

## 8 Magnetic and related properties of silicates and phosphates

### 8.1 Silicates

#### 8.1.1 Orthosilicates

(See subvolume III/27I1)

#### 8.1.2 Sorosilicates

(See subvolume III/27I2)

#### 8.1.3 Cyclosilicates

##### 8.1.3.1 Wadeite, walstromite, eudialyte and related silicates

The cyclosilicates from groups VIIC01-VIIC03 are listed in Table 1 [91N1]. The atomic coordinates of representative silicates are given in Table 2, while in Table 3 the lattice parameters are listed.

##### 8.1.3.1.1 Crystal structures. Lattice parameters

##### Wadeite, benitoite, bazirite, pabsite

The mineral **wadeite**, discovered in 1939 [39P1], is a rare natural zirconosilicate, but its structural motif was shown in a number of synthetic  $A_2MSi_3O_9$  compounds characterized by extensive isomorphic substitutions in the group of cations: K–Rb–Cs, Zr–Ti–Hf–Sn [55H1, 71A1, 71C1, 73C1]. Later on, by synthesis, of alkali and alkaline earth silicates at high pressure, was evidenced a class of framework structures with corner-linked 4- and 6-coordinated silicon. These compounds possess the structural formula  $(A^{+}_{4-2x}B^{2+}_x)^{[6]}Si_m([^{4}]Si_nO_{2(m+n)+2})$ . Appropriate values of  $m$  and  $n$  yield a wide range of high-pressure structures from fully 4-coordinated to fully 6-coordinated silicate frameworks [96H1, 99H1]. For  $m = 2$ ,  $n = 6$  wadeite,  $K_4^{[6]}Si_2^{[4]}Si_6O_{18}$  [75K1, 83S1], benitoite,  $Ba_2^{[6]}Si_2^{[4]}Si_6O_{18}$  [95F1], barium germanate-type structure of  $Ba_2^{[6]}Si_2^{[4]}Si_6O_{18}$  [94H1] or  $Na_4^{[6]}Si_2^{[4]}Si_6O_{18}$  [95F2, 96F1] type structure were obtained.

The first refinement was performed on the synthetic analog of the Ti wadeite structure [73S1]. This analysis revealed the inaccuracies in the original model [55H1] and stimulated the analysis of the structure of  $A_2MT_3O_9$  family, particularly of  $K_2ZrSi_3O_9$  wadeite [77B1]. In [77B1] the wadeite structure was refined initially in space groups  $P6_3/m$  and  $P3$ . The atomic positions for the latter space group are given in Table 2a. Analyzing the differences between the refined coordinates of the independent atoms within the space group  $P3$  and the coordinates of the same atoms multiplied by symmetry elements of  $P6_3/m$  with the corresponding standard deviations, it was shown that the symmetry of wadeite should be reduced. In this study was found that the crystal structure of  $K_2ZrSi_3O_9$  has an acentric  $P\bar{6}(C_{3h}^1)$  space group symmetry. The centrosymmetry of the structure is broken by the deviation of the O atoms from their ideal positions in the space group  $P6_3/m$ . The cation

distribution almost exactly obeys  $P6_3/m$  pseudosymmetry [77B1]. The basis of the wadeite structure is an infinite anion radical, a mixed framework  $\{Zr[Si_3O_6]\}^{2-\infty\infty}$  composed of discrete Zr octahedra and  $[Si_3O_9]$  triple rings threaded onto different  $\bar{6}$  axes and arranged in layers with an interval of four  $c$  translations. The triple rings on the  $\bar{6}$  axes in successive tetrahedral stages (coinciding with the  $m$  planes in the space group  $P6_3/m$ ) are mutually displaced by one third of the long diagonal of the hexagonal base. Ultimately, wide empty spaces develop along these  $\bar{6}$  axes, extending over the whole height of the cell between the three  $[Si_3O_9]$  rings along the equator and the two at the poles. Six Zr octahedra (connected in pairs by an  $m$  plane) take part in forming the elongated space – Fig. 1a [77B1]. Lying in the spaces on their axial lines are pairs of alkali cations  $K^+$ . As in the other mixed frameworks, there is no oxygen between them. For the highest possible symmetry of the wadeite framework ( $P6_3/mmc$ ), the spaces are too large even for potassium and the framework is distorted by twisting of the Si rings in one direction around the binding octahedra – Fig. 1a. The unperturbed framework exists in the Na analog of wadeite, **catapleiite**,  $Na_2ZrSi_3O_9 \cdot 2H_2O$ . Since Na has a smaller radius than K this paradox is resolved by introduction of  $H_2O$  molecules in catapleiite. These stabilize the framework, being built into the sixfold windows of the wadeite lanterns – Fig. 1a – and creating a more uniform environment for the  $Na^+$  ions [77B1]. Otherwise, the structure of catapleiite reproduces the motif on wadeite, a characteristic feature of which comprises infinite columns of Zr octahedra along the  $c$ -direction, linked by triads of Si tetrahedra and separated by a small cavity in the form of a trigonal prism – Fig. 2a [77B1]. The wadeite framework may be obtained from these fragments by parallel attachment one to another – Fig. 1c [77B1]. Island-like silicon-oxygen groups,  $Si_3O_9$ , furthermore, arise at the meeting place of three columns. In the other type of framework made up of the same parts of tetrahedra of neighbouring stories, while keeping one vertical edge intact, they are twisted in opposite directions – Fig. 1d. On the condensation of such columns – Fig. 1b – all the triple rings in the hexagonal cell occur on a single vertical at a distance of  $c/2$  [77B1]. The closed spaces of the wadeite type are disrupted, and it the structure of **benitoite**  $BaTiSi_3O_9$  can be obtained, or **bazirite**  $BaZrSi_3O_9$ , with broad channels along the  $z$ -direction [69F1]. In these channels  $Ba^{2+}$  ions, in compressed octahedra, are arranged as an infinite chain; these may supplement the O with second-coordination-sphere neighbours to form twelve-pointed polyhedra. This rearrangement of the framework is a consequence of the replacement of the monovalent fillers  $K^+$  of wadeite by half the number of divalent  $Ba^{2+}$  in benitoite. Thus, by virtue of different rotations of the Si tetrahedra there may be different numbers of settling places for the large cations in the same volume. The structure of wadeite is more compact, since it contains twice the number of filler ions. A fundamental characteristic of the wadeite and benitoite-type columns is the existence of mirror planes between neighbouring octahedra. This results in their alternation with empty trigonal prisms – Fig. 2a. There are also fragments in which the empty and occupied polyhedra are solely represented by octahedra – Fig. 2b – owing to the twisting of the columns into a corkscrew with the rotation of neighbouring M octahedra by  $60^\circ$ , the binding tetrahedra being sharply inclined [77B1].

As above mentioned, benitoite,  $BaTiSi_3O_9$ , like wadeite, contains rings of three linked tetrahedra,  $Si_3O_9$ . It belongs to space group  $P\bar{6}c2$  and has two formula units per unit cell [69F1]. In Fig. 3 is plotted the crystal structure, where each ring is shown as composed of tetrahedral units. The rings are located one above the other along the  $c$ -axis. The  $c$ -axis, passing through the origin, is the axis of threefold symmetry. Twofold symmetry axes are perpendicular to the  $c$ -axis, pass through the origin and through the Ba and Ti ions. The two rings are symmetrical with respect to rotation about the twofold axis. The  $c$ -axis and one of twofold symmetry axes were designated as the  $z$  and  $x$ -axes, respectively, in analyzing the normal modes of vibration – see section 8.1.3.1.4.

**Pabsite** is obtained from benitoite by partial replacing of Ti by Sn [65G1]. The silicate crystallizes in space group  $P\bar{6}c2$ .

### **$K_2Si_4O_9$ , $Na_2Si_4O_9$**

$K_2^{[6]}Si^{[4]}Si_3O_9$  single crystals were synthesized at high temperatures and pressures [75K1, 83S1]. The suggestion that this phase has a wadeite-type structure [74K1, 75K1], was confirmed later and the space group  $P6_3/m$  was attributed [83S1]. We note that in wadeite structure having space group  $P\bar{6}$  the centrosymmetry of the structure is broken by the deviations of the O atoms from their ideal positions in the space group  $P6_3/m$ . However, the cation distribution almost exactly obeys  $P6_3/m$  pseudo-symmetry. Thus,  $K_2^{[6]}Si^{[4]}Si_3O_9$  can be described as a framework structure containing parallel layers of  $Si_3O_9$  rings that are arranged in ABAB...stacking sequence

along [001] and linked together by octahedrally coordinated Si atoms. The  $K^+$  ions occupy the large cages that occur between the A and B layers of  $Si_3O_9$  and serve to charge balance the structure. The atomic charges (in  $e$ ) for  $^{[6]}Si$ ,  $^{[4]}Si$ , O1br and O2nbr are +3.29(15), 2.52(1), -1.43(8) and -1.43(4). These data suggest that an increase in the coordination number of a Si atom from 4 to 6 significantly increases the ionic character of that atom [83S1].

A low-pressure phase of  $K_2Si_4O_9$  was also reported [72S1, 74S1, 87G1]. The low-pressure phase with a complex sheet structure, contains solely tetrahedrally coordinated Si, having space group  $P\bar{1}$ .

The bulk modulus of  $K_2Si_4O_9$  is  $K_{0T} = 90$  GPa ( $K'_{0T} = 4$ ) for wadeite-type and  $K_{0T} = 40$  GPa ( $K'_{0T} = 4$ ) for sheet-type structure [87G1]. The thermal expansion coefficient is  $2.95 \cdot 10^{-5} K^{-1}$  [86S1].

