15} \cdot 3H_2O$**

The crystal structure of elpidite was solved by [63N1] and described in centrosymmetric space group Pmcm (the setting of crystallographic axes was changed [73C1] from various authors). Then in [65N1] the symmetry was lowered to P2cm, in order to explain certain features of electron density map. In [67C1] was reported that the  $b$  cell parameter is twice that previously reported. Then, the crystal structure was redetermined and found to agree essentially with that given by [65N1]. According to [73C1], it consists of a framework formed by chains of Si-tetrahedra, connected by Zr-octahedra. The anion framework is saturated by sodium atoms. Two independent Na atoms are present. Na2 has an octahedral coordination formed by four oxygens of tetrahedra and two symmetrically equivalent water molecules,  $H_2O1$ . The octahedra around Na2 and Zr form a column running parallel to [100]. The other sodium atom, Na1, occurs in a cavity formed by adjacent double chains of tetrahedra. It is bonded to seven oxygens and water molecule  $H_2O2$ . Na1 and the water molecule bonded to it are the atoms with the greatest deviation from the symmetry Pmcm.

We note that in [0211] were analyzed systematically topological structures of zirconosilicates and their analogs (60 minerals and 34 synthetic phases) where the simplest structure units are  $MO_6$  octahedra and  $TO_4$  tetrahedra united by vertices ( $[TO_4]:[MO_6] = 1.1$  to 6.1.)

**Davanite; synthetic  $K_2TiSi_6O_{15}$** 

Davanite  $K_2TiSi_6O_{15}$  crystallizes in a triclinic-type lattice [83G1, 84L1, 86W1, 87R1]. Synthetic  $K_2TiSi_6O_{15}$  crystallizes in a monoclinic-type structure having space group  $P2_1$  [01Z1]. An ORTEP plot of the asymmetric unit of synthetic  $K_2TiSi_6O_{15}$  with all the atoms labeled is shown in Fig. 5. The principal structural motif can be described as corrugated  $[Si_6O_{15}]_{\infty}$  layers. The layers are parallel to (*ab*) plane, zigzagged along the *b*-axis. The building units of the  $[Si_6O_{15}]_{\infty}$  layers are four- and six-membered rings, which are connected to each other forming chair-like eight-membered rings. The  $[Si_6O_{15}]_{\infty}$  layers are connected by isolated  $TiO_6$  octahedra and stacked along the *c*-axis to form a three-dimensional mixed framework. Three types of mixed rings are formed (T-T-T- $O_h$ ); (T-T-T-T- $O_h$ ) and (T-T- $O_h$ -T-T-T- $O_h$ ) membered rings (T =  $SiO_4$  tetrahedron and  $O_h$  =  $TiO_6$  octahedron). The two potassium cations are located in the cage formed by the six- and seven-membered rings. The only crystallographically unique  $TiO_6$  octahedron is slightly distorted. All the six  $SiO_4$  octahedra are corner shared with each other or with  $TiO_6$  octahedra. The lattice sites are listed in Table 2.

