

### 8.1.4.7 Jimthompsonite, babingtonite, zektzerite, batisite and related silicates

The silicates from the above mentioned groups, as well as their ideal compositions are listed in Table 1 [91N1]. We selected the representative silicates from each group, whose physical properties were analyzed, to give more details on the crystal structures.

#### 8.1.4.7.1 Crystal structures. Lattice parameters

The atomic sites for representative silicates from the above groups are listed in Table 2. In Table 3 we give the space groups and lattice parameters. For each silicate we mention also the compositions. For identifying the compositions of silicates mentioned in Tables 2, 3 and 7 see footnotes of Table 3. The physical properties of pyroxmangite, pyroxferroite and rhodonite were presented in Chap. 8.1.4.1 and consequently are not discussed here. The first report of species intermediate between amphibole and mica was a synthesized Na-triple chain silicate [75D1]. The triple-chain silicate, jimthompsonite, the mixed double- and triple-chain silicates and their monoclinic polymorphs were subsequently found [78V1].

#### Jimthompsonite group

**Jimthompsonite** (JT),  $(\text{Mg,Fe})_5\text{Si}_6\text{O}_{16}(\text{OH})_2$ , crystallizes in an orthorhombic structure having space group Pbca [78V2]. The triple A chain projection of the structure onto the (100) plane is shown in Fig. 1a while in Fig. 1b, the projection of the structure onto the (001) plane is plotted. The atomic sites are listed in Table 2. The I-beams, consisting of triple silicate chains and wide octahedral strips are connected in the orthopyroxene – orthoamphibole  $++--$  stacking sequence. Each silicate chain has two symmetrically independent chain rotating angles, an inner rotation angle (O1-O1-O1) and an outer rotation angle (O5-O6-O5), unlike the pyroxenes and amphiboles which have only one (see Chaps. 8.1.4.1 and 8.1.4.3). Both chains are **O**-rotated, the A chain with inner and outer rotation angles of  $179.6^\circ$  and  $173.5^\circ$  and the B chain with inner and outer angles  $166.9^\circ$  and  $161.7^\circ$ . As in pyroxenes and amphiboles, the outer M site is a distorted octahedron (M2 in pyroxene, M4 in amphiboles and M5 in jimthompsonite), while the inner M sites are more regular octahedra, slightly compressed in the [100] direction. By further analogy of the low Ca pyroxenes and amphiboles,  $\text{Fe}^{2+}$  is concentrated in the outer, distorted M site, while the regular M sites favor Mg. Chain warping or corrugation is apparent in a *c*-axis projection of the structure – Fig. 1b. The basal faces of the Si3A and Si3B tetrahedra are tilted significantly out of the (100) plane. As in orthopyroxenes and orthoamphiboles, the A chain is cut by a *b*-glide parallel to (100) and lies between octahedral layer of opposite skew, while the B chain is pierced by  $2_1$  axes and lies between octahedral layers of like skew. The only exception to these rules from atom nomenclature is in the B chain, where O6B is closer to the *c*-glide than O5B [78V2].

The *c*-axis projection of the **clinojimthompsonite** (CJT) structure is shown in Fig. 2 [78V2]. The structure consists of I-beams containing five crystallographically distinct M sites and symmetrically equivalent, **O**-rotated triple silicate chains with inner and outer rotation angles of  $171.4^\circ$  (O1-O1-O1) and  $170.0^\circ$  (O5-O6-O5). The I-beams are connected in  $++++$  stacking sequence, analogous to the stacking in monoclinic pyroxenes and amphiboles. As in the JT structure, the inner M sites are quite regular, but slightly compressed in the [100] direction, while M5, the outer M site, is a distorted octahedron. Fe is concentrated over Mg in this distorted outer site. The I-beams of CJT show the same type of chain warping as those of its orthorhombic polymorph.