Single crystals of sodium tetrasilicate  $Na_2Si_4O_9$  have been grown at 6 GPa and 1000°C to 9 GPa and 1500°C [96F1]. The high-pressure synthesized silicate crystallizes in a monoclinic-type structure having space group  $P2_1/n$  [96F1]. Nine-membered rings of  $SiO_4$  tetrahedra are collapsed around and interconnected by  $SiO_6$  octahedra, at shared corners, giving a framework structure that is analogous to, but distinct from those of  $K_2Si_3O_9$  (wadeite) and  $K_2Ge_3O_3$  (tetragermanate)-types. The structure accommodates Si in both tetrahedral and octahedral coordination ( $^{[6]}Si : ^{[4]}Si = 1 : 3$ ). The high-pressure phase has a large structure with three independent octahedral positions for  $^{[6]}Si$  and nine independent tetrahedral positions for  $^{[4]}Si$ , giving a formula  $Na_6Si_3[Si_9O_{27}]$  ( $z = 4$ ). The three-membered rings of  $SiO_4$  tetrahedra that characterize the wadeite and tetragermanate-type structures are not present. Instead, the  $SiO_4$  tetrahedra form a nine-membered ( $Si_9O_{27}$ ) ring in the (010) plane that is collapsed around and interconnected by isolated  $SiO_6$  octahedra at shared corners to form a framework of mixed  $SiO_4$  tetrahedra and  $SiO_6$  octahedra. In the wadeite-type structure, the three-membered  $Si_3O_9$  rings are too rigid to permit the distortion required to accommodate Na cations. The more open germanate ring apparently permits some distortions giving the twisted  $Ge_3O_9$  ring of the  $A_2Ge_4O_9$ -type structure that accommodates the smaller A cations. Hence, sodium tetrasilicate adopts a framework configuration with the pliable five-membered  $^{[4]}Si-^{[4]}Si-^{[4]}Si-^{[4]}Si-^{[6]}Si$  rings [96F1].

### BaSi<sub>4</sub>O<sub>9</sub>

The  $BaSi_4O_9$  silicate shows polymorphism. A sample synthesized at 4 GPa and 1000°C was determined to be trigonal, isostructural with barium germanate, having space group  $P3$  [99H1]. In [95F1] was described a barium tetrasilicate with hexagonal  $P\bar{6}c2$  benitoite structure.

The trigonal  $BaSi_4O_9$  structure is strikingly similar in topology to its benitoite polymorph [95F1] as well as to the trigonal  $P321$  structure of  $SrGe_4O_9$  [96N1] or  $BaGe_4O_9$  [68S1]. All of these framework structures contain three-membered silicate or germanate tetrahedral rings, with each ring linked to six individual silicate or germanate octahedra. Each isolated octahedron, in turn, is corner-linked to six three-membered tetrahedral rings. The result is a distinctive layering perpendicular to  $c$  of alternating tetrahedral and octahedral units – Fig. 4 [99H1]. This feature is common to several high-pressure alkali and alkaline-earth framework silicates [96H1]. In all these structures, the alkali or alkaline earth cations occupy large sites (eightfold or greater coordination) in the framework. In the  $P3$ -type structure the Ba cations occupy tenfold-coordinated sites in channels defined by the silicate framework. This structure is 4.2 % denser than the topologically similar benitoite form of high-pressure  $BaSi_4O_9$  which was induced by grinding of the barium tetragermanate-type crystal structure. The principal crystal chemical differences between barium tetragermanate and benitoite-type polymorphs of  $BaSi_4O_9$  are associated with framework distortions, as measured by Si–O–Si angles [99H1]. These distortions, in turn, influence the size of the Ba site. The lower density of benitoite polymorph (4.2 % less dense) arises from the more open framework, with significantly larger Si–O–Si angles. The relatively short Ba–O bonds in the  $P3$  structure suggests that the Ba site in a sample quenched to ambient pressure is, in effect, compressed and thus energetically unfavorable. By grinding single crystals, this induces a martensitic transition to benitoite-type structure [95F1].

### $A_{2-x}A'_x(B_{1-z}B'_z)Si_yGe_{3-y}O_9$ with A, A' = K, Rb, Cs, Tl and B, B' = Ti, Sn, Ge

The crystal structure of solid solutions  $A_{2-x}A'_x(B_{1-z}B'_z)Si_yGe_{3-y}O_9$  were studied [73C2, 73G2, 75C1]. For example in Fig. 5 are plotted the lattice constants of  $K_2BSi_yGe_{3-y}O_9$  with B = Ti(1) and B = Sn(2). In order to compare the experimental data of wadeite and tetragermanate, for wadeite-type structure  $a_w\sqrt{3}$  values were plotted. There is a discontinuity when the structure changes from tetragermanate (T) to wadeite (W). As

replacing Ge by Si after the T-W transition, the  $c$  values are higher and the  $a$  parameters are smaller. The authors analyzed the condition of stability based upon differences of the sizes between A and M and B and M (M = Si, Ge) atoms.

The presence of  $\text{BaSn}(\text{Si}_y\text{Ge}_{3-y})\text{O}_9$  solid solutions in entire composition range was reported [72C1].

#### **$\text{ATa}(\text{Ge}_{3-y}\text{Si}_y)\text{O}_9$ with A = K, Rb, Tl**

The  $\text{KTaGe}_{3-y}\text{Si}_y\text{O}_9$  and  $\text{RbTaGe}_{3-y}\text{Si}_y\text{O}_9$  silicates crystallize in a benitoite-type structure for  $y \leq 1.50$  while  $\text{TlTaGe}_{3-y}\text{Si}_y\text{O}_9$  form solid solutions up to  $y = 1$  [72C1]. For a given system, the lattice parameters  $a$  and  $c$  decrease when increasing the Si content.

#### **$\text{A}_3\text{Ta}_6\text{Si}_4\text{O}_{26}$ (A = Ba, Sr), $\text{K}_6\text{M}_6\text{Si}_4\text{O}_{26}$ (M = Nb, Ta)**

The  $\text{A}_3\text{Ta}_6\text{Si}_4\text{O}_{26}$  (A = Ba, Sr) and  $\text{K}_6\text{M}_6\text{Si}_4\text{O}_{26}$  (M = Nb, Ta) silicates crystallize in a structure related to benitoite, having space group  $\text{P}\bar{6}2\text{m}$  [70S1, 73G1, 76C1]. In this structure the  $\text{Si}_2\text{O}_7$  groups are linked with  $\text{NbO}_6(\text{TaO}_6)$  octahedra so as to create distorted pentagonal channels. These channels have a half occupancy by Ba and Sr in  $\text{A}_3\text{Ta}_6\text{Si}_4\text{O}_{26}$  (A = Ba, Sr) silicates and have full occupancy with K in  $\text{K}_6\text{M}_6\text{Si}_4\text{O}_{26}$ . The structure is basically the same for the two types of compounds. Supplementary potassium of  $\text{K}_6\text{M}_6\text{Si}_4\text{O}_{26}$  have two additional neighbour oxygen of the Si–O–Si bridge. Other compounds with benitoite-type structure were reported [70C1].

#### **Walstromite**

The walstromite,  $\text{Ca}_2\text{BaSi}_3\text{O}_9$ , crystallizes in a triclinic-type lattice having space group  $\text{P}\bar{1}$  [61G1, 65A1, 68D1]. The atom coordinates are given in Table 2 [68D1]. The  $(\text{Si}_3\text{O}_9)^{6-}$  rings are arranged in layers parallel to  $(10\bar{1})$  with calcium ions about half way between them – Fig. 6. The barium ions are roughly coplanar with the oxygen atoms. The oxygen positions were not well determined because of the presence of barium and since the structure was solved in projection only [68D1]. The  $\text{SiO}_4$  tetrahedra are all distorted so that the angles subtended at Si by the shared oxygen atoms (O3, O6, O9) are all less than the tetrahedral angle. The coordination polyhedra of divalent cations are irregular. Ca1 is coordinated by six charged and two uncharged oxygen atoms forming an irregular square antiprism; Ca2 by six charged oxygen atoms in a slightly irregular octahedron. Six charged and two uncharged oxygen atoms lie within 3.10 Å of the barium atom. Of these, O1', O2, O5, O7' and O9 form a fairly regular pentagon almost coplanar with Ba.

#### **Margarosanite**

The margarosanite,  $\text{PbCa}_2\text{Si}_3\text{O}_9$ , crystallizes in a triclinic structure having space group  $\text{P}\bar{1}$  [64G1, 69F2]. In this structure, planes of tetrahedral sites alternate with planes of calcium sites between sheets of close packing oxygen atoms parallel to  $(\bar{1}01)$ . The Pb and Ca atoms are ordered. Ca1 polyhedra form an infinite edges sharing chain parallel to  $[101]$ , and Pb and Ca2 sites alternate along the edge of this chain. Tetrahedral sites form three-membered rings which are linked to the Ca1 polyhedral chain. The two Ca atoms have sixfold coordination and the Pb atom has sevenfold coordination [69F2]. For structure see also Fig. 7b and corresponding comments.

#### **Roeblingite**

The ideal composition of roeblingite is  $\text{Pb}_2\text{Ca}_6(\text{SO}_4)_2(\text{OH})_2(\text{H}_2\text{O})_4[\text{Mn}(\text{Si}_3\text{O}_9)_2]$ . The first structure analysis on a natural sample reported the space group  $\text{C}2/\text{c}$  [66F1]. Later on [84M2], a monoclinic structure with space group  $\text{C}2/\text{m}$  was proposed. The basis of the structure is an infinitely extending planar trellis  $2_\infty [\text{Mn}^{2+}(\text{Si}_3\text{O}_9)_2]^{10-}$  fundamental building block (fbb). This sheet-like design is parallel to  $\{001\}$ , where the individual  $[\text{SiO}_4]$  tetrahedra and  $\text{MnO}_6$  octahedra are corner-linked to each other, forming the most rigid planar component in the structure. In Fig. 7 a polyhedral diagram of the structure down  $[100]$  is plotted. In fact bonds, other than O–H...O which penetrate the  $\{001\}$  plane, include ...Pb–O7–S–O9–Ca2... and ...Ca1–O8–S..., the  $[\text{SO}_4]$  insular unit acting as a bridge between  $[\text{Mn}(\text{Si}_3\text{O}_9)_2]$  parallel to  $\{001\}$ . These bonds which involve the large Ca1, Ca2 and Pb cations, have lower bond strength than Si–O–Si and Si–O–Mn linkages.