The synthetic  $K_2TiSi_6O_{15}$  has several similarities with other silicates, although it is not isostructural with any of them. It has the same/similar formula as for example the isostructural pair **davanite**,  $K_2TiSi_6O_{15}$  [83G1] and **dalyite**,  $K_2ZrSi_6O_{15}$  [65F1], **hydrated armstrongite**,  $CaZrSi_6O_{15} \cdot 2.5H_2O$  [78K1], synthetic epididymite  $K_2Be_2Si_6O_{15}$  [76N1],  $Cs_2TiSi_6O_{15}$  [97G1],  $Cs_2ZrSi_6O_{15}$  [96J1],  $K_2CeSi_6O_{15}$  [77K1],  $K_2GeSi_6O_{15}$  [92M1] and **sazhinite**  $Na_2CeSi_6O_{14}(OH) \cdot 1.5H_2O$  [80S1]. The structures of all the above compounds have infinite corrugated  $[Si_6O_{15}]_{\infty}$  layers. Three of them, davanite, armstrongite and epididymite (see Chap. 8.1.4.9) are more closely related to synthetic  $K_2TiSi_6O_{15}$ . The Si-Si connections in the  $[Si_6O_{15}]_{\infty}$  layers, for the above silicates, constitute an interesting sequence of structures [01Z1]. The building units of the  $[Si_6O_{15}]_{\infty}$  layers are the same in all the structures, i.e. four-, six- and eight-membered  $SiO_4$  tetrahedral rings. The eight-membered rings form a chair-like unit – Fig. 6A. In one direction (perpendicularly in Fig. 6A), the chair like units are connected by two shared  $SiO_4$  tetrahedra forming Si-O ribbons similar to eight-membered rings in xonotlite [55M1]. In the other direction (horizontally in Fig. 6A), the chair-like units are connected by two-corner-sharing  $SiO_4$  tetrahedra. As a result, four- and six-membered rings are formed in all cases. The relative orientation of the chair-like units in each structure is different. In davanite (Fig. 6Ab) and armstrongite (Fig. 6Ac) all the chair-like units are oriented in the same way, while in synthetic  $K_2TiSi_6O_{15}$  (Fig. 6Aa) and epididymite (Fig. 6Ad) they are oriented differently, such that a twofold screw axis is generated (horizontally in Fig. 6A). The  $[Si_6O_{15}]_{\infty}$  layers are complex and very much corrugated, as seen from their sideview – Fig. 6B. Among the above four silicates, the wave amplitude for the  $[Si_6O_{15}]_{\infty}$  layers of synthetic  $K_2TiSi_6O_{15}$  and epididymite are much larger than those for the  $[Si_6O_{15}]_{\infty}$  layers of davanite and armstrongite. The  $[Si_6O_{15}]_{\infty}$  layers in synthetic  $K_2TiSi_6O_{15}$ , davanite and armstrongite are connected into three-dimensional mixed framework by octahedrally coordinated atoms (Ti and Zr) – Fig. 6C – except epididymite (where the layers are connected by pairs of beryllium-oxygen tetrahedra). The octahedra in the synthetic  $K_2TiSi_6O_{15}$  are zig-zagged – Fig. 6Ca – while those in davanite – Fig. 6Cb – and armstrongite – Fig. 6Cc – are lying on a straight line. There are only two types of titanium involved polyhedral ring systems in the structure of davanite and armstrongite: 5-(T-T-T-T- $O_h$ ) and 6-(TT- $O_h$ -TT- $O_h$ ) rings, which are different from those in synthetic  $K_2TiSi_6O_{15}$ , as already denoted.

**Tinaksite,  $Ca_2K_2TiNa[Si_7O_{18}(OH)]O$ ; tokkoite,  $K_2Ca_4[Si_7O_{18}(OH)](F,OH)$** 

**Tinaksite** crystallizes in a triclinic lattice, having space group  $P\bar{1}$  [80B1]. We note that the crystal structure reported by [71P1] has been later refined [80B1]. There are two hybrid “dreierdoppelketten” in the unit cell with Si-O bond lengths varying from 1.566 to 1.657 Å, according to different linkages of the  $[SiO_4]$  tetrahedra.

