

8.1.3.7 Milarite group of silicates

As is apparent from Table 1, the group of double ring silicates having the general formula $^{[6]}A_2^{[9]}B_2^{[12]}C^{[18]}D^{[4]}T_2^{[4]}T_1T_2O_{30} \cdot (H_2O)_x$ [72F1] is quite large. Much of work on this family refers to the “milarite group”, whereas some more recent works refer to the “osumilite group”. Frequency of usage incline to the former designation. In addition, milarite has more of the possible cation sites filled (A, B, C, T1 and T2) than does osumilite (A, C, T1 and T2), which makes milarite more useful as the type of structure [91H1]. Consequently, in this chapter, the name “**milarite group**” has been preferred.

In addition to natural milarites, there are synthetic silicates having crystal structures of the milarite type. Many of these have technical utilizations [95W1]. For example, $BaMg_2Al_6Si_9O_{30}$ is a glass-ceramic for substrates in electronic devices or for reinforcement with SiC-fibres [79M1, 84B1, 87J1, 93W1, 95W1]. This silicate melts incongruently to mullite and becomes liquid at 1370°C. The thermal expansion coefficients (25...1000°C) are $\alpha_a = 2.4(3) \cdot 10^{-6}/K$ and $\alpha_c = 2.9(3) \cdot 10^{-6}/K$. Accordingly, glass-ceramics based on $BaMg_2Al_6Si_9O_{30}$ show a temperature stability up to 1300°C and linear thermal expansion coefficients between 2 and $3 \cdot 10^{-6}/K$ are observed. Reinforcement with SiC-fibres yields bending strengths between 400...700 MPa and K_{Ic} between $3...4 \text{ MPa m}^{1/2}$ [86B1, 86C1, 86G1]. $SrMg_2Al_6Si_9O_{30}$ shows similar properties as $BaMg_2Al_6Si_9O_{30}$, having a melting point at 1310°C and thermal expansion coefficients of $\alpha_a = 2.9(3) \cdot 10^{-6}/K$ and $\alpha_c = 2.3(3) \cdot 10^{-6}/K$ (25...700°C) [82V1, 93W2]. $Mg_2Al_4Si_{11}O_{30}$ osumilite was described [62S1] as metastable accessory compound in crystallization products of glasses with compositions close to the join cordierite-SiO₂. Addition of small amounts of BaO to an MgO-Al₂O₃-SiO₂ glass composition yields a product with $Mg_2Al_4Si_{11}O_{30}$ as the main phase [93W1, 93W3, 95W1]. Though metastable, this silicate can endure temperatures up to 1150°C for a long time. At higher temperatures it decomposes into cordierite and cristobalite. The thermal expansion resembles that of cordierite. While the *a*-axis expansion is low and positive, the *c*-axis shows a negative expansion: $\alpha_a = 2.6(3) \cdot 10^{-6}/K$ and $\alpha_c = -1.9(3) \cdot 10^{-6}/K$ (25...600°C) yielding an overall linear thermal expansion coefficient of $1.1 \cdot 10^{-6}/K$ which is nearly as low as that of cordierite.

8.1.3.7.1 Crystal structures. Lattice parameters

The greatest number of double ring silicates from the milarite group crystallizes in a hexagonal structure having space group P6/mcc – Fig. 1. Different space groups were evidenced only in armenite and roedderite. The atomic sites for some representative silicates are listed in Table 2. In the P6/mcc type structure, the hexagonal $Si_{12}O_{30}$ double rings of silicate tetrahedra are linked by tetrahedrally coordinated T2 cations and octahedrally coordinated A cations into a three-dimensional tetrahedral framework. Sandwiched between adjacent A octahedra are the B sites, each surrounded by nine oxygens. Alternating along the tunnels formed by the stacking of the double hexagonal silicate rings are C and D sites, each surrounded by twelve and eighteen oxygens, respectively. The milarite structure is extremely flexible from a chemical viewpoint and a considerable number of minerals [86H1, 91H1] and synthetic silicates [51R1, 64G1, 67S1, 69S1, 72P1, 77S1, 80N1] adopt the above basic atomic arrangement. The site occupancy for some members of the milarite group silicates are given in Table 3. The important substitutions in milarites are $Na(B) + Be(T2) = \square(B) + Al(T2)$ and $Y,R(A) + Be(T2) \rightleftharpoons Ca(A) + Al(T2)$ [91H1]. We denoted by R a rare-earth element. The first type of substitution is more common but the second can be significant in R enriched environments. The $\langle T2-O \rangle$ distance is linearly dependent on the Be/(Be+Al) ratio, supporting the structure refinement results that indicate direct $Be \rightleftharpoons Al$ substitution at the T2 site. The A cations (Ca,Y,R) always show positional disorder about the central position, even when the site is occupied by Ca. H₂O is always present in milarite and armenite; it is rarely present in other species of this group. The B site in milarite is occupied by (H₂O, Na,K) and shows positional disorder, that is a function of the Be/(Be+Al) ratio. The C site is completely occupied in milarite by K and there is no positional disorder at this site. In the silicate of milarite group, there is $Al \rightleftharpoons Si$ substitution at T1 and a wide variety of substitutions at T2. The sizes of the coordination polyhedra are linearly related to the ionic radii of constituent cations. A short description of the crystal structure of members of the milarite group will be given below.