**Chesterite** is a chain silicate having more than one set of topologically distinct chains [78V2]. There are two distinct types of I-beams, one similar to the I-beam of the anthophyllite, with A and B double chains, and the other very close to the I-beam of jimthompsonite, with A and B triple chains – Fig. 3. All the chains are **O**-rotated, except that the inner rotation angle of the A triple chain differs from  $180^\circ$  by less than its standard error. As in JT and CJT, the outer tetrahedra of both triple chains are more rotated than the inner ones. The stacking sequence of the I-beams is  $++--$ , the same as for orthopyroxenes, orthoamphiboles and JT. Because the structure is acentric, there are two nonequivalent  $++--$  stacking arrangements that are probably equally likely. The iron is concentrated over Mg in the distorted outer M sites and all four independent chains are warped out of the (100) plane.

The chesterite crystals were treated at  $\cong 1000^\circ\text{C}$  and were irradiated inside a 200 kV transmission electron microscope [04K1]. In this way the 2111 biopyribole was generated. The 2111 biopyribole indicates a chain sequence where 2 signifies a double (amphibole-like) chain and 1 indicates a single (pyroxene-like) chain. We

note that a pyribole consisting of double chains followed by three single chains (2111) was first observed in natural silicates [96G1]. Subsequently 2111 chain sequences were found that are intergrown with 3n single chains in natural samples [97K1]. In [04K1] was shown that many of the 2111 sequences are intergrown with narrow regions containing isolated single- and double-chain material that contains, respectively, 3n single chains and n double chains. The single chain triplets are presumably formed as a result of the decomposition of isolated triple-chain slabs that were originally intergrown with the chesterite. The 2111 sequence and the 3n single-chain slabs can be formed, respectively, by decomposition of chesterite and triple-chain material during observation in electron microscope.

As above mentioned, JT and CJT contain I-beams composed of triple silicate chains and wide octahedral strips [78V1, 78V2]. In JT these I-beams are stacked like those of orthopyroxenes and orthoamphiboles, while the I-beams of CJT are stacked like those in clinopyroxenes and clinoamphiboles. Chesterite contains both double and triple chain I-beams alternating in *b*-direction and assembled in the orthopyroxene – orthoamphibole stacking sequence. The above silicates are very similar to other low-calcium pyriboles with respect to several crystal-chemical attributes, including polytypism, chain rotation, chain warping, lamellar orientation and cation ordering patterns. Examination of the outermost polyhedra of chain silicate I-beams suggests that A chain rotations in orthorhombic pyriboles are a necessary consequence of edge-sharing between tetrahedra and octahedra [78V2]. As intermediate reaction products, these structures delineate a reaction path from anthophyllite and cummingtonite to talc. The amphibole to mica (see subvolume 27I5) transformation mechanism proceeds by reconstruction of double-chain I-beams to form alternating double and triple chains, and finally continuous sheets of silicate tetrahedra [78V2].

### Babingtonite group

**Babingtonite** is a chain silicate having chemical composition  $\text{Ca}_2(\text{Fe}^{2+}, \text{Mn}, \text{Mg})\text{Fe}^{3+}\text{Si}_5\text{O}_{14}\text{OH}$ . According to [72A1] babingtonite is triclinic with space group  $P\bar{1}$ . In [76K1] the structure was reinvestigated and the space group P1 was determined. Although the principal topology is very similar, the two papers present different settings of the structure and therefore different cell constants, atomic positions and distances. There are two chains of  $\text{SiO}_4$  tetrahedra (5 tetrahedra per repeat unit, parallel to [110] [72A1] or to [100] [76K1]). According to [72A1], these chains are connected by two crystallographically distinct  $\text{FeO}_6$  octahedra, differing in the degree of distortion and in the average cation-anion distance. In [76K1] similar results were reported. The Ca atoms are also located in two different sites in the large openings between the chains and the Fe octahedra. The babingtonite structure has similarities to rhodonite [63P1]. The Ca and Fe cations are located in Ca1, Ca2 and Fe1, Fe2 sites, respectively. Average Fe-O distances in the  $[\text{Fe1O}_6]$  and  $[\text{Fe2O}_6]$  octahedra are 2.1687 Å and 2.0477 Å, indicating that the larger  $\text{Fe}^{2+}$  and smaller  $\text{Fe}^{3+}$  ions are concentrated in the corresponding Fe1 and Fe2 sites. In the ideal babingtonite structure, the Ca coordination polyhedra and  $\text{FeO}_6$  octahedra share edges forming chains, eight polyhedra long, in the sequence  $\text{Ca2-Fe}^{3+}\text{-Ca1-Fe}^{2+}\text{-Fe}^{2+}\text{-Ca1-Fe}^{3+}\text{-Ca2}$  along the *c*-axis. These chains are cross linked by further edge sharing with adjacent polyhedral chains so that double bands of edge-sharing Fe and Ca coordination polyhedra extend on echelon along the *c*-axis [81C1, 91B1] – Fig. 4. In these bands, adjacent Fe atoms occur as isolated staggered tetrameric units in the sequence  $\text{Fe}^{3+}\text{-Fe}^{2+}\text{-Fe}^{2+}\text{-Fe}^{3+}$  – Fig. 4b. These units are separated by the  $\text{Ca}^{2+}$  ions – Fig. 4. Metal-metal distances across the shared edges are  $\text{Fe}^{3+}\text{-Fe}^{3+} \approx 3.30$  Å and  $\text{Fe}^{2+}\text{-Fe}^{2+} \approx 3.38$  Å, and lie within the range where  $\text{Fe}^{2+}\text{-Fe}^{3+}$  intervalence charge transfer transitions are induced in the visible region [81B1, 84A1]. However, because  $\text{Ca}^{2+}$  ions separate the  $\text{FeO}_6$  tetramers – Fig. 4 – electron delocalization along infinite bands of edge-shared  $\text{FeO}_6$  octahedra, such as those occurring in ilvaite etc., seems to be precluded in the ideal babingtonite structure [91B1].