The fundamental  $[\text{Si}_3\text{O}_9]$  units in roeblingite and margarosanite are featured in Fig. 7b [84M2]. In both structures, the geometrical similarities of the  $[\text{Si}_3\text{O}_9]$  rings are striking. Moreover, a weaker but still pronounced disposition of the Ca2 atoms in roeblingite and the Ca2 and Ca1 atoms in margarosanite can be noted. Beyond this, there is no further structural similarity between the remaining regions in roeblingite and in margarosanite. In roeblingite the large cations are tucked between the  $[\text{Mn}(\text{Si}_3\text{O}_9)_2]$  sheets. All vertices of  $\text{MnO}_6$  octahedron link to the  $(\text{Si}_3\text{O}_9)$  radicals which are oligosilicate three-membered rings and, as above stated, are geometrically similar to the rings in paragenetically related margarosanite. Coordination polyhedra include  $\text{Pb}\phi_7$  (maximal point symmetry  $\text{mm}2$ );  $\text{Ca}1\phi_8$  distorted square antiprisms,  $\text{Ca}\phi_7$  polyhedra similar to  $\text{Pb}\phi_7$ ;  $\text{MnO}_6$  octahedra;  $\text{SiO}_4$ ,  $\text{SO}_4$  tetrahedra.

### Scawtite

The properties of scawtite were determined by [55M1] considering an A-centered cell. In [55M2] were found cell parameters consistent with above, considering a probable space group  $I2/m$ . The transformation matrix from the A cell to I cell is  $-101/010/100$  with,  $Y = b$ ,  $Z \wedge a = 70^\circ$  and  $Z \wedge c = 30^\circ$ . Structure refinement of the scawtite,  $\text{Ca}_7(\text{Si}_6\text{O}_{18})(\text{CO}_3) \cdot 2\text{H}_2\text{O}$  [73P1] shows that the silicate crystallizes in a monoclinic structure having space group  $I2/m$  [73P1]. The structure, essentially, is composed of alternating layers of octahedrally coordinated calcium atoms and of  $\text{Si}_6\text{O}_{18}$  rings lying parallel to (010). The water molecules are bonded to Ca atoms forming part of the calcium-oxygen layer. The  $\text{CO}_3$  groups occupy space between the  $\text{Si}_6\text{O}_{18}$  rings [73P1]. Fig. 8 shows a projection of the structure onto (010) where diagram (a) is an idealized projection and (b) shows the actual atomic positions. Each  $\text{Si}_6\text{O}_{18}$  ring is bisected by the mirror plane of  $I2/m$  and each shaded tetrahedron is the superposition of two tetrahedra. Two Si1 tetrahedra link across the mirror plane and are joined by Si2 tetrahedra to another pair of Si1 tetrahedra. The linkage of the oxygen octahedra about calcium is very complex. As seen in Fig. 8b the calcium-oxygen polyhedra are very irregular, the layer is not continuous and the topological relation is not that of regular close-packed layer as suggested in Fig. 8a. Each Ca3 octahedron is bisected by a mirror plane and shares an edge with 2Ca1 and 2Ca1' octahedra, each pair of edges being superimposed in projection. The two Ca1 octahedra share a point O6, while the two Ca1' octahedra share an edge on the mirror plane. Each Ca2 octahedron had two vertices pointing in the same direction out of the plane of diagram. Pairs of Ca2 octahedra, one lying above the mirror plane and one below are also superimposed in projection, and share an edge with 2Ca1 and 2Ca1' octahedra. In Fig. 8c, the silicate layer is shown. The  $\text{Si}_6\text{O}_{18}$  rings are severely distorted from an ideal arrangement with sixfold rotation symmetry. Two tetrahedra point up, two point down, and two tetrahedra have one horizontal edge and one vertical edge. The  $\text{CO}_3$  triangles lie in the gaps between the  $\text{Si}_6\text{O}_{18}$  rings and appear as isosceles triangles because they are inclined to the plane of projection [73P1].

### Eudialytes

Eudialyte is a very complex cyclosilicate with varying amounts of Na, Ca, Sr, K, Fe, Mn, Zr, Ti, Si, R, Cl, F and some other elements. By R we denoted a rare-earth element. Since the first structure investigations [71G1, 71G2], eudialyte samples with different compositions were analyzed. Among them are **eudialyte** and **potassium oxonium eudialyte** [87R1, 88R1, 90R3], so-called **eucolite**, TR-Fe and TR-Mn **eucolites** [88R2, 90R1], **alluaivite** [90R4], “**barnasovite**” and “**red-brown barnasovite**” [87R2, 90R2], and a **Fe-low analogue of eudialyte** [98R1], **Ti-rich eudialyte** [99R1], **kentbrooksites** [98J1] or **Mn,Na-ordered analogue of eudialyte** [00R1]. After a short description of the classical eudialyte,  $\text{Na}_{16}\text{Ca}_6\text{Fe}_3\text{Zr}_3(\text{Si}_3\text{O}_9)_2(\text{Si}_6\text{O}_{27})_2(\text{OH,Cl})_4$ , structure, the more complex structures of eudialytes, particularly Ti-rich eudialyte [99R1], will be presented. The differences to other eudialyte compositions are also emphasized.

The structures of the eudialyte group of minerals are characterized by the presence of the same framework [71G1, 71G2] based on both discrete three-membered rings  $[\text{Si}_3\text{O}_9]$  and nine-membered rings  $[\text{Si}_9\text{O}_{27}]$  – Fig. 9a,b – combined with discrete and nearly regular Zr-octahedra and by six-membered rings of distorted  $[\text{Ca}_6\text{O}_{24}]$  octahedra – Fig. 9c,d. In classic eudialytes all these types of polyhedra are sandwiched parallel to (001) in proportion  $\text{Zr} : \text{Si} : \text{Ca} = 1 : 2 : 1$ . Thus, the unit cell contains 12 sheets. In this three-dimensional network, the holes are filled mainly with Na and variable amounts of additional atoms with different coordination. In case of Ti-rich eudialyte structure there are two crystallographically independent rings of each sort – Fig. 9 – and the

structure is characterized by the alternation along [001] of five layer types, formed by Si tetrahedra, M1, M2, M3 and M4 octahedra, respectively [99R2]. As a result, 24 polyhedral sheets are arranged along the z-axis in the following sequence: M4–Si–M1–Si–M3–Si–M2–Si–M4–... – Fig. 10a. They are connected along [001] by sharing the common vertices of polyhedra. Four sheets on  $z \cong 0.02...0.18$  levels are combined into a packet or microdomain with a thickness of  $\sim 10$  Å which corresponds to the classic Zr eudialyte structure, while the next four sheets form another microdomain close to the Ti-eudialyte (alluaivite) structure. Six of these microdomains alternate along the z-axis according to the rule of R-centering. The main differences between the two microdomains are associated with the Si, O-rings, M1–M4 polyhedra and several key sites [99R2].

Both the M1 and M2 sites – Fig. 10a – form nearly regular octahedra combining three and nine rings of two layers. The site population determined for Ti-rich eudialyte<sup>17)</sup> (for footnote see Table 3) are  $(\text{Zr}_{2.33}\text{Ti}_{0.67})$  and  $(\text{Ti}_{1.7}\text{Zr}_{1.3})$ , respectively. Among the nine tetrahedra of the large Si-rings – Fig. 9a,b, there are three tetrahedra with free oxygen vertices. In the central area of the ring these three inner oxygens form a triangle which can be used for the construction of additional polyhedra (tetrahedra or octahedra). If the sites on the triad axes accommodate Si atoms, the additional tetrahedra may have two orientations with the apex pointing towards or away from the hole between two rings. If other octahedra forming elements are present, the orientation is only away from the hole. Both of these variants of populations exists for the axial positions in the Ti-rich eudialyte structure. In one crystallographically independent pair of rings, combined with (Ti, Zr) octahedra, all the additional atoms form tetrahedra with two statistical orientations and shorted distances between them. The other pair of rings combined with Zr octahedra also contains Si tetrahedra. They also have two orientations along the triad axis. There is an additional polyhedron around the TM site – Table 2 – which statistically accommodates  $\text{Al}_{1.25}$  atoms per unit cell [99R2]. Similar to Zr2 [71G1] this axial M position is occupied by  $\text{Al}_{0.9}$  in eudialyte<sup>13)</sup> [87R1],  $\text{Ti}_{0.5}$  and  $(\text{Nb},\text{Al})_{2.2}$  in eucolite<sup>11)</sup> [88R2],  $\text{Ti}_{0.2}$  and  $[(\text{Zr},\text{Nb})_{1.8}\text{Al}_{0.4}]$  in “red-brown barsanovite” [87R2],  $\text{Nb}_{1.8}\text{Zr}_{0.8}$  and  $\text{Nb}_{1.7}\text{Zr}_{0.4}$  in “TR-Fe eucolite” and “TR-Mn eucolite”, respectively [90R1],  $\text{Nb}_{2.0}\text{Zr}_{0.9}$  in barsanovite [90R2] and  $\text{Nb}_{1.65}\text{Ti}_{0.3}\text{Zr}_{0.36}$  in kentbrooksite<sup>18)</sup> (for footnotes/compositions see Table 3) [98J1]. The TM position is coordinated by six anions, including three inner oxygens, O31, from the nine-membered ring and three OH4 shared with the Ti octahedra. The bond-valence sum on this anion point to an OH group. This key position, like O19 in kentbrooksite [98J1], participates in two octahedra (Al and Ti) and the Na5 polyhedron [99R2].

Another key site is a microregion with several subsites between two edges of the M3,4 octahedra from neighbouring six-membered  $[\text{M}_6\text{O}_{24}]$  rings. These subsites can be competitors for some elements. In Fe-rich eudialytes the position in the centre of an almost planar oxygen square is dominated by Fe. If Fe atoms are lacking, this site can be occupied by Na atoms, as in the alluaivite structure [87R2] or in the structure of Fe-low eudialyte [98R1]. There are no sufficient Fe atoms to dominate this position even in one microdomain of the Ti-rich eudialyte structure [99R1]. In the “Zr-part” of the structure, determined by using the method described by [89A1], allowed to localise the Fe1 and Ti sites. A similar splitting of the two positions was reported in kentbrooksite [98J1]. In Ti-rich eudialyte the Fe1 position is accompanied by the Na10 position on the other side of square at a distance of 1.42 Å. All these three positions can only be statistically occupied. Ti is sixfold coordinated in a rather distorted octahedron [99R2].