The crystal structure of **tokkoite** consists of corrugated walls of calcium octahedra parallel to (100), between which bands of silicon-oxygen tetrahedra are situated. One of the non-bridging end anions is a OH group. K atoms are located within zig-zag channels formed by curved silica bands [89R1]. Thus, the crystal structure of tokkoite can be considered as composed of the following structural units: (1) corrugated walls parallel to (100) and (2) curved bands with the composition  $[Si_7O_{18}(OH)]^{9-}$  consisting of a hybrid three-repeat double chain (hybrid dreier double chain [78L1]) with four- and eight-membered rings. These structural units are connected by corner sharing and alternate along *a*-axis. K and H atoms occur in large zig-zag channels between the silicon-oxygen bands. A general design of the tokkoite structure is identical to tinaksite, the octahedral walls being geometrically similar. These two structures are related by the substitution  $2Ca^{2+} \leftrightarrow Ti^{4+} + Na^+$  and  $(F,OH)^- \leftrightarrow O^{2-}$  which occurs simultaneously in cationic and anionic parts of silicates. The silicon-oxygen band

$[\text{Si}_7\text{O}_{18}(\text{OH})]_\infty$  is analogous to that of tinaksite and can be considered as two polymerized chains of wollastonite-type with an additional tetrahedron or condensed chains of wollastonite-type (see Chap. 8.1.4.1 [73P1]). Bands of silicon-oxygen tetrahedra are connected to the octahedral wall on both sides by sharing oxygen atoms. K1 and K2 atoms are located in a zig-zag channel between the two centro-symmetrical tetrahedral bands and have tenfold coordination. The structural similarity of tinaksite and tokkoite suggests that they are the end members of the hypothetical isomorphous series  $\text{K}_2\text{Ca}_4[\text{Si}_7\text{O}_{18}(\text{OH})](\text{O},\text{OH},\text{F}) - \text{K}_2\text{Ca}_2\text{NaTi}[\text{Si}_7\text{O}_{18}(\text{OH})]\text{O}$ .

### Sazhinite, $\text{Na}_2\text{Ce}[\text{Si}_6\text{O}_{14}(\text{OH})]\cdot n\text{H}_2\text{O}$

The crystal structure of sazhinite is based on infinite corrugated networks of silicon tetrahedra built up to xonotlite bands of the dalyite type  $[\text{Si}_6\text{O}_{15}]_\infty$  [80S1]. The principal component of this layer is the xonotlite band composed of eight-membered rings of tetrahedra running parallel to [100]. Adjacent bands (along  $y$ ) are related by a mirror plane, and owing to their condensation there arises a network with eight-membered, six-membered and four-membered loops, infinite in two dimensions. This network is not plane but wavy. The silicon radicals of this type were found in the structure of dalyite [65F1], armstrongite [78K1] and synthetic  $\text{K}_3\text{NdSi}_6\text{O}_{15}$  [77P1].

### $\text{K}_2\text{CeSi}_6\text{O}_{15}$

$\text{K}_2\text{CeSi}_6\text{O}_{15}$  crystallizes in a monoclinic-type lattice [77K1]. The structure consists of the silicon-oxygen anion framework of xonotlite strips, which extend along the  $y$ -axis and suffer considerable deformation as a result of the corrugation of the rings and their mutual rotation in the  $(xy)$  plane. The direct condensation of the strips at the levels  $z = 0$  and  $z = \frac{1}{2}$  leads to a skeletal binding of the centro-symmetrical eightfold (xonotlite) and (perpendicular to them) to the sixfold (lovozerite – Chap. 8.1.3.4 (subvolume 27I3)) rings. The coupling of the rings gives spirals of tetrahedra around the  $2_1$  axis parallel to the  $z$ -directions. Inside the channels of xonotlite rings lie the K atoms occupying large, eight-pointed polygons which, when viewed along the  $y$ -axis, are alternatively linked by common faces and common edges into a zig-zag column with projections of single Ce octahedra (on the twofold axes) in accordance with the characteristic olivine motif. - See also section on  $\text{A}_n\text{MSi}_6\text{O}_{15}\cdot x\text{H}_2\text{O}$  silicates.