High-resolution transmission electron microscopy (HRTEM) studies of babingtonite [81C1] have revealed errors in the periodicity of the "fünfer" single-chain linkages of  $[\text{SiO}_4]$  tetrahedra, analogous to those observed in the isotypic rhodonite and other pyroxenoids [80C1, 80R1]. Examples of such chain periodicity faults (CPFs) are shown schematically in Fig. 4. Here "siebener" and "dreier" chain units are seen to interrupt the "fünfer" silicate chains of babingtonite [91B1]. These CPFs affect the sequence of edge-shared Ca and Fe coordination polyhedra causing kinks and shortening the polyhedral chains where "siebener" chains occur – Fig. 4 left – but extending the sequence of edge-shared  $\text{FeO}_6$  octahedra where "dreier" chains exist – Fig. 4 right. Babingtonite from hydrothermal vein (USA) was found to contain fewer CPFs than crystals from Norwegian skarn deposits [81C1] and the babingtonite samples studied by [80A1]. No evidence was found for Fe atoms in Ca sites or for disordering of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  over their sites.

**Santaclaraite**, ideally  $\text{CaMn}_4[\text{Si}_5\text{O}_{14}(\text{OH})](\text{OH})\cdot\text{H}_2\text{O}$ , crystallizes in a triclinic-type lattice. According to [81O1] the structure has a centric triclinic symmetry ( $P\bar{1}$  for the primitive cell). An I-centered cell was employed ( $I\bar{1}$ ). In [84E1] a B-centered cell was selected. Santaclaraite is a five-tetrahedral-repeat single chain silicate. The crystal structure consists of alternating tetrahedral and octahedral layers. The octahedral layer includes rows of ten octahedra with adjacent octahedral rows displaced along their length to form bands two or three octahedra wide. As isolated units, the tetrahedral chain and octahedral bands are similar to the corresponding portions of the rhodonite structure. The structure of santaclaraite, however, differs in that: (1) two adjacent chains (or bands) in a given layer are displaced by a half  $c$  translation, and (2) the octahedral layer is rotated by a half turn in the plane parallel to the layer with respect to the adjacent tetrahedral layer. The three roles of hydrogen as hydrogen bond, hydroxyl group, and water molecule are responsible for the above half-translation and half-rotation. Three octahedral sites (M1,M2,M3) are essentially occupied by Mn atoms. The Ca atoms are ordered in M5 and the small amount of Mg is probably concentrated in M4 [81O1]. The dehydration of santaclaraite occurs at  $\approx 550^\circ\text{C}$ .