The fivefold coordination, in a distorted square pyramid, is a common feature of the eudialyte structures [91P1, 99R2]. A square pyramid of Fe with an almost full occupation of its position was found in barnasovite [90R4], whereas the corresponding pyramid accommodates mainly Mn atoms in kentbrooksite [98J1]. The octahedron on the triad axis and three octahedra (or square pyramids) around it link to form a cluster. Such clusters are the main reason for the strong deviation from centrosymmetry which causes the piezoelectric effect in eucolites [88R2, 90R1], especially barnasovites [87R2, 90R2]. In the kentbrooksite structure [98J1], three Mn pentagonal groups are linked together by the (Nb,Ti,Zr) octahedron into a similar cluster. In the Ti-rich eudialyte – as mentioned before – the Ti,Al-cluster appears only in the “Zr part” – Fig. 10b – of the structure, while the “Ti part” accommodates mainly Na atoms in a similar microregion – Fig. 10c [99R2].

There are 17Na sites in the Ti-rich eudialyte structure – Table 2. Five of them, M5–M9 are dominated by Na atoms and nine positions are occupied by Na only. Moreover Na participates also in the M4 position together with Ca and in Na10 together with OH. Most of these positions are splitted, statistically occupied, with short distances between them. They are characterized by different coordination numbers and distances [99R2]. All the Na atoms are placed in the 9 sites with point symmetry m except Na8b and Na9b which are disordered and distributed over 18c sites with 25 % occupancy [99R2]. Such disordering of Na atoms in the cavity between two nine-membered rings is a characteristic feature of some eudialytes [88R2, 90R1, 90R2, 99R2]. As a whole, there

are 15.93 and 18.5 Na atoms in the Zr and Ti parts, respectively in Ti-rich eudialyte [99R2]. Mn atoms occupy in Ti-rich eudialyte two different sites: in six-membered rings with Ca and in the center of nine-membered ring tetrahedron. R atoms participate in the other six-membered ring. Moreover, R and Sr atoms are distributed over Na positions, and R only in the “Ti-part” [99R2].

Cl and H<sub>2</sub>O molecules are localized on triad axes with statistical occupation of their sites. Predominance of Cl and H<sub>2</sub>O in the “Ti-part” is a feature of the structure. In addition, H<sub>2</sub>O<sub>4</sub> molecule occupies one of the compact holes between two three-membered Si-rings, inside the six-membered M4-ring. As a rule, these cavities remain empty in the eudialyte structure. Water molecules were detected in one of them but only in the alluaivite structure [99R2].

So far there are only two known eudialyte minerals with 2c lattice constants: alluaivite [90R4] and Ti-rich eudialyte [99R2]. Due to centrosymmetry, the alluaivite structure is nonmodulated. The non-centrosymmetrical Ti-rich eudialyte structure can be regarded as commensurately modulated, with the modulation vector *c*. The partial substitution of smaller Ti cations for larger Zr cations leads to structural modulation. The oxygen atoms forming Ti and Zr octahedra participate in Si tetrahedra which are modulated with keeping of triad axes in the rings [Si<sub>9</sub>O<sub>27</sub>] and [Si<sub>3</sub>O<sub>9</sub>]. Atomic displacements in the rings are primarily connected to tilt angle changes between these tetrahedra. The two nine-membered rings, related by translation  $(1/2)c \cong 30 \text{ \AA}$ , are significantly rotated from their average positions in opposite directions – Fig. 9a,b. Such a rotation is also observed in the six-membered M3 and M4 rings – Fig. 9c,d. As a result, some structural positions are connected with displacement and occupational modulation.

The Ti-rich eudialyte [99R2] has the most complex eudialyte structure. This comprises the unusual framework with the predominance of Zr in one octahedron and Ti in the other which determines the existence of two individual parts with the same structure. The Ti-rich eudialyte is an intermediate member between classic eudialyte, i.e. Zr, Ca and Fe-rich eudialytes and alluaivite, i.e. Ti, Na, R-rich eudialyte, characterized by an intermediate value of the *a* parameter. The replacement of one independent Zr by Ti leads to R elements concentrating in only one part of the structure. The partial substitution of Zr for smaller Ti is the main reason for the modulation of the framework atoms.

The **kentbrooksite**, ideally (Na,R)<sub>15</sub>(Ca,R)<sub>6</sub>Mn<sub>3</sub>Zr<sub>3</sub>NbSi<sub>25</sub>O<sub>74</sub>F<sub>2</sub>·2H<sub>2</sub>O crystallizes in space group R3m [98J1]. This silicate belongs to the eudialyte group and has the framework characteristic for this group, consisting of three-membered and nine-membered rings of SiO<sub>4</sub> tetrahedra cross-linked by Zr and M1 in octahedral coordination. The major differences in crystal structure are shown when compared with natural eudialyte [71G1], namely: <sup>55</sup>Mn substitution for <sup>56</sup>Fe in M2, <sup>93</sup>Nb (M3) substitution for <sup>28</sup>Si (M4) and high content of R and F substitution for Cl. Kentbrooksite represent the Σ Nb,R,Mn,F end member of series within the eudialyte group [98J1].

The **low-Fe eudialyte** (space group R3m) has a structure similar to Fe-rich eudialyte but the Fe position is occupied mainly by Na [98R1].

We note in the eudialyte family silicates with an unusually low symmetry, R3 [98J1, 99R1, 00R1]. Such a low symmetry was explained by the deficiency of calcium and a differentiation of the elements isomorphically replacing calcium in the octahedra entering six-membered rings. For example in the Mn, Na-ordered analogue of eudialyte, the structure consists of the six-membered rings built by two octahedra of substantially different volumes, one occupied mainly by manganese and the other mainly by sodium [00R1] – Fig. 11. The above sample is also characterized by a high silicon content which favours the transformation of nine-membered Si-rings into ten-membered planar radicals containing statistically disordered additional Si-tetrahedra.

### Catapleiite, Na<sub>2</sub>ZrSi<sub>3</sub>O<sub>9</sub>·H<sub>2</sub>O, calcium catapleiite, CaZrSi<sub>3</sub>O<sub>9</sub>·2H<sub>2</sub>O

The crystal structure of catapleiite, at 300 K, is monoclinic, described by the hemisymmmorphic, centrosymmetrical space group B2/b and is characterized by marked pseudo-hexagonal symmetry [81I1, 88I1]. There is octahedral coordination of zirconium atoms and tetrahedral coordination of silicon atoms. The condensation of the M octahedra of Zr and the T tetrahedra of Si leads to the formation of two- and three-dimensional MT framework in which all the vertices of the polyhedra are bridging: M–O–M, T–O–T, M–O–T. Spatial thinning of the polyhedra (not having face and edge contacts) involves the appearance of a large number of gaps in the MT structure. Location of the alkali metals in these gaps determines a characteristic network of ion transport channels. In the structure there are five regular systems of points, in a special position with local symmetry  $\bar{1}$  and 2 which are occupied by Na and Zr atoms; the order of the group is equal to eight. The cross

section of the framework along the pseudoaxis 6 is shown in Fig. 12a, while in Fig. 12b, the cross section of the Na, Zr sublattice is given [88I1]. The independent part of the B2/b cell contains 19 atoms: 2Zr, 5Na, 3Si, 9O and 2H<sub>2</sub>O molecules. In the cross sections perpendicular to the *b*-axis (pseudo axis 6) the atoms can be divided into those located in layer L<sub>1</sub> (section *b* = 0.00, Zr1(4a), Na1(4b), Na5(8f)) and in layer L<sub>2</sub> (*b* = 0.25, Zr2(4e), Na2(4c), Na3(4d), Na4(4e)). The number of crystallographically independent Na atoms in a layer is different from that of the other layer, but the ratio of Na sites to Zr ones, is the same Na/Zr = 3. The probability, *w*, of populations of the Na positions is *w* = 2/3. The Na/Zr atomic ratio, for any layer, is equal to two. The structural motifs of arrangement of the Na and Zr atoms in the layers are topologically equivalent. Each Zr atom is surrounded by six statistically located Na atoms, and each Na atom by two Zr atoms – Fig. 12b.

The possible directions of fast ionic transport in the structure of catapleiite are channels lying in a plane perpendicular to the hexad pseudoaxis intersecting at 60° with filling of four of the possible positions along the channel. The cross section of such a channel is shown in Fig. 12a. The walls of the channel are sixfold rings of two Zr octahedra linked by diorthogroups Si<sub>2</sub>O<sub>7</sub>, with an Na atom at the center of the ring [88I1].

Calcium catapleiite is a catapleiite with 2Na replaced by Ca [64P1].

### Gaidonnayite, georgechaoite

The gaidonnayite, Na<sub>2</sub>ZrSi<sub>3</sub>O<sub>9</sub>·2H<sub>2</sub>O, crystallizes in an orthorhombic structure having space group P2<sub>1</sub>nb [74C1, 85C1]. The same structure was reported for georgechaoite, NaKZrSi<sub>3</sub>O<sub>9</sub>·2H<sub>2</sub>O [85B1, 85G1]. The structure of gaidonnayite is composed of single chains of SiO<sub>4</sub> tetrahedra, repeating every six tetrahedra. The chains extend alternatively along [101] and [10 $\bar{1}$ ] and are cross-linked by a Zr-O octahedron and distorted Na-O octahedra – Fig. 13.a,b [85C1]. There are three independent Si-O tetrahedra in each chain. Both Na1 and Na2 are coordinated with four oxygen atoms and two H<sub>2</sub>O molecules to form a highly distorted octahedron. The water molecules are situated at opposite corners in the Na1-O octahedron and at adjacent corners in the Na2-O octahedron. In both Na-O octahedra, the oxygen atoms are contributed from three different chain, two from one chains, and one each from two others. The zirconium atom is octahedrally coordinated with six oxygen atoms. The oxygen atoms are contributed from three different silicate chains (two from each) [85C1].

Similar, as for gaidonnayite, the georgechaoite structure consists of sinusoidal single chains with six-tetrahedron repeat, running parallel to [10 $\bar{1}$ ] and [101] directions which are cross linked by regular [ZrO<sub>6</sub>] octahedra and highly distorted [NaO<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>] and [KO<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>] octahedra [85B1, 85G1]; georgechaoite has a slightly larger unit cell – Table 3.