The crystal structure of **milarite**, the mineral from which the group is named was described by [49B1, 51B1, 52J1] and commented by [53P1]. The silicate crystallizes in hexagonal P6/mcc type structure – Fig. 1 and Table 2. The natural milarites were studied by [63C1, 65O1, 66R1, 68C1]. Milarite has a beryllio-alumino-silicate framework structure. The framework is a four-connected three-dimensional net, one of a series of seven simple

nets, with prominent double rings of tetrahedra [86H1]. The T1 tetrahedron of the $\text{Si}_{12}\text{O}_{30}$ double six-membered ring – Fig. 1 – shares three corners with adjacent T1 tetrahedra and one corner with a T2 tetrahedron. The T2 tetrahedron links the $[\text{Si}_{12}\text{O}_{30}]$ clusters into a framework; it shares four corners with adjacent T1 tetrahedra and two edges with adjacent A octahedra. This site is occupied by variable amounts of Be and Al. The A octahedron lies between the $[\text{Si}_{12}\text{O}_{30}]$ clusters, sharing corners with the T1 tetrahedra and further strengthening the framework linkage. It also shares edges with three flanking T2 tetrahedra, edges that are extremely contracted relative to the other edges of both the A octahedron and T2 tetrahedron. In normal milarite, this site is ideally completely occupied by Ca. In nearly all the refinements, the A cation showed extremely anisotropic displacement parameters with the long axis of the ellipsoid oriented along the c -axis [75B1, 80C1, 91H1]. This site was modeled by a split atom [89A2, 89K1, 91H1]. The amount of splitting varies nearly linearly across the series using either $\langle \text{T2-O} \rangle$ or $\text{Be}/(\text{Be}+\text{Al})$ as a measure of the Be content. When the A site is partly occupied by Y and R, the constituent cations still show the splitting and the amount of splitting still increases as function of the $\text{Be}/(\text{Be}+\text{Al})$ ratio. A splitting of the B site was also evidenced. The reason for the A- and B-site splitting was analysed by refining the structure of both natural and dehydrated milarites [89A2]. In dehydrated milarite, both the A- and B-site splittings do not occur. If H_2O occupies the split B site and the cations occupy the central B site, dehydration will remove the H_2O from the split site but will not affect the cations at the central B site. This is what is observed in dehydrated milarite, leading to the conclusion that H_2O occupies the split B site [91H1]. On dehydration, the splitting of the A site also does not occur. This suggests that the A-site splitting observed in milarite is the result of a $^{\text{A}}\text{Ca}-^{\text{B}}\text{H}_2\text{O}$ interaction along the \bar{c} axis [89K1]. In [89A2] was proposed that the A site ($= \text{Ca}$) is coordinated by seven anions with a $\text{Ca}-\text{H}_2\text{O}$ bond of 2.84 Å augmenting the six shorter $\text{Ca}-\text{O}$ bonds (2.35 Å) and that lowering of symmetry that gives rise to optical anomalies in milarite is due to the polar nature of A site coordination and the resulting disorder along $\pm c$. We note that in [66B1, 72F2, 75B1] site populations were proposed that intended to explain dehydration induced changes in the structure. The B site lies on the threefold axis between the $[\text{Si}_{12}\text{O}_{30}]$ clusters, and directly above and below the A octahedron – Fig. 1 – surrounded by nine O atoms [91H1]. The ideal B site occurs at $z = 0$, and it has three O neighbours at ≈ 2.78 Å and six O neighbours at ≈ 3.30 Å. In the refinements made on milarites [75B1, 80C1, 91H1] the B cations, as above mentioned, showed very anisotropic displacement behaviour that was modeled by a split atom position. The splitting of the B cation site is much greater than that observed for the A atoms. The C site occurs on the sixfold axis at $z = 1/4$ sandwiched between two $[\text{Si}_{12}\text{O}_{30}]$ clusters – Fig. 1. The central atom is bonded to 12 O atoms, all of which are at distance of ≈ 3.0 Å. This site is occupied completely by K. Unlike the A and B cations, the C cation is not significantly displaced from the high symmetry position at the center of the C-polyhedron [91H1]. The D site occurs at the center of the $[\text{Si}_{12}\text{O}_{30}]$ cluster – Fig. 1 – surrounded by 18 O atoms arranged at the vertices of an augmented hexagonal prism. In the study of [91H1], no significant density was detected within this cavity; if small numbers of atoms were disordered about this cavity, it would be difficult to detect them with conventional diffraction techniques.

The structure of milarite was also analysed in the model proposed by [86H1, 88H1]. In [86H1] were developed 46 four-connected three-dimensional nets based on an insertion of two connected vertices into the three-connected two-dimensional nets 6^3 , $3 \cdot 12^2$, $4 \cdot 8^2$ and $4 \cdot 6 \cdot 12$. One of the topological consequences of developing four-connected three-dimensional nets by out-of-plane linkages between stacks of two-dimensional nets is that the initial three-connected vertices must lie in infinite paths within a single prototype two-dimensional net [88H1]. The milarite framework has double six-membered rings of such vertices and is one of a family of possible structures based on sigma transformation nets [73S1] containing double n -membered rings. The net characteristic for milarite has six-membered silicate and nine-membered silicate-beryllate rings, each of which is arranged coaxially along $[001]$ to form a hollow tube. These tubes contain A, B, C and D sites. These are occupied by alkali and alkaline earth cations and by the H_2O group, which thus support the fairly open framework.