**Bostwickite** has composition  $\text{CaMn}^{3+}_6\text{Si}_3\text{O}_{16}\cdot 7\text{H}_2\text{O}$  [83D1].

**Inesite**, ideally  $\text{Ca}_2\text{Mn}_7\text{Si}_{10}\text{O}_{28}(\text{OH})_2\cdot 5\text{H}_2\text{O}$ , crystallizes in a triclinic lattice having space group  $P\bar{1}$  [68R1, 78W1]. The crystal structure of inesite consists of two components: (a) a polyhedral band, consisting of a sequence of seven edge-sharing Mn octahedra and two Ca pentagonal bipyramids, connected to two similar sequences on either side by edge sharing and (b) double silicate chains with a five-tetrahedral-repeat period, which contain alternating six- and eight-membered rings. These silicate double chains knit the adjacent Ca, Mn polyhedral bands into a three-dimensional framework [78W1]. The three crystallographically independent water molecules serve as apical ligands to the Ca and Mn atoms. The site of one of the water molecules is statistically occupied half the time, accounting for five water molecules in the unit cell. All seven hydrogen atoms are involved in hydrogen bonding. The recipient of a hydrogen bond is either a water molecule or a bridging oxygen atom bonded to two silicon atoms only. The average Si-O bond lengths within the five different Si tetrahedra are 1.621, 1.626, 1.623, 1.627 and 1.630 Å. The Si-O-Si angles range from  $130.0^\circ$  and  $143.5^\circ$ , the smaller Si-O-Si angles being associated with longer Si-O bonds and vice versa. The six- and eight-membered silicate rings are nearly planar. The oriented thermal transformation of inesite to high-calcium rhodonite at  $\sim 800^\circ\text{C}$  involves considerable cation migration and breakage of Si-O bonds [78W1].

**Marsturite**,  $\text{NaCaMn}_3\text{Si}_5\text{O}_{14}(\text{OH})$ , crystallizes in a triclinic-type structure having space group  $P1$  or  $P\bar{1}$  [78P1]. Marsturite is isostructural with other minerals mentioned below.

**Lithiomarsturite**,  $\text{LiMn}_2\text{Ca}_2\text{HSi}_5\text{O}_{15}$ , crystallizes in a triclinic structure having space group  $P\bar{1}$  [90P1]. It has a structure based on "fünferketten", but chain-periodicity faults are common. This is isostructural with marsturite [78P1], nambulite [72Y1], natronambulite [85M1] and babingtonite [72A1]. These structures are characterized by bands of octahedra that are constructed of parallel columns of eight octahedra joined through edge sharing in an offset manner. The octahedra at opposite ends of the column (M4) are significantly larger than the others and are occupied preferentially by Ca. As two of the four  $\text{M}^{2+}$  cations per formula unit lithiomarsturite are Ca, whose radius is significantly greater than that of Mn, the analogy with isostructural babingtonite or nambulite implies that one of the two Ca atoms is ordered in M4.

**Nambulite** has the ideal formula  $\text{LiNaMn}_8\text{Si}_{10}\text{O}_{28}(\text{OH})_2$  [72Y1]. The silicate crystallizes in a triclinic structure having space group  $P\bar{1}$  [75N1]. The structure consists of infinite silicate chains with a repeat unit of five tetrahedra, and Mn polyhedral bands, both parallel to  $[110]$ .

**Natronambulite**,  $(\text{Na,Li})(\text{Mn,Ca})_4\text{Si}_5\text{O}_{14}\text{OH}$  ( $\text{Li} > \text{Na}$ ,  $\text{Mn} > \text{Ca}$ ) crystallizes in a triclinic structure having space group  $P1$  or  $P\bar{1}$  [85M1, 87H1].

### "Fowlerite"

A Zn-rich rhodonite, "fowlerite" has been recently studied [05N1]. With the recognition that "fowlerite" is a Zn-rich variety of rhodonite (up to 10 wt% ZnO), its treatment as distinct mineral species was eventually discontinued. As mentioned already (Chap. 8.1.4.1), rhodonite is a triclinic pyroxenoid that typically contains Ca, Fe and Mg. Although the conventional space group  $P\bar{1}$  was originally used in characterizing the unit cell, the unconventional space group  $C\bar{1}$  was considered for a more intuitive comparison with pyroxenes and other pyroxenoids [75O1]. The rhodonite structure [59L1, 63P1] contains silicate chains made up of repeating five