### $\alpha\text{-K}_3\text{NdSi}_6\text{O}_{15}\cdot 2\text{H}_2\text{O}$ ; $\beta\text{-K}_3\text{NdSi}_6\text{O}_{15}$

In [77P1] the structure of  $\text{K}_3\text{NdSi}_6\text{O}_{15}$  was reported. The structure of silicates, having closely related compositions, were further analyzed [91H1, 93H1, 97H1, 00H1, 00H2]. The structure of  $\alpha\text{-K}_3\text{NdSi}_6\text{O}_{15}\cdot 2\text{H}_2\text{O}$  is orthorhombic of Pbam type and is based on highly corrugated  $[\text{Si}_2\text{O}_5^{2-}]_\infty$  layers which can be generated by the condensation of xonotlite-like ribbons, which can, in turn, be generated by the condensation of wollastonite-like chains [00H1]. The silicate layers are connected by Nd octahedra to form a three-dimensional framework. Potassium ions and water molecules are located in interstitial sites within this framework, in particular within channels that extend along [001]. In  $\alpha\text{-K}_3\text{NdSi}_6\text{O}_{15}\cdot 2\text{H}_2\text{O}$  a sequence of transformations was observed as function of temperature. When aging of as-grown crystals at room temperature, for periods of six months or more,  $\alpha\text{-K}_3\text{NdSi}_6\text{O}_{15}\cdot 2\text{H}_2\text{O}$  undergoes an ordered transition to  $\alpha'\text{-K}_3\text{NdSi}_6\text{O}_{15}\cdot 2\text{H}_2\text{O}$ , having space group Pnnm and  $c$  parameter twice that of  $\alpha$ -silicate. The sequence of phase transformations can be summarized as function of temperature:

$\alpha \text{ (or } \alpha') \xleftarrow{400(30)\text{K}} \alpha_1 \xleftarrow{425(25)\text{K}} \alpha_{\text{II}}$ . The  $\alpha_{\text{II}}$  phase was supposed to be anhydrous and  $\alpha_1$  may or may not contain residual water. The high-temperature phase,  $\alpha_{\text{II}}$ , is stable up to temperatures of at least 1373 K [00H1].

The structure of  $\beta\text{-K}_3\text{NdSi}_6\text{O}_{15}$  is orthorhombic, having space group Bb2<sub>1</sub>m, and is based on  $[\text{Si}_2\text{O}_5^{2-}]_\infty$  layers connected by Nd polyhedra to form a three-dimensional framework [00H2]. Potassium ion sites, some of which are only partially occupied, are located within channels that run between the silicate layers. The silica-neodymium framework of  $\beta\text{-K}_3\text{NdSi}_6\text{O}_{15}$ , in particular the linkages formed between the silicate layers and Nd polyhedra, bears some similarities to that of essentially isocompositional phase  $\alpha\text{-K}_3\text{NdSi}_6\text{O}_{15}\cdot 2\text{H}_2\text{O}$ . In both, the silicate layers are corrugated so as to accommodate a simple cubic array of  $\text{NdO}_6$  octahedra with lattice constant  $\sim 7.5$  Å. The  $\text{Si}_2\text{O}_5$  layers in  $\beta\text{-K}_3\text{NdSi}_6\text{O}_{15}$  are topologically identical to those of the sazhinite. Although  $\beta\text{-K}_3\text{NdSi}_6\text{O}_{15}$  and sazhinite are not isostructural, the structure of each can be described as slight distortions of a high-symmetry parent structure with space group Pbmm.