### Loudounite

Only the strongest six lines in X-ray diffraction pattern were reported [83D1]. No crystal structure determination was available.

#### 8.1.3.1.2 Nuclear gamma resonance (NGR) data

### Eudialytes

A large number of eudialyte samples were studied by the <sup>57</sup>Fe NGR method [87P1, 91P1]. The data thus obtained were correlated with optical properties of eudialytes – see section 8.1.3.1.5. The <sup>57</sup>Fe NGR spectra were divided in three groups – Fig. 14 [91P1]. (1) An asymmetric Fe<sup>2+</sup> doublet (denoted Fe1<sup>2+</sup>) is predominant in the spectra of optically positive eudialyte<sup>(12)</sup>. In the high-velocity range a weak peak of another Fe<sup>2+</sup> doublet is observed. In the low-velocity range of the spectrum a broadened weak peak near 0.2 mm/s corresponds to it. The peak can be split in two lines assigned to Fe<sup>2+</sup> doublet and Fe<sup>3+</sup>, respectively. The Fe1<sup>2+</sup> doublet was given by separate peaks, while doublets of Fe<sup>3+</sup> and Fe<sup>2+</sup> ions by symmetric doublets – Fig. 14a. A noticeable asymmetry in component areas and half widths of the main Fe1<sup>2+</sup> doublet, was observed at room temperature. At 77 K, the asymmetry of the areas in the doublet practically vanishes while the difference in widths increases – Table 4. (2). In the spectra of eucolite<sup>(14)</sup>, the intensity of a Fe<sup>2+</sup> doublet increases and becomes predominant – Fig. 14b. The relative intensity of the doublet increases with decreasing temperature. (3) Spectra of red-brown eucolite<sup>(15)</sup>, in this respect, become intermediary – Fig. 14c.



In the structure of optically positive eudialyte,  $\text{Fe}^{2+}$  was considered initially to take the only position (a planar oxygen quadrangle built by edges of Ca octahedra from neighbouring six-membered  $\text{Ca}_6\text{O}_{24}$  rings) – Fig. 15 [91P1]. The  $\text{Fe}^{2+}$  doublet is attributed to this position. The quadrangle planes make an angle of  $17.5^\circ$  with the symmetry axis. According to [71G2, 73G1], the quadrangles are equalsided trapezes, while according to [87R1, 88R2] their shape is close to a rectangle. The iron ion is slightly shifted beyond the plane. A single nonidentical element of the point symmetry group of the  $\text{Fe}^{2+}$  site is the reflection plane. It coincides with the symmetry plane of the crystal. The quadrupole splitting of the  $\text{Fe}^{2+}$  doublet is smaller than in gillespite and does not depend on temperature. This was explained, as in case of gillespite [67C1], that in a planar "eudialyte" coordination, the lattice and valency contributions to the electric field gradient on the nucleus are approximately equal and compensate for each other to a great extent. The high-velocity component  $\text{Fe}^{2+}$  is broader than the low-velocity component. This feature has been attributed mainly to relaxation processes [91P1].

In earlier stages of structure determination of eucolite, the presence of only one type of site for iron was shown [71G1, 71G2, 73G1]. Later on [87R2, 88R2] the presence of the additional M2 site for  $\text{Fe}^{2+}$  ions was evidenced. The M2 polyhedron, statistically occupied by  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{Mn}^{2+}$  ions, is built on the basis of the considered planar oxygen quadrangle completed by OH group – see section 8.1.3.1.1. M2 cation is shifted from the rectangle plane by  $0.5 \text{ \AA}$  towards the OH-group. The point symmetry of the cationic position in the formed quadrangle pyramid is C1. The isomer shift value of  $\text{Fe}^{2+}$  doublet agree quite well with fivefold coordination. Three M2 pyramids appear simultaneously in the void in which OH-groups together with oxygen atoms of a nine-membered silicon-oxygen ring form an axial octahedral M1 position (additional Al, Zr or Nb cations). Besides, OH group coordinates one more M3 position with large Na, Sr and R cations, i.e. it is common and necessary for a simultaneous existence of three cationic sites in the void near the nine-membered ring [91P1]. The formation of a cluster built of M1, M2 and M3 polyhedra in eucolite – Fig. 15 – leads to a shift of the gravity centre of positive charges towards the centre of a nine-membered ring in eucolite in which oxygen atoms have the highest deficiency of valence forces. The  $[\text{Si}_9\text{O}_{27}]$  ring in this case operates as a sort of cationic pump. Thus, the doublet of  $\text{Fe}^{2+}$  ions is an indicator of complex structural transformation attributed to charge redistribution in the voids. The doublet intensity is proportional to the degree of cluster occupation from M1, M2, M3 polyhedra.

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

##### **BaTiSi<sub>3</sub>O<sub>9</sub>, K<sub>2</sub>TiSi<sub>3</sub>O<sub>9</sub>**

The  $^{29}\text{Si}$  NMR chemical shift has been studied in benitoite [84M1, 97B1]. As mentioned in section 8.1.3.1.1 the benitoite contains octahedral titanium which connect  $\text{Si}_3\text{O}_9$  rings [69F1]. The overall bonding configuration consists of three Si–O–Si and six Si–O–Ti. Therefore, six of the available Si–O bonds are occupied by titanium which can be designated Si(2Ti). The experimental  $^{29}\text{Si}$  NMR spectrum exhibits one sharp, high-intensity resonance at  $-94.2 \text{ ppm}$  [84M1] or  $-94.3 \text{ ppm}$  [97B1] representing a Si(2Ti) environment.

$\text{K}_2\text{TiSi}_3\text{O}_9$  was expected to have bonding configurations similar to those of benitoite, as evidenced by a single high-intensity peak at  $-94.4 \text{ ppm}$  which is representative of Si(2Ti) [97B1] – Table 5.

##### **Na<sub>2</sub>Si<sub>4</sub>O<sub>9</sub>, K<sub>2</sub>Si<sub>4</sub>O<sub>9</sub> crystalline phases and glasses**

The wadeite type,  $\text{K}_2\text{Si}_4\text{O}_9$  was found to be stable over a large pressure range from  $\cong 2$  up to  $12 \text{ GPa}$  [74K1, 75K1]. As mentioned in section 8.1.3.1.1, both  $^{41}\text{Si}$  and  $^{61}\text{Si}$ , are present in the structure. The  $\text{SiO}_4$  tetrahedra and  $\text{SiO}_6$  octahedra share corners with each other forming a three-dimensional network. There are two types of O sites in the structure:  $^{41}\text{Si-O1-}^{41}\text{Si}$  and  $^{41}\text{Si-O2-}^{61}\text{Si}$  with a ratio 1:2 [83S1, 86D1].

The  $^{17}\text{O}$  MAS NMR spectrum of crystalline  $\text{K}_2\text{Si}_4\text{O}_9$  has sharp features than can be simulated by considering two O sites with a ratio 1:2 – Fig 16a [94X1]. The O site with larger isomer shift was assigned to O2 and the other to O1 – Table 5. The static NMR spectrum was fitted taking into account chemical shift anisotropy, assuming that the principal axes of the chemical shift tensor are coincident with those of the electric field gradient tensor. Values  $\delta_{xx} = 81$ ,  $\delta_{yy} = 81$  and  $\delta_{zz} = 25.5 \text{ ppm}$  were obtained for the O1 site and  $\delta_{xx} = 117$ ,  $\delta_{yy} = 117$  and  $\delta_{zz} = 57 \text{ ppm}$  were determined for the O2 site [94X1].

The  $^{17}\text{O}$  MAS NMR spectrum of the  $\text{K}_2\text{Si}_4\text{O}_9$  glass, quenched from melt at  $1 \text{ atm}$  – Fig 16c, can be simulated with a narrow NBO (nonbridging oxygen atom) peak and a broader BO (bridging oxygen atom) doublet. For the

sample quenched from melt at 6 GPa – Fig. 16b - both the narrow NBO peak and the broad BO doublet shift by about 3 ppm to higher frequency as compared with glass obtained at  $p = 1$  atm. This was explained by an increase of the mean intertetrahedral angle with pressure [91X1]. The increased intensity and the apparent broadening and shift to a higher frequency of the NBO peak was suggested to be caused by the formation of new O sites in the  $^{[4]}\text{Si-O-}^{[6]}\text{Si}$  (possibly also  $^{[4]}\text{Si-O-}^{[5]}\text{Si}$ ) linkages.

The  $^{17}\text{O}$  MAS NMR spectra of  $\text{Na}_2\text{Si}_4\text{O}_9$  glass, quenched from 1 atm, can be simulated with a narrow NBO peak and a broader BO doublet, similar as for the  $\text{K}_2\text{Si}_4\text{O}_9$  glass – Fig. 17 and Table 5 [94X1]. The  $^{17}\text{O}$  MAS NMR spectrum of the glass, quenched at 6 GPa, shows that the large, unresolved intensity increases on both sides of the narrow NBO peak – Fig. 17. Its relative height decreases and the maximum of the NBO peak shifts slightly toward high frequency. This behavior may be correlated with the development of new O sites in the Si-O-Si linkage, as for  $\text{K}_2\text{Si}_4\text{O}_9$  glass. The  $^{17}\text{O}$  static NMR spectra of  $\text{Na}_2\text{Si}_4\text{O}_9$  glasses, quenched at increased pressure, show also a continuous decrease in the relative intensity of the NBO doublet consistent with the development of additional O-type sites that have broader quadrupolar patterns.

The  $^{29}\text{Si}$  MAS NMR spectra of  $\text{Na}_2\text{Si}_4\text{O}_9$  glasses quenched from different temperatures and pressures are plotted in Fig. 18 [91X1] – Table 5. We note that the spectra at 1 atm reported by various authors are similar [84D1, 87S1, 91X1]. Two new peaks, near –147 ppm and –198 ppm, first appear in the glass quenched at 6 GPa and increase in intensity with pressure. These were attributed to the presence of  $^{[5]}\text{Si}$  (–147 ppm) and  $^{[6]}\text{Si}$  (–198 ppm) in an amorphous phase.