tetrahedron units (fünferketten). The silicate chains extend along *c* and are stacked with tetrahedral, alternatively pointing along reciprocal lattice vectors  $+a^*$  and  $-a^*$  in (100) layers, in a manner analogous to pyroxenes. As in pyroxenes juxtaposed tetrahedral chains define M sites. In rhodonite M1, M2 and M3 sites are six-coordinated and M5 is seven-coordinated. These are marked differences in the crystal chemistry of rhodonite and fowlerite. Cations in Zn-poor rhodonites and in fowlerites exhibit distinct substitutional trends. Substitution of Zn in fowlerite occurs entirely at M4 and Ca displays a stronger preference for M5 in fowlerite than in Zn-poor rhodonite [05N1]. The most striking distinctions occur in the geometrical details of M4 and M5. Distortion in the M4 site of magnesian rhodonite, typical Mn-rich rhodonite and fowlerite increases with both increasing electron population and mean electronegativity. The M4 site assumes increasing amounts of tetrahedral character with increasing electron density (i.e. Zn concentration). As M4 becomes more Zn-rich, tetrahedral and covalent in character, M5 becomes more Ca-rich, less distorted and more ionic in character. This suggests that “pure” fowlerite (nominally  $\text{Ca}_{0.2}\text{Zn}_{0.2}\text{Mn}_{0.6}\text{O}_3$  or  $\text{CaZnMn}_3\text{O}_{15}$ ) may contain an unequivocally four-coordinated M4 site occupied solely by Zn, and Ca largely restricted to M5.

### Zektzerite group

In [77D1] the unit-cell dimensions and possible space group of **zektzerite** were determined, and the similarity of its cell dimensions and chemical composition with those of tuhualite was noted. The crystal structure was refined later [78G1]. Zektzerite,  $\text{NaLiZrSi}_6\text{O}_{15}$  crystallizes in an orthorhombic-type lattice having space group Cmca. The crystal structure is a tridimensional framework, consisting of three types of polyhedral chains – Fig. 5: (a) an edge-sharing Na polyhedral chain; (b) an octahedral-tetrahedral chain, formed by alternating  $\text{LiO}_4$  tetrahedra and  $\text{ZrO}_6$  octahedra sharing edges and (c) a corrugated silica double chain, with six tetrahedral repeat [78G1]. The sodium atoms occur within cylindrical channels formed by the corrugation of the silicate double chains. Each Na polyhedron (highly distorted octahedron) shares two opposite edges with two adjacent Na polyhedra to form a chain parallel to the *c*-axis. The Li tetrahedron shares two opposite edges with two Zr octahedra on either side, thereby forming a chain parallel to the *c*-axis with alternating  $\text{LiO}_4$  tetrahedra and  $\text{ZrO}_6$  octahedra. The Zr octahedron is nearly regular. The most interesting part of the structure is the corrugated silica chain with six tetrahedral repeat parallel to the *c*-axis. Such a single silicate chain is connected to an identical chain across a mirror plane, by sharing corners, giving rise to a double silicate chain (“sechserdoppelkette”). These double chains contain three different four-membered tetrahedral rings. Each octahedral-tetrahedral chain is connected to four adjacent silicate double chains by sharing corners. Likewise, each silicate double chain is connected to four adjacent octahedral-tetrahedral chains by corner sharing. The Na polyhedral chains are connected to a pair of silicate double chains on the one side and an octahedral-tetrahedral chain on the other by sharing polyhedral edges and corners. A three-dimensional framework structure is formed in this fashion. The atomic sites are given in Table 2.

The **synthetic silicate**  $\text{Na}_2\text{Mg}_2\text{Si}_6\text{O}_{15}$  crystallizes in an orthorhombic structure having space group Cmca. Fig. 6 shows their structure projected along *a* [72C1]. The silicate anions are corrugated ribbons running parallel to *c*. There are two such ribbons to the height of the cell in the *a*-direction which are shown in Fig. 6 as chains of open and shaded triangles, respectively. Each ribbon is two tetrahedra wide in the *a*-direction, and repeats at intervals of six such pairs of tetrahedra. The ribbon can also be described as a series of rings of four tetrahedra which are fused together and which lie in planes parallel to [100]. Each triangle in Fig. 6 represents an  $\text{Si}_2\text{O}_7$  group with its Si-Si direction normal to the plane of the paper, the two tetrahedra in the group coinciding in projection because the oxygen atoms that link them lie on the plane perpendicular to *a*.