### $A_nMSi_6O_{15} \cdot xH_2O$ silicates

In [97H1] the structural features of  $A_nMSi_6O_{15} \cdot xH_2O$  silicates were compared where A is an alkaline metal or alkaline rare earth,  $M = Y, Ti, Zr$  or a rare-earth and  $n = 1, 2$  and 3. This analysis has in view single layer  $\alpha$ - $K_3NdSi_6O_{15} \cdot 2H_2O$  [97H1, 00H1],  $\beta$ - $K_3NdSi_6O_{15}$  [97H1, 00H2] and isomorphous sazhinite [80S1],  $Na_3NdSi_6O_{15} \cdot 2H_2O$  [97H1], double ring  $\alpha$ - $Na_3YSi_6O_{15}$  [97H1], double chain  $\beta$ - $Na_3YSi_6O_{15}$  [94B1] and their isomorphous  $Na_2LiYSi_6O_{15}$  [82G1], zektzerite,  $NaLiZrSi_6O_{15}$  [78G1] (Chap. 8.1.4.7)  $NaLiTiSi_6O_{15}$ ,  $NaLiSnSi_6O_{15}$  [79M1], emeleusite,  $Na_2LiFeSi_6O_{15}$  [78J1] (Chap. 8.1.4.7),  $Li_2ZrSi_6O_{15}$  [81Q1], tuhualite  $(Na,K)Fe^{+2}Fe^{+3}Si_6O_{15} \cdot 0.5H_2O$  [69M1] (Chap. 8.1.4.7) and  $Na_2Mg_2Si_6O_{15}$  [72C1] (Chap. 8.1.4.7). Related structures include elpidite  $Na_2ZrSi_6O_{15} \cdot 3H_2O$  [73C1], epididymite,  $Na_2Be_2Si_6O_{15} \cdot H_2O$  [70R1] (Chap. 8.1.4.9), where two edge-sharing  $BeO_4$  groups play the role of a single  $MO_6$  group; single layer dalyite  $K_2ZrSi_6O_{15}$  [65F1] and its isomorph  $K_2TiSi_6O_{15}$  [83G1, 84L1], single layer armstrongite [78K1],  $Cs_2ZrSi_6O_{15}$  [96J1] and the framework structure  $K_2CeSi_6O_{15}$  [77K1]. As mentioned above, in addition to the layered configuration  $[Si_6O_{15}]_{\infty}$ , structures of  $Si_6O_{15}$  based silicates can also adopt double chain, double ring and framework configurations.

In the following we present the discussion on the matter given by [97H1]. The *single layer structures*  $\alpha$ - $K_3NdSi_6O_{15} \cdot 2H_2O$ ,  $\beta$ - $K_3NdSi_6O_{15}$ ,  $Na_3NdSi_6O_{15} \cdot 2H_2O$ , dalyite and armstrongite have in common a wollastonite-type chain [78O1] as the basic structure building block – Fig. 7a [97H1]. In the terminology of [85L1], this is a dreier-single chain meaning that the translational repeat unit along the chain consists of three silicate tetrahedra and that the tetrahedra are linked only to others that extend along the direction of the chain. Viewed along the direction of the chain, the wollastonite-type chain [61B1] has the width of two silicate tetrahedra. Condensation of two wollastonite-type chains produces the xonotlite-like chain [79K1], a dreier double chain – Fig. 7b. This chain is characterized by the presence of eight-membered silicate rings. Further condensation of xonotlite-like chains produced the connectivity of tetrahedra in the sheets found within all of the single layer  $A_3MSi_6O_{15} \cdot xH_2O$  analysed structures. Thus, all the corrugated layer structures are based on the xonotlite double chains, although in compounds such as  $K_2ZrSi_6O_{15}$  [65F1] they are so distorted so as to be barely recognizable [00H2]. The xonotlite-like double chains may be linked together in one of the three ways so as to generate the  $(Si_2O_5)_{\infty}$  layer – Fig. 7. The chains may be linked after simple translation in a direction perpendicular to the chain extension – Fig. 7c; after translation in a direction perpendicular to the chain extension and translation in a direction parallel to the chain extension by half the periodicity of the chain – Fig. 7d or the chain may be linked in an alternating manner between the first two types of linkages – Fig. 7e. The silicate sheets in which the xonotlite-like chains are all directly linked, as in Fig. 7c, are the more common, as in  $\beta$ - $K_3NdSi_6O_{15}$  [97H1, 00H2],  $\alpha$ - $K_3NdSi_6O_{15} \cdot 2H_2O$  [97H1, 00H1], sazhinite [80S1],  $K_2TiSi_6O_{15}$  [83G1],  $K_2ZrSi_6O_{15}$  [65F1] and  $CaZrSi_6O_{15}$  [78K1]. The silicate  $Na_3NdSi_6O_{15} \cdot H_2O$  [97H1] crystallizes in a structure with a layer having alternating direct and sheared linkages – Fig. 7e and  $Cs_2ZrSi_6O_{15}$  [96J1] crystallizes in a structure with a layer in which there are only sheared linkages – Fig. 7d [00H2].