A number of synthetic milarites were prepared, as for example $\text{A}_2\text{Mg}_5\text{Si}_{12}\text{O}_{30}$ with $\text{A} = \text{K}, \text{Na}$ [51R1, 69S1] or $\text{AM}_3\text{M}'_2(\text{Si},\text{Al})_{12}\text{O}_{30}$ with $\text{A} = \text{K}, \text{Ba}$; $\text{M} = \text{Zn}, \text{Mn}, \text{Al}, \text{Fe}$; $\text{M}' = \text{Mg}, \text{Mn}, \text{Fe}$ [64G1, 67S1, 72P1]; $\text{K}_2\text{Mn}_5\text{Si}_{12}\text{O}_{30} \cdot \text{H}_2\text{O}$ [77S1], $\text{A}_x\text{M}_3\text{M}'_2\text{Si}_{12}\text{O}_{30}$ with $\text{A} = \text{Na}, \text{K}, \text{Rb}$; $\text{M} = \text{Mg}, \text{Zn}, \text{Fe}^{2+}, \text{Cu}^{2+}, \text{Li}$ and $\text{M}' = \text{Mg}, \text{Cu}^{2+}, \text{Fe}^{2+}$ [80N1] etc. In the last series of compounds, $\text{A}_x\text{M}_3\text{M}'_2\text{Si}_{12}\text{O}_{30}$, M sites show tetrahedral coordination and M' sites an octahedral coordination. The A elements, with larger sizes ($\text{Na}, \text{K}, \text{Rb}$) occupy two types of sites formed by the host lattice: 12 coordinated sites in the tunnels bounded by the $\text{Si}_{12}\text{O}_{30}$ rings and 9 coordinated

sites between these rings. The latter type of site is half occupied for $x = 2$ and fully occupied for $x = 3$. The Cu^{2+} ions exhibit a site preference for a flattened tetrahedral coordination [80N1].

The **brannockite** [73W1, 88A3], **chayesite** [89V1], **darapiosite** [75S1], **eifelite** [83A1], **merrihueite** [65D1, 72K1], **osumilite** [56M1, 62S1, 69B1, 73C1, 95W1], **poudretteite** [87G1], **sogdianite** [68D1, 75B1, 95F1, 99C1], **sugilite** [76K1, 88A3, 91H1] and **yagiite** [69B2] crystallize in a hexagonal structure having space group P6/mcc. In **brannockite**, Li occupies strongly angularly distorted tetrahedra, sharing two edges with Sn octahedra [73W1, 88A3]. The **chayesite** composition, $\text{K}(\text{Mg}^{2+}, \text{Fe}^{2+})_4\text{Fe}^{3+}\text{Si}_{12}\text{O}_{30}$, is related to roedderite, $(\text{Na}, \text{K})_2(\text{Mg}, \text{Fe})_5\text{Si}_{12}\text{O}_{30}$, by the substitution $\text{Fe}^{3+} + \square = \text{Fe}^{2+} + (\text{Na}, \text{K})$ [89V1]. The **merrihueite** is the name for natural silicates from the milarite group having $\text{K} > (\text{Na} + \text{Ca})$, $(\text{Fe} + \text{Mn}) > \text{Mg}$, $\text{Al}/(\text{Al} + \text{Si}) < 0.2$ [65D1]. As mentioned already there are synthetic milarites [51R1, 67O1, 69S1, 72F2, 72K1]. For example, the $^{61}\text{Mg}_2^{91}\text{K}^{112}\text{K}^{44}\text{Mg}_3\text{Si}_{12}\text{O}_{30}$ merrihueite was synthesized hydrothermally at 790°C at 2 kbar $p_{\text{H}_2\text{O}}$ [72F2, 72K1].