The **tuhualite**,  $(\text{Na},\text{K})\text{Fe}_2\text{Si}_6\text{O}_{15}$ , crystallizes in an orthorhombic-type structure having space group Cmca [56H1, 69M1]. According to [69M1], tuhualite contains double chains of silicate tetrahedra with a period of six (sechser-doppelkette), linked by vertex-sharing to chains of iron coordinated polyhedra. The latter chains consist of alternating edge-sharing  $\text{Fe}^{3+}\text{O}_6$  octahedra and  $\text{Fe}^{2+}\text{O}_4$  tetrahedron. This anomalous ordering of smaller, higher valence cations in the larger octahedral site was explained as being necessary for local charge balance in the structure. This situation is not necessary in zektzerite since the higher-valence cation ( $\text{Zr}^{4+}$ ) is well suited to octahedral coordination by oxygen and the lower valence ion ( $\text{Li}^+$ ) is likewise appropriate in tetrahedral coordination.

The **emeleusite**,  $\text{Na}_2\text{LiFe}^{3+}\text{Si}_6\text{O}_{15}$ , crystallizes in an orthorhombic structure having space group Acam [78J1, 78U1]. The axial setting of emeleusite [78U1] differs from the ones quoted for tuhualite, zektzerite and  $\text{Na}_2\text{Mg}_2\text{Si}_6\text{O}_{15}$ . The *abc* sequence for emeleusite corresponds to *cba* one for tuhualite and others. In [78J1] the original orientation of emeleusite was maintained. The essential feature of the structure is the formation of

double silicate chains running in the [100] direction and corrugated in an S-like manner with a six-tetrahedral repeat, thus forming a "sechserdoppelkette" [72L1]. The double chain is developed during condensation of two single chains across a mirror plane and all the tetrahedra take part in this condensation. The double silicate chains are linked by chains of Na2 polyhedra and chains of alternating Li tetrahedra and Fe octahedra. Na1 is located on the mirror plane coordinated by nine oxygens.

The zektzerite, tuhualite, emeleusite and  $\text{Na}_2\text{Mg}_2\text{Si}_6\text{O}_{15}$  are isostructural. All phases have double silicate chains equally corrugated, their unit cell parameters containing the double chain direction are: emeleusite ( $a = 10.07 \text{ \AA}$ ), tuhualite ( $c = 10.11 \text{ \AA}$ ), zektzerite ( $c = 10.16 \text{ \AA}$ ) and  $\text{Na}_2\text{Mg}_2\text{Si}_6\text{O}_{15}$  ( $c = 10.21 \text{ \AA}$ ). Their chemistry presents the following variations [78J1]:

Coordination	9	10	4	6
Emeleusite	Na1	Na2	Li	$\text{Fe}^{3+}$
Tuhualite		Na2	$\text{Fe}^{2+}$	$\text{Fe}^{3+}$
Zektzerite		Na2	Li	Zr
$\text{Na}_2\text{Mg}_2\text{Si}_6\text{O}_{15}$	Na1	Na2	Mg	Mg

The Na1 position is vacant in tuhualite and zektzerite. The Na2 polyhedra, the Li,  $\text{Fe}^{2+}$ , Mg tetrahedra and Mg,  $\text{Fe}^{3+}$ , Zr octahedra are very similar in shape in different phases. In tuhualite and  $\text{Na}_2\text{Mg}_2\text{Si}_6\text{O}_{15}$  the octahedral-tetrahedral chains consist of alternating  $\text{Fe}^{2+}$  tetrahedra and  $\text{Fe}^{3+}$  octahedra and alternating Mg tetrahedra and Mg octahedra, respectively. The angular distortion within the  $\text{Fe}^{2+}$  and  $\text{Mg}^{2+}$  tetrahedra, respectively, in the two structures are closely comparable to the angular distortion found within the Li tetrahedra in zektzerite and emeleusite.