The  $^{29}\text{Si}$  MAS NMR spectra of  $\text{K}_2\text{Si}_4\text{O}_9$  glasses quenched at 1 atm [84D1, 86G1, 87S1, 89S1, 91X1] and at higher pressures [91X1] were also analysed. The characteristic features is a broad double peak with maxima at  $\approx -95.2$  and  $-103.8$  ppm [89S1] or  $-92.6$  and  $-105.5$  ppm [91X1]. These were attributed to the tetrahedral  $\text{Q}^3$  and  $\text{Q}^4$  species, respectively. The  $^{29}\text{Si}$  MAS NMR spectra of  $\text{K}_2\text{Si}_4\text{O}_9$  glasses show that both  $^{[5]}\text{Si}$  and  $^{[6]}\text{Si}$  appear for samples quenched at 4 and 6 GPa and the corresponding peaks increase with pressure. The  $\text{K}_2\text{Si}_4\text{O}_9$  glasses have more  $^{[5]}\text{Si}$  than the  $\text{Na}_2\text{Si}_4\text{O}_9$  glass, both at 4 and 6 GPa.

The  $^{23}\text{Na}$  MAS NMR spectra of  $\text{Na}_2\text{Si}_4\text{O}_9$  glasses quenched at 1 atm and 8 GPa were also studied [91X1]. The spectra of samples prepared at high pressures are similar to those obtained at 1 atm although there is a decrease of the linewidth. This can be caused by a slight reduction in the mean quadrupolar coupling constant or by reduction in the range of values. Either possibility suggests a more regular or more symmetrical average coordination polyhedron for Na at higher pressures [91X1].

The above data show that  $^{17}\text{O}$  NMR spectra of a  $\text{K}_2\text{Si}_4\text{O}_9$  glass quenched from the melt at 6 GPa and  $\text{Na}_2\text{Si}_4\text{O}_9$  glasses quenched from 6 to 10 GPa are consistent with the presence of O sites in the  $^{[4]}\text{Si-O-}^{[6]}\text{Si}$  (and possible also  $^{[4]}\text{Si-O-}^{[5]}\text{Si}$ ) linkage, in agreement with  $^{29}\text{Si}$  MAS NMR results. In addition,  $^{17}\text{O}$  static NMR data reveal the development of another new type of O site, possibly one that is connected with two or three  $^{[6]}\text{Si}$  or  $^{[5]}\text{Si}$  atoms in the  $\text{Na}_2\text{Si}_4\text{O}_9$  glass quenched from 10 GPa. Thus  $^{[6]}\text{Si}$  and  $^{[5]}\text{Si}$  may be largely isolated from one another below 10 GPa, whereas at higher pressures, clustering of these Si species may become significant in  $\text{Na}_2\text{Si}_4\text{O}_9$  melts [94X1].

#### 8.1.3.1.4 Heat capacity

##### $\text{K}_2\text{Si}_4\text{O}_9$

The calculated low-temperature heat capacities, determined from vibrational spectra, of low- and high-pressure forms of  $\text{K}_2\text{Si}_4\text{O}_9$  are plotted in Fig. 19 [87G1]. The entropy of transition at 298 K from the sheet-type phase to wadeite-type phase is negative and in the range –17 to –32 J/K mol. These data indicate that the wadeite-type phase is stable, at low temperatures, relative to sheet-type phase. According to [98F1] the heat capacity of wadeite is described by the relation  $C_p = 4.991 \cdot 10^{-2} - 4.350 \cdot 10^{-5} T^{-0.5}$  J/K mol. For the measured drop-solution enthalpy see [04A1].

### 8.1.3.1.5 Optical properties

#### Benitoite, BaTiSi<sub>3</sub>O<sub>9</sub>

The infrared (IR) reflectance spectrum of benitoite was reported by [36M1]. The Raman spectra of benitoite were first presented by [69G1]. In [76A1] was reported the IR reflectance spectra of single crystal benitoite. The authors were able to show almost all of the lines predicted from the factor group analysis and assigned their symmetry species quite unambiguously. The Raman and IR spectra of benitoite were then measured by [93M1] and they observed frequencies which are constantly lower by 12 cm<sup>-1</sup> than those reported in [76A1]. In [49M1, 63S1] were calculated the normal frequencies of the silicate ring, Si<sub>3</sub>O<sub>9</sub>, in benitoite, assuming its symmetry to be D<sub>3h</sub> ( $\bar{6}m2$ ). Later, it was reported that the ring actually has C<sub>3h</sub>( $\bar{6}$ ) symmetry. The normal modes of vibration and their frequencies were calculated later considering  $\bar{P}6c2$ -type structure [93K1]. Factor group analysis dictates that certain normal modes involve the motion of only the ring atoms. On the assumption that mode mixings and splittings due to inter-ring interactions are small, the normal frequencies of the isolated ring of C<sub>3h</sub>( $\bar{6}$ ) symmetry were determined by fitting to suitable averages of selected frequencies in the Raman spectra. A valence force potential consisting of only central interactions between nearest neighbours and bond-bending interactions centered at the silicon atoms was used. This potential was then extended to the full crystal structure by including interactions involving the Ba<sup>2+</sup> and Ti<sup>4+</sup> ions. The frequencies estimated were in good agreement with IR and Raman spectra, requiring only minor adjustment of the force constants obtained for the isolated ring.

The factor group analysis for benitoite predicts 54 vibrational modes, two of which are acoustic modes: 1E' + 1A''<sub>2</sub>. Of the 54 vibrational modes, 34 are Raman active: 7A'<sub>1</sub> + 15E' + 12E''. The external ring modes, considering a ring unit with  $\bar{6}(C_{3h})$  symmetry yields one A'<sub>1</sub> (ring rotation about the *c*-axis), two E' (ring translations perpendicular to the *c*-axis) and two E'' (ring rotations about an axis perpendicular to *c*) ring rotation modes. There are 20 internal vibrational modes for an isolated three-membered ring (6A' + 6E' + 4A'' + 4E''). Since the primitive cell of benitoite has two three-membered rings, each A', E', A'' and E'' mode for isolated ring has two corresponding modes for benitoite. This doubling of each mode (Davydov splitting) [93K1] is caused by in-phase and out-of-phase vibrations of each internal ring mode that relate one ring to other by a twofold rotation axis. Thus the Raman active A' mode for the isolated ring corresponds to an A'<sub>1</sub> and A'<sub>2</sub> mode pair where only A'<sub>1</sub> modes being Raman active. The infrared-active A'' mode for isolated ring corresponds to A''<sub>1</sub> and A''<sub>2</sub> mode pair, where only A''<sub>2</sub> is IR active. Each E' and E'' mode for the isolated ring corresponds to a pair of Raman active E' or E'' modes for the crystal. Thus, the six A' modes correspond to six of the seven A'<sub>1</sub> modes for benitoite, the remaining A'<sub>1</sub> mode is due to ring rotation. The six E' modes for the isolated ring correspond to 12 of the 15 Raman active E' modes for benitoite. The remaining three E' modes are due to one translational mode each for Ba, Ti and the ring. The four E'' modes for the isolated ring correspond to eight of the 12E'' modes, the remaining four E'' modes are due to one translational mode each for Ba and Ti and two ring rotational modes [93M1].

The Raman spectra of benitoite, BaTiSi<sub>3</sub>O<sub>9</sub>, are plotted in Fig. 20 [93M1]. The spectra were analyzed considering three frequency ranges. The lattice dynamics calculations mentioned above [93K1] show that the 50 to 300 cm<sup>-1</sup> range contains Ba, Ti ring translational and ring rotational modes. The 300 to 800 cm<sup>-1</sup> range contains three-membered silicate ring breathing, stretching and deformation modes. The 800 to 1200 cm<sup>-1</sup> range contains Si–O bond stretching modes. The orientation of the incident and scattered light polarization and propagation directions with respect to the benitoite crystal structure is depicted in Fig. 21 for each of the three spectra of Fig. 20. The *z*-axis in the laboratory reference frame is parallel to the *c*-axis of the crystalline structure, while the *x*-axis in the laboratory reference frame is parallel to one of the *a*-axes of the crystal structure. In Fig. 20a is plotted the *z(xx)y* spectrum which has both A'<sub>1</sub> and E' species. This spectrum best depicts the A'<sub>1</sub> species line [64L1]. The relative weak E' lines are due to polar modes for point group  $\bar{6}m2$ , where LO–TO frequency shifts occur for this species.

The Raman lines within the 50 to 300 cm<sup>-1</sup> range were associated with eigenmodes that primarily involve Ba, Ti and external ring motions. The A'<sub>1</sub> species has only one mode in this frequency range, at 256 cm<sup>-1</sup> which was assigned to ring rotation [93M1]. The E' modes in this frequency range are associated with Ba, Ti, and ring translations. The E'' modes in this frequency range are mixtures of Ba, Ti ring translations, ring rotations and  $\nu_{13}$ . The ring mode  $\nu_{13}$  is an O2–Si–O2 motion that can be considered as a response of the ring atoms to Ba and Ti

translations. Eigenmodes associated with lines in the 300...800  $\text{cm}^{-1}$  frequency range mostly contain atomic displacements and mixtures of atomic displacements, that involve Si–O1–Si and O2–Si–O2 bond-bending vibrations. Four  $A'_1$  species lines are in this frequency range: ring breathing ( $\nu_3$ ), wagging of O2–Si–O2 parallel to the ring plane ( $\nu_6$ ), ring deformation and O2 displacements perpendicular to the ring plane that involve bond bending ( $\nu_2 + \nu_4$ ), and O1 displacements within the ring plane ( $\nu_3 + \nu_4$ ) [93M1]. Four Davydov [62D1] pairs of  $E'$  species line are present which were associated with eigenmodes that are similar to those for  $A'_1$  lines in this frequency range. The  $E'$  eigenmodes are mixtures of internal ring displacements:  $\nu_{12}$ ,  $\nu_{14}$ ,  $\nu_{16}$  and  $\nu_{18}$ . The 337  $\text{cm}^{-1}$  lines exist for both  $A'_1$  and  $E'$  since these eigenmodes are dominated by  $\nu_3$  and  $\nu_{14}$  motions, respectively that involve similar atomic displacements.  $E''$  lines in this frequency range include two Davydov pairs which were associated with eigenmodes that contain O2 torsion ( $\nu_{19}$ ) and ring puckering ( $\nu_{20}$ ). The calculations predict an  $E''$  line to be at 549  $\text{cm}^{-1}$  that is associated with the Ti translation and  $\nu_{19}$ . The Raman lines in the 800...1200  $\text{cm}^{-1}$  frequency were associated with eigenmodes that involve Si–O1 and Si–O2 bond stretching. Two  $A'_1$  lines and two pairs of  $E'$  lines occur in this frequency range which are due to Si–O2 bond stretching  $\nu_1(A'_1)$  and  $\nu_{11}(E')$  and Si–O1 bond stretching  $\nu_{10}(A'_1)$  and  $\nu_{15}(E')$ . A pair of  $E''$  modes occurs in this frequency range and is due to Si–O2 bond stretching vibrations ( $\nu_{17}$ ).