Only half of the B-sites are occupied by K. However, probably, due to the larger size of K relative to Na, K does not lead to an ordered distribution with symmetry reduction. In addition, K is not displaced along the c -axis [72F2, 72K1]. The crystal structure of **osumilite** was determined by [56M1] and refined by [69B1]. According to [73C1] the osumilite composition is characterized by $\text{K} > \text{Na}$, $\text{Fe} > \text{Mg}$, $\text{Si}/\text{Al} < 7$ and of osumilite – Mg by $(\text{K}, \text{Mg}) > \text{Na}$, $\text{Mg} > \text{Fe}$, $\text{Si}/\text{Al} < 7$. In case of sample²²⁾ (for footnote composition see Table 4), 10.22 Si + 1.78 Al were restricted to the 12 T1 tetrahedra in the double hexagonal rings and 2.63 Al + 0.37 Fe^{3+} occupy the three T2 tetrahedra outside the rings. K, Ca, Na atoms are coordinated between the double six-membered rings in a hexagonal antiprism which shares an edge with the T1 tetrahedron [69B1]. The crystal structure of **poudretteite**, $\text{KNa}_2\text{B}_3\text{Si}_{12}\text{O}_{30}$, is isotypic with that of osumilite and is ordered with K in 12-coordinated C site, Na in octahedrally coordinated A-site, boron in tetrahedrally coordinated T2 site, Si in tetrahedrally coordinated T1 site and the B site is vacant [87G1]. The **sogdianite** was first described by [68D1] and its structure was reported by [75B1]. The general structural arrangement has the space group P6/mcc and the non-silicate T2 tetrahedra link the 12-membered double rings of silicate tetrahedra into $[\text{T}\Phi_2]$ 4-connected three-dimensional framework [86H1]. The general formula of sogdianite may be written as $(\text{Zr}, \text{Ti}^{4+}, \text{Fe}^{3+}\text{Al})_2(\square, \text{Na})_2\text{K}[\text{Li}_3\text{Si}_{12}\text{O}_{30}]$. According to [99C1] the ideal end-member formula has Zr dominant at the A site and \square dominant at the B site. These Li-bearing silicates were divided in two subgroups: (1) those with vacancy \square , at the B site and (2) those with (Na, K) at the B site. In sogdianite, the T1 site is completely occupied by Si. In [75B1] (Li+Al) was assigned to the T2 site. In [99C1] a complete occupancy of T2 site by Li was suggested. It was shown [91H1] that Al can occur at the A, T1 and T2 sites in the milarite-type structure. For sogdianite³³⁾ the minor Al content (0.13 apfu) occurs at the A site, as the T1 site is completely occupied by Si and the T2 site is completely occupied by Li. The A site is occupied by Zr, Fe^{3+} , Ti and Al [99C1]. In sogdianite the B site is occupied by $(\square + \text{Na})$ and there is no positional disorder at the A site. The C site is completely occupied by K. The crystal structure studies on **sugilite** [76K1, 88A3] and **brannockite** [73W1, 88A3] showed that both silicates crystallize in space group P6/mcc. The T2 sites are occupied by Li. The fairly large T2 tetrahedron is extremely distorted in its angles, whereas the A site – which is occupied by $(\text{Fe}^{3+}, \text{Mn}^{2+}$ and Al) in sugilite and by Sn in brannockite – reveals a rather regular octahedral environment. In both silicates, K resides in a large cavity (C site) situated between two double rings. In [88A3] it was suggested for sugilite³⁴⁾ that Na is disordered on a position of the type $(1/2, 2/3, 0.0134)$ which is up to 49(1) % occupied and that Na possesses distorted ninefold coordination. A similar coordination of Na has been found in the double-ring silicate eifelite (see below) [83A1]. The corresponding position in brannockite is vacant. We note that in [76K1] was suggested that in sugilite, Na shares the B site with H_2O , in [88A3] was indicated that the B site is predominantly occupied by Na and slightly displaced along c (site B'). In addition, in [80D1] the presence of volatiles was not indicated in sugilite.

The name of **yagiite** was proposed for minerals having $\text{Na} > \text{K}$, $\text{Mg} > \text{Fe}$ and $\text{Si}/\text{Al} < 7$ [69B2]. In the above paper it was shown that at least two substitutional pairs were possible ($\text{K} \leftrightarrow \text{Na}$; $\text{Fe} \leftrightarrow \text{Mg}$). As reported for eifelite [83A1], milarite [89A2] and sugilite [88A3] (see above), Na is not centered on the B site but is slightly displaced along c . In P6/mcc type structure, the displaced site was called B' – Table 2b. The lattice parameters are listed in Table 4 and the end member compositions for Li-bearing milarites are given in Table 5.

The dependence of structural parameters on the chemistry of milarites, crystallizing in space group P6/mcc, was analysed [88A3]. In the double ring silicates, the a cell edge is dependent on the length of the shared edge between the T2 tetrahedron and the A octahedron and thus related to the lengths of the A–O3 and T2–O3 distances, a (in Å) = $5.610 + 1.59d_{\text{A-O3}} + 0.63d_{\text{T2-O3}}$. In case of the c lattice parameter, there is a dominant influence of the C–O distance c (in Å) = $-1.600 + 1.126d_{\text{T2-O}} + 4.48d_{\text{C-O}}$. According to [88A3] large T2

tetrahedra show a strong angular distortion in sugilite and brannockite but are connected to fairly undistorted A octahedra. Small T2 tetrahedra in milarite have minor distortions in their angles. However, the edge sharing A octahedra are strongly compressed along the *c*-axes. Thus, Li, which accepts highly distorted coordination tetrahedra, is almost ideal in combination with cations favouring a regular octahedral environment within the double-ring silicate structure. The large cations, as Ca, that allow fairly distorted octahedral coordination on A may be associated with cations that need rather regular tetrahedral coordination on T2.

The crystal structures of **armenite** and **roedderite** have lower symmetry than the hexagonal one, reported for the above described milarites. Initially, [60T1, 75B1] reported and refined an average structure of a pseudohexagonal twin of armenite in space group P6/mcc, but this assignment has been shown to be erroneous. In a study of milarites, having a closely related double ring silicate with $\text{Ca}_2\text{KNa}_{1-x}(\text{Be}_{3-x}\text{Al}_x)\text{Si}_{12}\text{O}_{30}\cdot n\text{H}_2\text{O}$ [89A2], it was suggested that optical sectors resembling a trilling pattern in (001) sections were caused by variable ordering of H_2O . Nonstoichiometric H_2O increases, as above mentioned, the oxygen coordination of Ca from six to seven. In [88A1] the optical sectors in armenite were related to (Si,Al) ordering. Heat treatments of armenite for four days at 950°C [84P1] or 1000°C [89B1] cause expulsion of the H_2O and lead to uniaxial optical properties with decreased refractive indices. These data raised problems concerning the armenite P6/mcc crystal structure. Space group Pnna [92A1] and Pnc2 [99A1] were later reported.