### Batisite group

**Batisite** is the barium-rich member of the solid solution series with the approximate formula  $(\text{Ba},\text{K})(\text{K},\text{Na})\text{Na}(\text{Ti},\text{Fe},\text{Nb},\text{Zr})_2(\text{Si}_2\text{O}_7)_2$ . The potassium rich end member is **shcherbakovite**. The possible existence of solid solution series between batisite and shcherbakovite was discussed [64S1] and an intermediate member of this series was described [65P1]. The structure of batisite was first determined by [62N1] who assigned the acentric group Ima2, since in [60K1] a strong piezoelectric effect was observed. According to [87S1] batisite crystallizes in space group Imam. The structure involves three different atomic positions Cat1, Cat2 and Na – Table 2 – for large, weakly charged cations, one octahedrally-coordinated position Oct for smaller, more electronegative cations, and the tetrahedrally-coordinated position for silicon.  $\text{Si}_4\text{O}_{12}$  vierer single chains and  $\text{Oct}_2\text{O}_{10}$  zweier single chains, running parallel to the  $c$ -axis – Fig. 7 – are joined by common corners in such a way that each chain of octahedra is surrounded by four chains of tetrahedra and each chain of tetrahedra is flanked by four chains of octahedra. According to [87S1], although batisite is commonly classified as a chain silicate with vierer single chains parallel to [001], the structure can be regarded as a composite three-dimensional network of composition  $[\text{Si}_4^{4+}\text{Ti}_2\text{O}_{14}]^{4-}$  with the larger cations in voids of the framework. The network of batisite has free channels parallel to the  $a$ - and  $c$ -axis (Fig. 7). The largest cations ( $\text{Ba}^{2+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ) are situated in the crossing of these channels (Cat1, Cat2). There is a further void which is occupied by sodium atoms (Na sites). The atoms – Fig. 7 – are packed in nearly planar layers normal to the  $c$ -axis. There are two distinct types of layers. Most of the strong bonds of the structure form the layers in  $z \cong 0.25$  and  $z \cong 0.75$  planes. There, the oxygen atoms belonging to the Oct-O-Si and Si-O3-Si bridging bonds are arranged in a planar net of triangles (tetrahedral faces) and squares (cross sections of octahedra). All hard cations including silicon are strongly connected to that layer. The geometry of the twelvefold coordination of the Cat1 position can be derived from a cubooctahedron. Consequently, the arrangement of  $\text{TiO}_6$  polyhedra around the Cat1 position corresponds to that of perovskite-type barium titanate [96B1]. The large cation in batisite is flanked only by four octahedra (or two octahedral chains). The two remaining coordinating oxygen ions O4, at larger distance, belong to silicate chains and are strongly displaced from an ideal "cubooctahedral" position. The eight nearest neighbours of the position occupied by K and Na (Cat2) form a slightly distorted cube. The Na site has an irregular sixfold coordination.

**Krauskopfite**,  $\text{BaSi}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$  crystallizes in a monoclinic-type structure having space group  $\text{P2}_1/\text{a}$  [65A1].

### 8.1.4.7.2 Magnetic properties

#### Babingtonite

The dependence of the magnetic ordering temperatures,  $T_m$ , to paramagnetic phase on Mn content is shown in Table 4 [91B1]. The magnetic ordering temperatures, as well as the  $^{57}\text{Fe}$  hyperfine fields (section 8.1.4.7.3) decrease generally when increasing the Mn content. But factors others than Mn concentration influence also the magnetic ordering temperatures. According to [91B1] one of such factors may be the frequency of chain periodicity faults. The faults – Fig. 4 – disrupt the octahedral sequence of  $\text{Ca}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  and alter the periodicities of adjacent Fe atoms. This also occurs when  $\text{Mn}^{2+}$  substitutes for  $\text{Fe}^{2+}$ .