Optical spectroscopy studies of blue benitoite showed a broad peak at  $\approx 700$  nm, most of which resides in the near-infrared region [97R1]. Its origin has been considered rather as due to a paramagnetic impurity than to an electron trapped at an anion vacancy. The possible explanation includes the  $\text{Fe}^{2+}\text{-Ti}^{4+}$  or  $\text{Fe}^{2+}\text{-Fe}^{3+}$  intervalence charge transfer [97R1] since traces of  $\text{Fe}^{3+}$  have been found in benitoite by EPR [91V1]. Such a mechanism has not been verified [04G1].

Benitoite is a luminescent silicate [04G1]. Under short-wave excitation of a mercury lamp, at 254 nm, benitoite fluoresces in an intense blue-white, the paler-coloured crystal cores frequently more vividly than the edges. Under long-waved excitation at 365 nm, the cores fluoresce in a dull red, while the edges are non-fluorescent [80M1, 04G1]. The blue luminescence from benitoite is characterized by a broad band peaking at 420 nm under short UV excitation [90W1]. Such a blue emission band has been interpreted as possibly connected with  $\text{TiO}_6$  centers [90W1, 04G1]. Other potential emission centers include impurities such as  $\text{Bi}^{3+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Sn}^{2+}$ ,  $\text{Ag}^+$  and  $\text{Cu}^+$  substituting for  $\text{Ba}^{2+}$  [01G1]. In [04G1] the spectral and kinetic parameters of blue luminescence from benitoite were studied in the temperature-range 40...465 K. The emission was shown to be connected with isolated  $\text{TiO}_6$  octahedra. The  $\text{TiO}_6$  luminescence center has a  $d^0$  configuration. The energy level scheme, for blue luminescence, determined from experimental data, obtained by steady-state luminescence spectroscopy, is given in Fig. 22a [04G1]. After excitation, the metastable level 1 is populated due to nonradiative fast transitions from the excited level (broken arrow). Between levels 1 and 2 the equilibrium population is established due to nonradiative transitions. The energetic barriers,  $U$ , between the two closely spaced emitting excited states and the excited level obtained by fitting the experimental data was  $U = 0.145$  eV (1150  $\text{cm}^{-1}$ ). The determined energy difference between the first and the second excited emitting states was  $W = 0.06$  eV (460  $\text{cm}^{-1}$ ). By  $A_1$  and  $A_2$  was shown the radiation transition probabilities between ground state and the first (1) and second (2) excited emitting states, respectively. The energy levels scheme for the  $\text{TiO}_6$  luminescence center is plotted in Fig. 22b [04G1]. The absorption band at 240 nm (41670  $\text{cm}^{-1}$ ) was assigned to the allowed  $^1A_{1g} \rightarrow ^1T_{2u}$  transition and a weaker band, at 280 nm, assigned to the formally forbidden  $^1A_{1g} \rightarrow ^1T_{1u}$  transition. The excitation spectrum of the blue luminescence exhibits the same bands as in the absorption spectrum, but with different intensities. The analysis of the data shows that the metastable level  $^3T_{1u}$  is the emitting level (1) at low temperatures, with a long decay time of 1.1 ms. At higher temperatures an energy level (2) with higher radiation probability must be involved in the emission process, and this level is situated at 0.06 eV higher energy than the lowest level. These two levels may be connected with  $^3T_{1u}$  level splitting or with closely spaced  $^3T_{1u}$  and  $^3T_{2u}$  levels. Decay time shortening and thermal quenching are connected with nonradiative decay within the  $\text{TiO}_6$  luminescence center, while energy migration does not take place at least up to RT [04G1].

The luminescence of impurity  $\text{Ti}^{4+}$  centers has been studied in  $\text{BaSnSi}_3\text{O}_9\text{-Ti}^{4+}$  and  $\text{BaZrSi}_3\text{O}_9\text{-Ti}^{4+}$  [81K1]. The broad blue green emission bands in many minerals, were connected with  $\text{TiO}_6$  luminescence [81G1]. The maximum in the excitation spectra of  $\text{Ti}^{4+}$  impurity in  $\text{BaSn}_{1-x}\text{Ti}_x\text{Si}_3\text{O}_9$  system, shifts from 225 nm for  $x = 0.01$  to 240 nm for  $x = 0.1$  and remains in this position for  $0.1 \leq x \leq 0.7$  [81K1].

**Wadeite,  $K_2ZrSi_3O_9$** 

The Raman spectra of  $A' + E'$  and  $E'' + E'$  symmetries are plotted in Fig. 23 [96M1]. Some conclusions can be drawn about the eigenmodes determined for wadeite and benitoite, by comparing the nearly identical geometries and bonding within the rings, and the different atomic arrangements and bonding external to the rings for the two structures. For both silicates, the highly localized internal ring modes, at frequencies above  $800\text{ cm}^{-1}$ , are virtually identical. On the other hand the less localized internal ring modes between  $300$  and  $800\text{ cm}^{-1}$  are predominantly mixtures of idealized planar three-membered ring modes which can be unique to each crystal structure. In the case of wadeite, the most striking difference when compared to benitoite is the absence of a bridging oxygen breathing mode which appears to have been replaced by ring breathing motions. The nonbridging oxygens in benitoite are more tightly clamped to the surrounding Ba and Ti cations, restricting internal and whole ring motions and leading to an eigenmode having only bridging oxygen motions. In wadeite, where the nonbridging oxygens are more weakly clamped to the surrounding K and Zr cations, there is more freedom of ring motion. Therefore, no bridging oxygen breathing mode is found, while several intermediate and low-frequency eigenmodes are dominated by ring breathing and rotation motions that can mix with other ring modes. In eigenmodes at frequencies below  $250\text{ cm}^{-1}$ , mixing of K and Zr motions with those of the ring is present. Similar behaviour was found for benitoite, where mixing of Ba and Ti motions with those of the rings is found for modes below  $300\text{ cm}^{-1}$ .

 **$K_2Si_4O_9$** 

The infrared and Raman spectra for the  $K_2Si_4O_9$  high-pressure and low-pressure forms are given in Fig. 24 [87G1]. The Raman spectrum of the low-pressure form [76V1] showed a Raman line near  $1100\text{ cm}^{-1}$  indicative of units of Si plus one nonbridging oxygen in a range of silicate glass [75B1] and crystals. The Raman spectrum of low-pressure  $K_2Si_4O_9$  reported by [87G1] shows no such feature. The major high-frequency lines occur at  $1154$  and  $1074\text{ cm}^{-1}$  – Fig. 24b. These modes have not been assigned to any particular vibrations of the  $K_2Si_4O_9$  lattice [87G1]. The strong sharp Raman modes in the  $400\ldots 525\text{ cm}^{-1}$  region – Fig. 24b – likely correspond to vibrations of bridging oxygens in the Si-O-Si linkages. It is possible that one or both of the  $524$  and  $511\text{ cm}^{-1}$  peaks in the Raman spectrum of the low-pressure  $K_2Si_4O_9$  are due to vibrations of the bridging oxygens in the four-membered rings. The infrared bands in the region of  $600\ldots 750\text{ cm}^{-1}$  – Fig. 24a – may also be assigned to vibrations associated with bridging oxygens in Si-O-Si linkages. However, the weak Raman modes near  $750\ldots 800\text{ cm}^{-1}$  and infrared bands in the same region may be also associated with Si “cage” motions which appear for highly polymerized silicates [75M1, 84M3]. For this reason it was not possible to assign the bands between  $600$  and  $750\text{ cm}^{-1}$  in the IR spectrum of the low-pressure form of  $K_2Si_4O_9$ .

The high-pressure (wadeite-type) polymorph of  $K_2Si_4O_9$  shows a strong infrared band at  $746\text{ cm}^{-1}$  – Fig. 24c. This was suggested to correspond to the asymmetric stretch of the  $SiO_6$  groups sharing corners with  $SiO_4$  tetrahedra. This may be also due to  $Si_3O_9$  rings. Similar alternatives exist for the interpretation of the Raman bands of high-pressure  $K_2Si_4O_9$  in the  $550\ldots 650\text{ cm}^{-1}$  region – Fig. 24d. This region corresponds to vibrations involving bridging oxygens in intertetrahedral Si–O–Si linkages and it is possible that tetrahedral-octahedral Si–O–Si linkages may also vibrate in this region. An assignment to the symmetric stretching of  $SiO_6$  groups in wadeite would be possible for one or more of the Raman bands near  $500\text{ cm}^{-1}$ . It is possible that the  $645\text{ cm}^{-1}$  Raman peak of high-pressure  $K_2Si_4O_9$  – Fig. 24d – also corresponds to the Si–O–Si vibrations within the three-membered rings of the wadeite structure. From analysing the above data it may be concluded that there are no simple and unambiguous assignments for either Raman and infrared vibrations for both the low- or high-pressure polymorphs. The vibrational models based on  $K_2Si_4O_9$  predict that the low-pressure polymorph of  $K_2Si_4O_9$  has significant higher entropy than the high-pressure polymorph [87G1]. The low-temperature heat capacities were also calculated (see section 8.1.3.1.4). The heat capacity,  $C_p$ , of the low-pressure polymorph below  $200\text{ K}$  is notably larger than that of the high-pressure polymorph. At higher temperatures, the difference decreases because the modes at higher frequencies begin to make significant contributions to  $C_p$  [87G1].