The type and extent of corrugation in the layered  $A_nMSi_6O_{15} \cdot xH_2O$  silicates was shown to be determined by the nature of the M cation. The large cations such as  $Nd^{3+}$  and  $Ce^{3+}$  force a corrugation determined by the local connectivity of  $NdO_6$  polyhedra to  $(Si_2O_5^{2-})_{\infty}$  layers. Entirely different linkages are formed between  $ZrO_6$  ( $TiO_6$ ) octahedra and the  $Si_6O_{15}$  layer. The corrugations are such that  $NdO_6$  ( $CeO_6$ ) polyhedra span three silicate tetrahedra (in direction normal to the wollastonite type chain) whereas  $ZrO_6$  ( $TiO_6$ ) octahedra span four [00H2]. The degree of warping of the layers is therefore greater in the former than in the latter. The layers in the Zr silicates are stacked in a staggered, two layers sequence that gives rise to a centered unit cell. The neighbouring layers in neodymium silicates are stacked essentially by translation normal to the layers. The two general types of  $MSi_6O_{15}$  frameworks which result from the two general types of linkages with  $MO_6$  octahedra are shown in Fig. 8. The larger M cations necessarily generate a framework – Fig. 8a – which is more open than that generated by the smaller cations – Fig. 8b and that this is true regardless of the specific details of the topology of the  $Si_6O_{15}$  layer and the nature of the A cation [00H2]. Analyzing a number of single layer silicate structures, it was concluded that as the octahedrally coordinated M cation decreases in size, from  $Nd^{3+}$  to  $Zr^{4+}$ , the degree of corrugation of the layers increases commensurably [97H1]. This occurs because a high degree of corrugation permits terminating O atoms to come within sufficient proximity to one another to satisfy the coordination requirement of a small M cation.

The  $\text{K}_2\text{CeSi}_6\text{O}_{15}$  takes an **interrupted framework** structure. In [77K1] xonotlite-like chains were identified as the basic structural unit. The structure can also be understood in terms of  $\text{Si}_6\text{O}_{15}$  layers containing six- and ten-membered silicate rings that are linked together by bridging O atoms to form a three-dimensional silicate anion. The adoption of framework structure was explained in terms of a combined valence-cation size arguments [85L1]. In [97H1] was suggested that the absence of a single layer structure results from synthesis conditions that favoured the framework structure.

The structure of  $\alpha\text{-Na}_3\text{YSi}_6\text{O}_{15}$  [95H1] contains discrete  $\text{Si}_6\text{O}_{15}$  units – Fig. 9a. According to [85L1] a **dreier double ring** indicates that it is composed of two three-membered rings that share a common interfacial plane. The  $\text{Si}_6\text{O}_{15}$  units are linked by  $\text{YO}_6$  octahedra to form a three-dimensional network – Fig. 9b. In this case, unlike that of layered silicates, the octahedron is essentially free to take on the most favorable configuration without the need to conform to O-O distances in the silicates anion.

The  $\text{Cs}_2\text{TiSi}_6\text{O}_{15}$  silicate crystallizes in a monoclinic structure, having space group  $\text{C2/c}$  [97G1]. In the structure, isolated titanium-centered octahedra and silica-centered tetrahedra share all corners to form an open framework structure containing large cavities in which the cesium ions are located. Each cavity is bound by three 5-rings, two 6-rings and two 8-rings. The cavities are linked via the 8-rings into channels parallel to [101]. The cesium ions occur in pairs along the channels, separated by 3.765(2) Å.