In analysing the structure of armenite in space group Pnc2, a parallel comparison with structures of cordierite and beryl was made [99A1]. For a direct comparison between structures with single- and double-six-membered rings, a labeling was introduced where T_c designates tetrahedra connecting ring units (single or double) to a tetrahedral framework, T_s denoted tetrahedra in single six-membered rings (beryl and cordierite) and T_d denoted the tetrahedra assembled to six-membered double rings (e.g. armenite and milarite). With respect to Si, Al ordering, cordierite seems to be an analogue of armenite [99A1]. In both silicates, $T_{s,d}$ and T_c tetrahedra may be occupied by Si and Al in a way that Al tetrahedra are always adjacent to Si tetrahedra, in agreement with Loewenstein's rule [54L1]. The Al concentration in both silicates corresponds to the maximum value allowed by this Al-avoidance rule. The structure analyses on two optically untwinned armenites [91F1, 92A1], in orthorhombic space group Pnna, lead to different Si, Al distributions. The orthorhombic symmetry was considered to be caused by displacements of CaO_6 octahedra and neighboring water molecules [91F1]. In the Pnna refined model of armenite²⁾ [92A1], it was reported that well-ordered Si,Al clusters alternate with Si, Al disordered T_c and T_d tetrahedra. But the presence of both (Si,Al) ordered and disordered clusters within the same structure were considered as unusual [92A1]. A later refinement of armenite²⁾ was made in space group Pnc2 [99A1]. In Pnc2 type structure there are 12 symmetry independent T_d (all on general positions) and 5 T_c sites (only one on a general position). There are four T_d and three T_c sites filled with Al; thus Si and Al are completely ordered. A partially occupied (11%) position, labeled CC, occurred at the cage center of the six-membered double-rings that was assigned to H_2O – Table 2. It locally increases the Ba coordination from 12 to 14. This H_2O site is 3.28(6) Å away from two neighbouring Ba positions [99A1]. In armenite [92A1] and milarite [89A2], H_2O occupies structural interstices (B sites). Completely occupied H_2O sites (W1, W2) increase the Ca coordination from sixfold to sevenfold. The distribution of W1 and W2 associated with the related structural distortions were considered to be responsible for the primitive lattice [99A1]. The completely ordered Si,Al arrangement in tetrahedral framework fulfills requirements of a C-centered lattice – Fig. 2 and Table 2e. Both Si,Al ordering and H_2O distribution were considered as responsible for the deviation from hexagonal symmetry. Armenite is completely hydrated and has 2 H_2O pfu. Milarite has non-stoichiometric H_2O ($\ll 2$ pfu) and additional Na, K and Ca may enter the ninefold-coordinated B site which is $\cong 0.7$ Å apart from B'. Upon heating at $\sim 1000^\circ\text{C}$ [41N1, 84P1, 89B1, 92A1], H_2O is expelled from armenite. The superstructure reflections, after heating 24 h at 1000°C, become unobservable and the crystal becomes pseudohexagonal and possesses the same Si,Al arrangement as natural armenite. The corresponding group symmetry is Amma (in a setting corresponding to Pnna; standard setting is Cccm) [92A1]. Fig. 2b shows the local environment of W1 in a completely Si,Al ordered armenite (space group Pnc2) [99A1]. There are three O3-type O atoms (O37, O312 and O310) close to W1 ($\cong 2.9$ Å) and participating in Ca–O bonds. These O3-type O atoms connect an Si tetrahedron and an Al tetrahedron with Ca and are slightly overbonded. W1 is additionally coordinated by three O1-type O atoms (O14, O11, O12) with O14 and O11 connecting Si and Al tetrahedra whereas O12 links two Si tetrahedra. Thus, the slight underbonding of O14 and O11 makes those O atoms preferred acceptors of weak hydrogen bonds. The IR spectra (subsection 8.1.3.7.5) support a H_2O model where one is hydrogen bonded to the closest O14 with the second proton rotationally disordered. A similar situation was found around W2 [99A1].

In [72K1] the crystal structure of **roedderite** end member, $\text{K}_2\text{Mg}_5\text{Si}_{12}\text{O}_{30}$, was refined. They showed that the D site is vacant, the A- and T2-sites are occupied by Mg, while Si resides exclusively in the T1 site, leading to the hexagonal double-ring of silicate tetrahedra. The C site is occupied by K, as is one of the two B sites (with six long and three short K–O bonds), the other B site being vacant. Thus, its structural formula is $^{[12]}\text{K}^{[6+3]}\text{K}\square^{[6]}\text{Mg}_2^{[4]}\text{Mg}_3\text{Si}_{12}\text{O}_{30}$, \square indicating the vacancy in the B site. The $\text{Na}_2\text{Mg}_5\text{Si}_{12}\text{O}_{30}$ and $\text{K}_2\text{Mg}_5\text{Si}_{12}\text{O}_{30}$ form solid solutions. Crystal structure refinements of roedderite solid solutions with $\text{Na}/(\text{Na} + \text{K}) \cong 0.54$ [83A1, 89A1] indicated that K is completely fractionated into the $^{[12]}\text{C}$ site and Na into $^{[6+3]}\text{B}$ sites. While [83A1] observed the P6/mcc symmetry with a statistical distribution of Na between the two B sites, the data obtained at 100 and 300 K on roedderite³⁰⁾ [89A1] suggested that Na preferentially occupies one of the two B sites leading to $\text{P}\bar{6}2\text{c}$ symmetry. In spite of the reduced symmetry, roedderites show the same main structural units as other double ring silicates. As mentioned above, the B site in the space group P6/mcc splits into two different types of B positions within the space group $\text{P}\bar{6}2\text{c}$ – Fig. 3. One is at 1/3, 2/3, 0.25 (called B1') and the other at 1/3, 2/3, 0.75 (called B2') – Table 2d. Site occupancy refinements indicated that the B1' site is preferentially occupied by Na, while B2' shows only very low Na content. All other structural positions maintain a P6/mcc pseudo-symmetry. Thus, the preferred Na occupation is responsible for the lower symmetry.