 **$K_2TiSi_3O_9$** 

The IR absorption spectra of  $K_2TiSi_3O_9$  were also studied [61P1, 73S1].

### **Na<sub>2</sub>Si<sub>4</sub>O<sub>9</sub>, K<sub>2</sub>Si<sub>4</sub>O<sub>9</sub> glasses**

The Raman spectra of Na<sub>2</sub>Si<sub>4</sub>O<sub>9</sub> glass obtained at 1 atm, as reported by various authors [75B1, 81F1, 83M1, 91X1], are identical. The strong peak at 1090 cm<sup>-1</sup> is caused by symmetric Si-O stretching vibration of Q<sup>3</sup> species and the weak peak near 940 cm<sup>-1</sup> was assigned to Si-O stretching of a small proportion of Q<sup>2</sup> species – Fig. 25 [91X1]. The 776 cm<sup>-1</sup> band may correspond to motions of Si against its oxygen cage. The sharp low-frequency peak at 522 cm<sup>-1</sup> may be attributed to the Si-O-Si bending vibrations associated with Q<sup>3</sup> species, and the 598 cm<sup>-1</sup> maximum on its high-frequency shoulder is caused by a population of Si-O-Si linkages in the glass with narrower Si-O-Si angles possibly associated with Q<sup>2</sup> species or three-membered siloxane rings containing both Q<sup>4</sup> and Q<sup>3</sup> species [83M1, 90D1, 91X1]. The band near 450 cm<sup>-1</sup>, forming a low-frequency shoulder on the 522 cm<sup>-1</sup> peak, was assigned to Si-O-Si bending vibrations of Q<sup>4</sup> species in the glass. The presence of Q<sup>4</sup> species may also be responsible for the maximum near 1156 cm<sup>-1</sup> on the high-frequency shoulder of the 1090 cm<sup>-1</sup> band [71F1, 83M1, 84M3]. For samples quenched at 4 GPa, the 522 cm<sup>-1</sup> peak shows a slight shift to higher frequency (526 cm<sup>-1</sup>) consistent with a slight decrease in the Si-O-Si angle within the Q<sup>3</sup> units. The low-frequency shoulder on this peak associated with Q<sup>4</sup> species also shifts to higher frequency, suggesting a decrease in the mean Si-O-Si angle within Q<sup>4</sup> units. For glasses quenched above 4 GPa, there are marked changes in Raman spectra [91X1]. The intensity of band near 600 cm<sup>-1</sup> increases with pressure and becomes the dominant low-frequency band for the sample quenched at 12 GPa. There is a large intensity increase in the 250...550 cm<sup>-1</sup> region. An increase in the peak intensity occurs in the region of the band near 940 cm<sup>-1</sup> and an extra weak band near 990 cm<sup>-1</sup> develops in the 8...12 GPa quenched glasses. The 1156 cm<sup>-1</sup> maximum on the high-frequencies side of the 1090 cm<sup>-1</sup> band is no longer resolved from the main peak for the 6...12 GPa quenched samples. The band near 780 cm<sup>-1</sup> shifts slightly to higher frequency. These spectral changes bear a general resemblance to those of the 1 atm prepared A<sub>2</sub>Si<sub>4</sub>O<sub>9</sub> glass series, when A is changed from Cs to Rb, to K, to Na, to Li, during which a disproportionation reaction involving Q<sup>3</sup> is known to occur [83M1]. An extended discussion on this matter was given by [91X1].

The IR reflectance spectra of Na<sub>2</sub>Si<sub>4</sub>O<sub>9</sub> glasses were also analysed [91X1]. These are also consistent, as Raman spectra, with the occurrence of high coordination Si species in the samples prepared at high pressures, although the peak assignments to the vibrational modes involving these species are not unique. Reduction of Si-O-Si angle within Q<sup>3</sup> and Q<sup>4</sup> units, with pressure, are again suggested by Raman spectra.

The Raman spectra of K<sub>2</sub>Si<sub>4</sub>O<sub>9</sub> glasses are plotted in Fig. 26 [91X1]. The Raman spectra of the glass obtained at 1 atm, reported by various authors, are identical [75B1, 83M1, 91X1]. There is less intensity in the 400...500 cm<sup>-1</sup> region than in the spectra for Na<sub>2</sub>Si<sub>4</sub>O<sub>9</sub> glasses probably because fewer Q<sup>4</sup> species are present [83M1]. The 592 cm<sup>-1</sup> peak is well resolved from the 520 cm<sup>-1</sup> band. These peaks can be attributed to bending vibrations of Si-O-Si linkages [91X1]. The 592 cm<sup>-1</sup> band is caused by Si-O-Si linkages within the glass with smaller Si-O-Si angle than those associated with the predominant Q<sup>3</sup> species. The narrower Si-O-Si angles might be associated with either the presence of Q<sup>2</sup> species indicated by the weak shoulder in the 900...1000 cm<sup>-1</sup> region, or with three-membered siloxanes rings in the glass [83M1, 90D1, 91X1]. The band at 774 cm<sup>-1</sup> may be due to Si motion against its oxygen cage. In the high-frequency region, there is a well developed shoulder at 1158 cm<sup>-1</sup> on the 1102 cm<sup>-1</sup> band. This shoulder is also present in the 1 atm quenched Na<sub>2</sub>Si<sub>4</sub>O<sub>9</sub> glass and was associated with the presence of Q<sup>4</sup> species. Raman spectral changes with increasing pressure are similar to those observed for the Na<sub>2</sub>Si<sub>4</sub>O<sub>9</sub> glass. Only minor changes occur in the spectra of glasses prepared below 5 GPa. For samples prepared between 5...8 GPa, there is a continued increase in the intensity of the bands in the 900...1000 cm<sup>-1</sup> region [91X1].

The IR reflectance spectra of the K<sub>2</sub>Si<sub>4</sub>O<sub>9</sub> glasses, prepared at 1 atm, show peaks at 1018 and 1082 cm<sup>-1</sup> and a shoulder at 1140 cm<sup>-1</sup> [90D1, 91X1]. Between 1 atm and 1 GPa, the 1018 and 1082 cm<sup>-1</sup> bands coalesce to give a band with principle maximum near 1035 cm<sup>-1</sup> and the shoulder moves to about 1130 cm<sup>-1</sup> [91X1]. At 6 and 8 GPa the high-frequency band increases in frequency to about 1078 cm<sup>-1</sup>, and a new band develops in the 940...970 cm<sup>-1</sup> region. As in high-pressure quenched Na<sub>2</sub>Si<sub>4</sub>O<sub>9</sub> glass, the growth of the band in the 940...970 cm<sup>-1</sup> region may be correlated with the increase of the proportion of <sup>5</sup>Si and <sup>6</sup>Si species in the glass, in agreement with <sup>29</sup>Si NMR studies.

### Eudialyte

The optical absorption spectra of eudialytes can be divided into three groups – Fig. 27 [91P1]: (1) Spectra of crimson<sup>12, 13)</sup> and pink optically positive varieties. They are characterized by a weakly polarised absorption band around  $18900\text{ cm}^{-1}$  dominating in intensity. There are absorption bands at  $10900$ ,  $7150$  and  $4000\text{ cm}^{-1}$  in the near infrared range with polarization  $N_o(\mathbf{E} \perp \mathbf{c}) > N_e(\mathbf{E} \parallel \mathbf{c})$ . Lowering the temperature to  $77\text{ K}$ , decreases the intensity of the  $18900\text{ cm}^{-1}$  band and increases that of the  $10900\text{ cm}^{-1}$  band. The above bands appear due to different mechanisms and belong to different optical centre. (2) the spectra of brown and yellow-brown optically negative varieties in which the  $10900$  and  $4000\text{ cm}^{-1}$  bands are predominant while the  $18900$  and  $7150\text{ cm}^{-1}$  bands are either missing or have insignificant intensity. Spectra configuration and colour of the eudialytes are determined by the long-wave edge of a strong absorption band with wavenumbers  $> 20000\text{ cm}^{-1}$ , obviously due to charge transfer  $\text{O}^{2-} \rightarrow \text{Fe}^{3+}$ ; (3) optical spectra of red-brown, brown-red and other eudialytes, intermediate in optical spectra between the first and second variety groups with chromaticity points lying within the range  $\lambda_0=590\dots605\text{ nm}$ .

In Fig. 28, in a  $\text{Fe}^{12+}\text{-Fe}^{22+}$  diagram, the fields of optically positive and optically negative varieties are shown [91P1]. An almost complete absence of  $\text{Fe}^{22+}$  ions is characteristic for optically positive samples. The optical sign of the silicates becomes negative when the cluster occupation reaches  $40\%$  of  $\text{Fe}^{12+}$  sites occupancy.

The leading role of  $\text{Fe}^{3+}$  in colouring of yellow, brown and red-brown varieties of eudialytes was discussed [91P1]. Different explanations were given to crimson and pink colours, attributing them to  $\text{Mn}^{2+}$  ions [67D1],  $\text{Mn}^{3+}$  [76P1, 79F1] or  $\text{Ti}^{3+}$  [73B1]. Another interpretation of optical absorption bands in eudialyte was proposed by [91P1]. Crimson colour of optically positive eudialytes was accounted for by optical transitions in the system of energy levels of  $\text{Fe}^{2+}$  ions in a planar fourfold coordination ( $18900\text{ cm}^{-1}$  band). The influence of  $\text{Mn}^{3+}$  ions on the colour of eudialyte was not observed. Red-brown and brown colour of eucolites was accounted by a competing influence of the  $18900\text{ cm}^{-1}$  band and the edge of charge transfer band  $\text{O}^{2-} \rightarrow \text{Fe}^{3+}$  whose center is positioned in the UV part of the spectrum. The presence of a large number of  $\text{Fe}^{3+}$  ions in eucolites, as compared to eudialytes is due to a comparatively easy oxidation of  $\text{Fe}^{2+}$  ions. Optically bands of the latter do not affect the colour of the sample [91P1].

The refractive indices for some silicates are given in Table 6.