According to [97H1] the energy differences between the various configurations are quite small. In contrast to  $\text{Na}_3\text{YSi}_6\text{O}_{15}$  both Nd and Zr silicates crystallize as layered structures, despite the significant difference between these ions in terms of charge and size. The  $\text{Si}_6\text{O}_{15}$  sheets in these structures assume highly corrugated configurations to conform to the geometry of the  $\text{MO}_6$  (or  $\text{MO}_7$ ) polyhedron. The differences in size between  $\text{NdO}_6$  (or  $\text{NdO}_7$ ) and  $\text{ZrO}_6$  produces differences in the manner in which corrugation occurs, generating much more open structures in the case of Nd(Ce) silicates than obtained in Zr (Ti) silicates. This openness results in large channels within the structures.

### Yuksporite

Yuksporite is a complex titanosilicate of calcium, potassium and sodium. Different crystal structures were reported in literature, as orthorhombic [85K2], triclinic [03M1] or monoclinic [04K1]. The lattice parameters given by different authors are listed in Table 3. According to [04K1], the structure of yuksporite is based upon complex rods consisting of corner-sharing  $\text{TiO}_6$  octahedra and  $\text{SiO}_4$  tetrahedra – Fig. 10. The rods are parallel to **a** and have an elliptical cross section. Silicate tetrahedra consist of nine independent types.  $\text{Si1O}_4$ ,  $\text{Si4O}_4$  and  $\text{Si5O}_4$  tetrahedra are linked via common O atoms to form xonotlite-like double dreier chains  $\infty^1[\text{Si}_6\text{O}_{17}]$  (i.e. double chains with three tetrahedra within their identity periods) – Fig. 10c. These chains are parallel to **a** and are oriented perpendicular to **c**. Similar  $\infty^1[\text{Si}_6\text{O}_{17}]$  chains are made up of  $\text{Si2O}_4$ ,  $\text{Si6O}_4$  and  $\text{Si8O}_4$  tetrahedra – Fig. 10d. Two  $\infty^1[\text{Si}_6\text{O}_{17}]$  chains are linked into a rod via  $\text{Ti1O}_6$  and  $\text{Ti2O}_6$  octahedra and  $\text{Si}_2\text{O}_7$  double tetrahedra formed by Si3 and Si7 atoms – Fig. 10e. Another  $\text{Si}_2\text{O}_7$  group composed of two corner-sharing  $\text{Si9O}_4$  tetrahedra is located within the rod and is oriented parallel to **b**. This group provides linkage of two opposite walls of the rod along the **b**-axis – Fig. 10b. There are two different  $\text{TiO}_6$  octahedra and both of them show an out-of-center distortion of octahedral geometry typical for  $d^0$  transition metal cations [95K1]. These octahedra are predominantly occupied by Ti(Nb). Of the six O atoms, coordinating the  $\text{Ti}^{4+}$  cations, five are shared with silicate tetrahedra and one is not. The titanosilicate nanorod  $\{(\text{Ti,Nb})_4(\text{O,OH})_4[\text{Si}_6\text{O}_{17}]_2[\text{Si}_2\text{O}_7]_3\}$  is negatively charged. The above nanorods are porous. The internal pores are defined by eight-membered rings (8MRs) oriented perpendicular to (100). These 8MRs consist of two octahedra and six tetrahedra each – Fig. 10b. Within the rod the 8MRs are arranged in two parallel internal channels separated by the  $\text{Si}_2\text{O}_7$  groups formed by  $\text{Si9O}_4$  tetrahedra. From the outside, the rods are bounded by 8MRs formed solely by silicate tetrahedra – Fig. 10c. The plane of these rings is parallel to (001). Other outside rings are 6MRs – Fig. 10e. These rings consist of two octahedra and four tetrahedra. The interior of the titanosilicate nanorods is occupied by alkali metal cations (Na,K). In addition, there is a low-occupancy M site located within the rod between two  $\text{Si}_2\text{O}_7$  groups formed by Si9 atoms. The rods are separated by walls composed of Ca coordination polyhedra. The walls are parallel to (010) and provide linkage of the rods into a three-dimensional structure [04K1]. The titanosilicate nanorods of yuksporite are of interest as potential technological applications [02P1].