Roedderite and **eifelite** form a solid solution series which is characterized by the substitution $^{[9]}\text{Na} + ^{[6]}\text{Na} \rightarrow ^{[9]}\square + ^{[6]}\text{Mg}$. Members with $(\text{Na} + \text{K}) > 3$, $\text{Na} > \text{K}$, $\text{Mg} > \text{Fe}$ and $\text{Si}/\text{Al} > 7$ should be named eifelite [83A1]. As mentioned above, an ordered arrangement of the two Na atoms per unit cell over four available B-cages leads to space group $\text{P}\bar{6}2\text{c}$. In the end member eifelite all B sites are occupied by Na and thus the assignment of space group P6/mcc [83A1] is probably correct. In [91W1, 93B1] roedderites were synthesized along $(\text{K}_{1-x}\text{Na}_x)_2\text{Mg}_5\text{Si}_{12}\text{O}_{30}$ compositions. Both a and c parameters were observed to vary in a non-linear manner with composition, c passing through a broad maximum around $x = 0.5$ [91W1] or $x = 0.6$ [93B1] as seen in Fig. 4 [93B1]. In [91W1], considering the contrasting effect of $\text{K} \leftrightarrow \text{Na}$ substitution on the B- and C-sites, it was argued that $\text{KNaMg}_5\text{Si}_{12}\text{O}_{30}$ is in fact an intermediate compound, splitting the binary solid solutions into two subsystems. We note that although the space group $\text{P}\bar{6}2\text{c}$ was proposed [89A1, 92T1], in [93B1] indexed the X-ray data in P6/mcc type structure. Starting from the lattice parameters – Fig. 4 – an equation of state was developed assuming the simplest possible model of a two-site K–Na mixing [93B1].

In synthetic **merrihueite**, $^{[6]}\text{Mg}_2^{[9]}\text{K}^{[12]}\text{K}^{[4]}\text{Mg}_3\text{Si}_{12}\text{O}_{30}$ [72K1] only half of the B sites are occupied by K. Probably, due to the larger size of K relative to Na, K does not lead to an ordered distribution with symmetry reduction. In addition, K is not displaced along the c -axis of merrihueite [89A1].

The $\text{MMg}_2\text{Al}_6\text{Si}_9\text{O}_{30}$ ($\text{M} = \text{Sr}, \text{Ba}$) and $\text{Mg}_2\text{Al}_4\text{Si}_{11}\text{O}_{30}$ osumilites crystallize in a P6/mcc type structure [95W1]. The C site between consecutive double-ring units is occupied by Ba^{2+} and Sr^{2+} in $\text{BaMg}_2\text{Al}_6\text{Si}_9\text{O}_{30}$ and $\text{SrMg}_2\text{Al}_6\text{Si}_9\text{O}_{30}$, respectively – Table 2c – while it is empty in $\text{Mg}_2\text{Al}_4\text{Si}_{11}\text{O}_{30}$ osumilite. This leads to increased C–O2 distances in $\text{Mg}_2\text{Al}_4\text{Si}_{11}\text{O}_{30}$ compared to the Ba- and Sr-bearing silicates. The larger C–O2 distances are compensated by a stronger distortion of the neighbouring T1 double-rings at T2 tetrahedra. In $\text{BaMg}_2\text{Al}_6\text{Si}_9\text{O}_{30}$ and $\text{SrMg}_2\text{Al}_6\text{Si}_9\text{O}_{30}$, Mg is constrained to the octahedral A site whereas in $\text{Mg}_2\text{Al}_4\text{Si}_{11}\text{O}_{30}$ the A octahedron and the T2 tetrahedron have a mixed Mg,Al occupancy. Osumilite-type compounds with partial Al in six-membered double-rings show a different T1–O–T1 angular distortion compared to double-ring silicates with pure $\text{Si}_{12}\text{O}_{30}$ units. The reason for this difference is not primarily the Al concentration on T1, but the higher ionic valences on A and T2 which become necessary for charge balance [95W1].

8.1.3.7.2 Nuclear gamma resonance (NGR) data

The osumilites having various compositions were studied by the ^{57}Fe NGR method [78G1]. In all the spectra the presence of Fe^{2+} was evidenced – Table 6. We note that the Fe^{3+} content in osumilite³⁷⁾ is very low. A comparative analysis of two- and three-doublet fits suggest that a three-doublet fit of the spectrum provides a better overall agreement with experimental data than the two-doublets one. The electronic absorption spectra of osumilite suggest that Fe^{2+} resides in only two types of sites, the octahedral and in channel sites [78G1]. Starting from the above data it was suggested that the outer doublet arises mostly from Fe^{2+} in the octahedral site and the inner two doublets were mostly due to Fe^{2+} in the channels. The broad linewidths of the doublets were attributed to local environment effects. The two- and three-doublet fits indicate that about 68 % and 53 %, respectively, of the total iron is octahedral Fe^{2+} . The physical interpretation for a third doublet was not clear [78G1]. Local

environment effects can probably be considered. No major changes in the hyperfine parameters were shown after heating the sample, as shown in Table 6 for sample³⁸⁾. The RT spectrum of osumilite³⁹⁾ was fitted considering five doublets. The three Fe²⁺ doublets have hyperfine parameters moderately similar to those evidenced in sample³⁷⁾. In addition, the spectrum shows the presence of Fe³⁺ in two type of sites [78G1]. One of the doublet ($\delta = 0.25$ mm/s, $\Delta Q = 1.71$ mm/s) was attributed to Fe³⁺ in tetrahedral coordination. The peak with $\delta = 0.40$ mm/s, attributed to an “octahedral” Fe³⁺ improve the fit, but their physical significance is also not certain [78G1].

8.1.3.7.3 Nuclear magnetic resonance (NMR) data

The ²⁹Si MAS NMR spectra of **milarites**^{40, 41)} show only one strongly broadened line of Lorentzian peak shape, assigned to T_d tetrahedra – Fig. 5 and Table 7 [99A1]. For sample⁴⁰⁾ the line is positioned at –104.5 ppm and for sample⁴¹⁾ at –104.3 ppm. After heat treatment, at 800°C, the lines remains broad and centered at –104.5 ppm. There is no indication of Si on T_c tetrahedron. In the crystal structure of milarite [89A2, 91H1, 99A1], each Si tetrahedron is connected to three additional ring SiO₄ tetrahedra (T_d) and, in addition, to one Be or Al tetrahedron (T_c) interconnecting the Si₁₂O₃₀ double-rings. Si with neighbouring Be amounts to 73...79 %, the remaining Si being linked to Al. Thus, in the ²⁹Si MAS NMR spectra one should expect one weak peak for T_d(3Si,1Al) and one strong peak for T_d(3Si,1Be). The spectra, however, indicate only one broad band. The broadening of the milarite ²⁹Si NMR line was attributed to: 1) a mixture between Si (3Si,1Be) and Si (3Si,1Al) contributions or (2) the fact that milarite possesses a disordered and distorted structure because B-type interstices are either vacant or occupied by Na, K, Ca or H₂O and Al, Be are disordered on T_d, (3) the possible presence of paramagnetic elements (Fe, Mn), in low concentrations.

The fully ordered structure model of armenite [99A1] leads to 44.44 % T_d(Si,3Al), 44.44 % T_d(2Si,2Al) and 11.11 % T_c(4Al). The three MAS NMR lines observed in armenite⁴²⁾ agree in intensity and chemical shifts with a fully ordered Si, Al distribution in agreement with Loewenstein rule [54L1]. The line at –82.3 ppm was assigned to T_c(4Al) and the lines at –95.0 and –101.6 to T_d(Si,3Al) and T_d(2Si,2Al), respectively. Armenite⁴³⁾ has ²⁹Si MAS NMR bands that agree in their positions with those of an ordered structure, but the intensity ratios are significantly different. Either a more complicated Si, Al distribution pattern or a mixture between various Si,Al distribution was suggested. No convincing structural model was possible to be elaborated for this armenite [99A1].

Solid state ²³Na and ²⁹Si MAS NMR spectroscopy on Na₂Mg₅Si₁₂O₃₀ end member **roedderite**, suggests two symmetrically distinct ⁴¹Si sites within the hexagonal double ring of silicate tetrahedra, an observation compatible with the space group P6₂c [92T1]. According to [90H1] only one peak was shown in roedderite sample.

8.1.3.7.4 Heat capacity

The heat capacity of natural **osumilite**⁴⁵⁾ was measured from 298 K to 1000 K by differential scanning calorimetry – Fig. 6 [84H1]. The data can be described by the relation C_p [J/g K] = $0.58332 + 1.2742 \cdot 10^{-3} T - 6.4871 \cdot 10^{-7} T^2 - 1.554 T^{-0.5} - 3.961 \cdot 10^3 T^{-2}$.

8.1.3.7.5 Optical properties

Electronic absorption spectra of three osumilite samples are plotted in Fig. 7 [78G1]. In case of osumilite^{46),39)} – Fig. 7a,b – the spectra consist of absorption features at 10280, 15480, 22220 and 24150 cm^{–1} in ω polarization and 4650, 7020 and 10280 cm^{–1} in ϵ polarization. The asymmetry and breadth of the band at 15480 cm^{–1} in the ω spectrum of osumilite³⁹⁾ was attributed to a superposition of a dominant lower-energy band assigned to intervalence charge transfer between tetrahedral Fe³⁺ and octahedral Fe²⁺ and a subordinate higher-energy band assigned to tetrahedral Fe³⁺ [72F1]. The weak band near 22220 cm^{–1} was assigned to tetrahedral Fe³⁺ and the band near 10280 cm^{–1} to octahedral Fe²⁺ [72I1]. The electronic absorption spectrum of osumilite³⁷⁾ ($2V \cong 40^\circ$) indicates three distinct optical directions – Fig.7c [78G1]. The γ spectrum (which has the same crystallographic orientation as ϵ in Fig. 7a,b) consists of bands at 4686, 7020 and 10280 cm^{–1}. Peak maxima differ slightly for the main band in α and β polarizations and occur at 10360 and 10400 cm^{–1}, respectively. The band in the visible region, in α and β , has a broad maximum between 18000 and 21000 cm^{–1} and a weak shoulder at 22220 cm^{–1}.

corresponding to the position of the band observed in ω in the other samples. Some of the intensity of the 4686 cm^{-1} band occurs in α , but is only observed in mm-thick section. The bands at 10280 and 7020 cm^{-1} in γ (or ϵ) were assigned to Fe^{2+} in the octahedral site. Bands in the 10200...10400 cm^{-1} region in α and β (or ω) and the 4650...4700 cm^{-1} region in γ (or ϵ) were assigned to Fe^{2+} in the channels. The two absorption bands arising from each type of Fe^{2+} were considered to represent electronic transitions to the components of the split ${}^5\text{E}_g$ state. The barycenter (median) energies of the two transitions for octahedral and channel Fe^{2+} are 8650 and 7590 cm^{-1} , respectively. The bands assigned to octahedral Fe^{2+} retained the same intensity after heat treatment in air at 700°C for 13.5 h, whereas both bands assigned to channel Fe^{2+} were reduced to $\approx 85\%$ of their intensity prior to heating. From the spectra (namely the 10280 cm^{-1} band), it was concluded that in case of osumilite³⁷⁾ about 60 % of iron ions are in the octahedral site and 40 % in the channels [78G1], in agreement with ${}^{57}\text{Fe}$ NGR data.