#### 8.1.4.6.2 Nuclear magnetic resonance (NMR) data

##### Xonotlite

The  $^{29}\text{Si}$  MAS NMR studies were performed both on synthetic and natural xonotlites [80L1, 87E1, 90B1, 96C1, 98N1]. In [80L1, 87E1, 90B1, 96C1] the presence of two resonance lines at  $-86.8$  ( $Q^2$ ) and  $-97.8$  ( $Q^3$ ) was reported, with a 2:1 intensity ratio. Later on, in [98N1] was shown that the  $^{29}\text{Si}$  NMR signals of  $Q^2$  both in natural and synthetic xonotlites were split – Fig 10 and Table 4. As discussed in Sect. 8.1.4.6.1 for Si1 and Si2 – Fig. 2 – the mean Si-O bonds (Si1 - 1.613 Å, Si2 - 1.635 Å) and Si-O-Si bond angles (Si1 -  $140.8^\circ$ , Si2 -  $141.0^\circ$ ) are different and consequently the presence of different lines are expected. Thus, the  $Q_H^2$  and  $Q_L^2$  signals were attributed to Si1 and Si2. The signal at  $-79.6$  ppm ( $Q^1$ ) was observed only in a synthetic crystal and was interpreted in terms of chain truncations, whereas a corresponding signal was not observed in spectra of natural xonotlites of high crystallinity. Consequently this has been correlated with a rather poor crystallinity of synthetic xonotlite [94N1, 98N1].

The  $^1\text{H}$  wideline and MAS NMR signals of synthetic xonotlite were reported by [71G1] and [79R1, 98N1], respectively, as well as for a natural sample [98N1]. The  $^1\text{H}$  MAS NMR spectra – Fig 10c,d – were deconvoluted into three lines – Table 4. The signals at 5.26, 1.86 and 2.19 ppm were attributed to molecular water, Si-OH and structural Ca-OH [93R1, 98N1], respectively. Protons associated with  $\text{SiO}_4$  tetrahedra have not been located in the structure.

#### 8.1.4.6.3 Electrical resistivity

##### $\alpha\text{-K}_3\text{NdSi}_6\text{O}_{15}$

The conductivity of  $\alpha\text{-K}_3\text{NdSi}_6\text{O}_{15}$  single crystal was measured in the temperature range  $573\text{ K} \leq T \leq 1193\text{ K}$  [00H1]. Lower-temperature measurements could not be made because of the high resistivity of the samples. The conductivities, as function of temperature along different directions, increase at a faster rate than would be expected for a simple activated process – Fig. 11. From the slopes of these curves the values of the activation energies were obtained – Table 5. The conductivities at 873 K are also listed. The  $\sigma_{33}$  is the largest value, indicating that the [001] channels, present in the room temperature structure, are preserved at high temperatures as to serve as pathways for easy ion transport. The greater value of  $\sigma_{22}$  than  $\sigma_{11}$  suggest that the motion through the layers is easier than motion perpendicular to the corrugation.

#### 8.1.4.6.4 Optical properties

Infrared studies were performed on xonotlite. The OH stretching frequencies at  $3636\text{ cm}^{-1}$  indicate that the O-H-...O distance is rather long [57K1, 99L1].

Some refractive indices are listed in Table 5.