Polarized infrared (IR) spectra in the region of OH absorptions were recorded both in **milarites**^{40,47)} [91H1, 99A1] and **armenite**⁴²⁾ [99A1]. Typical spectra are shown in Fig. 8. The spectra are similar for all milarites but with different absolute intensities of absorption bands and with minor shifts in band positions – Table 8. The data were used to analyse the H_2O orientation in milarite and armenite [91H1, 99A1]. In milarite, cations on the nine-fold coordinated cavities (B site) prefer the center of cavity, whereas non-stoichiometric H_2O (Ow) is displaced parallel to c and has 3 O1 and 3 O3 nearest neighbours. Calcium octahedra in such idealized milarite are edge-linked with three T_c tetrahedra (two occupied by Be and one for Al). This local arrangement reduced the observed 3 average symmetry of Ca. In addition, O3 coordinating Ca is corner linked with a $\text{T}_d(\text{Si})$ tetrahedron. Depending on whether O3 links a Be or an Al tetrahedron, the Pauling bond strength of O3 is either underbonded (5/6) or overbonded (13/12). From the view of bond strength O3 is the favorable to accept a hydrogen bond from Ow [99H1]. Steric constraints, however, exclude a H_2O proton oriented towards O3 because of short H–Ca distances. The most favorable H_2O proton arrangement in **milarite** is obtained by bifurcated hydrogen bonds to O1 and O3 with H1 and H2. This proton arrangement is either statically or dynamically disordered, governed by the threefold axis passing through Ow – Fig. 2b. The model has the H–H vector in (001) and is suggested by the polarization of the $\nu_2\nu_3$ combination and the ν_3 asymmetric stretch mode [91H1, 99A1]. In the above model the diad of the H_2O molecule is inclined by about 66° to the c -axis of milarite. A stronger hydrogen bond to O1 decreases the inclination of the H_2O diad. The IR spectra [91H1, 99A1] show no polarization for the ν_1 mode in milarite and incomplete polarization for the ν_2 mode. The polarization of the modes ν_1 and ν_2 determines the orientation of the diad of the H_2O molecule. However, the ν_1 , ν_2 , ν_3 band assignment of H_2O vibrations suggested by [91H1] and adopted in the above model are problematic because ν_1 and ν_2 should show the same polarization (not observed) [99A1]. According to [99A1] the assumption of a “symmetric” H_2O molecule is questionable. More probable is a H_2O molecule with one “free” OH vector leading to the $\approx 3600\text{ cm}^{-1}$ absorption and another with a medium strong hydrogen bond causing the $\approx 3500\text{ cm}^{-1}$ absorption.

The local environment of W1 in the Pnc2 type structure of armenite was discussed in subsection 8.1.3.7.1 – Fig. 2b. The slight underbonding of O14 and O11 makes those O atoms preferred acceptors of weak hydrogen bonds [99A1]. This would cause the H–H vector to be almost parallel to pseudohexagonal (001), a model which is not supported by IR data because the single crystal spectra show no significant polarization for $\nu_2\nu_3$ and ν_3 modes. The IR spectra support a H_2O model where one proton is hydrogen bonded to the closest O14 with the second proton rotationally disordered. A similar situation was found around W2, where O16 and O13 have distances of 2.793 Å and 2.821 Å to W2 [99A1].

For IR spectra of some synthetic $\text{A}_x\text{M}_3\text{M}'_2\text{Si}_{12}\text{O}_{30}$ with $\text{M} = \text{Mg}, \text{Zn}, \text{Fe}^{2+}, \text{Cu}^{2+}, \text{Li}$ and $\text{M}' = \text{Mg}^{2+}, \text{Cu}^{2+}, \text{Fe}^{2+}$ milarites see [80N1].

Some refractive indices for silicates from the milarite group are listed in Table 9. In [89A2] was suggested, that in **armenite**, optical sectors resembling a trilling pattern in (001) section were caused by variable ordering of H_2O . In [84P1, 89Z1] biaxial and uniaxial armenite domains with one-crystal aggregate were described. Heat treatment of armenite for 4 days at 950°C [84P1] or 1000°C [89B1] causes expulsion of the H_2O and leads to uniaxial optical properties with decreased refractive indices. The structurally related milarite $\text{KNa}_{1-x}\text{Ca}_2(\text{Be}_{3-x}\text{Al}_x)\text{Si}_{12}\text{O}_{30}\cdot n\text{H}_2\text{O}$, which contains nonstoichiometric H_2O , described in space group P6/mcc, exhibits also unusual biaxial sectors in (001) sections [86J1, 89A2]. These sections were explained, as for armenite, by symmetry reduction owing to the ordering of the H_2O molecule that may occupy a position above and below a CaO_6 octahedron [89A2].