### 8.1.4.7.3 Nuclear gamma resonance (NGR) data

#### Babingtonite

The  $^{57}\text{Fe}$  NGR spectra in babingtonite,  $\text{Ca}_2(\text{Fe},\text{Mn})\text{FeSi}_5\text{O}_{14}\text{OH}$ , were studied [80A1, 80L1, 82B1, 84A1, 91B1]. Typical  $^{57}\text{Fe}$  NGR spectra, at RT and 4.2 K, are shown in Fig. 8. Because the babingtonite structure contains  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions, each located in a single structural position, the spectrum at RT consists of one ferrous and one ferric doublet. In [80A1]  $\text{Fe}^{2+}$  were assigned in the sixfold coordinated sites and  $\text{Fe}^{3+}$  at the octahedral position. Thus, the  $\text{Fe}^{2+}$  most probably occupy Fe1 sites and  $\text{Fe}^{3+}$  the Fe2 site – Fig. 4b. The temperature dependence of the isomer shift is nearly linear – Fig. 9a – with  $d(\delta)/dT = -7.68(2) \cdot 10^{-4}$  mm/s K for  $\text{Fe}^{2+}$  and  $-7.25(2) \cdot 10^{-4}$  mm/s K for  $\text{Fe}^{3+}$ , near the theoretical value ( $-7.32 \cdot 10^{-4}$  mm/s K) caused by the second-order Doppler shift [76A1]. The strong temperature dependence of the  $\text{Fe}^{2+}$  quadrupole splitting is in agreement with that assignment, as is the nearly complete invariance of the  $\text{Fe}^{3+}$  quadrupole splitting with temperature. The analysis of the spectra revealed that the area of  $\text{Fe}^{3+}$  doublet is higher than that of the  $\text{Fe}^{2+}$  doublet as would be the case for an ideal babingtonite composition with both Fe1 and Fe2 sites completely filled by iron – Table 5. This was explained by a partial substitution of  $\text{Fe}^{2+}$  and to a minor amount also of  $\text{Fe}^{3+}$  by other cations such as Mn, Mg, Al.  $\text{Mn}^{2+}$  appears to substitute for  $\text{Fe}^{2+}$  [80A1]. According to [80A1], the  $^{57}\text{Fe}$  NGR spectra revealed no resonant absorption features which could be attributed to electron exchange or hopping between  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  although these ions are located in neighbouring octahedra sharing common edges. The above studies show that the  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions occupy distinct crystallographic sites with little evidence of electron delocalization between adjacent iron cation. Although an optically induced  $\text{Fe}^{2+} - \text{Fe}^{3+}$  intervalence charge transfer transition occurs in babingtonite at 680 nm and is responsible for its dark green color in transmitted light [84A1], electron delocalization appears to be less extensive than it is in associated minerals [80A1]. The analysis of the correlations of isomer shifts for  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  in babingtonite with other mixed valence  $\text{Fe}^{2+}\text{-Fe}^{3+}$  minerals indicate that the low velocity  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  peaks are almost exactly superimposed in 295K  $^{57}\text{Fe}$  NGR spectra of babingtonite [91B1].

We note that in [91B1] the paramagnetic spectra were fitted by three methods. In Table 5 we give the data only in case when no constraints were imposed to fit the spectra. The  $^{57}\text{Fe}$  NGR spectra show a hyperfine splitting at low temperatures – Fig. 9b. This indicates that magnetic ordering of  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  ions has occurred [91B1]. In all babingtonites, magnetic ordering of both  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  sublattices occurs simultaneously. The  $^{57}\text{Fe}$  hyperfine fields determined at 4.2 K decrease when increasing the Mn content.

### 8.1.4.7.4 Nuclear magnetic resonance (NMR) data

#### Zektzerite

The electric field gradient (EFG) tensors of  $^7\text{Li}$  and  $^{13}\text{Na}$  in a zektzerite single crystal,  $\text{NaLiZrSi}_6\text{O}_{15}$ , have been determined by NMR [89G1]. The quadrupole coupling constants  $e^2qQ/h$  and the asymmetry parameters  $\eta$  are listed in Table 6. In both cases, the EFG tensors show the twofold site symmetries at the Li and Na sites. For  $^7\text{Li}$ , the magnitude of the quadrupole coupling constant and the principal axis of the EFG tensor reflect the large angular distortion of the  $[\text{LiO}_4]$  tetrahedron. The large quadrupole coupling constant of  $^{23}\text{Na}$  indicates a high degree of distortion of the Na coordination polyhedra.

### Krauskopfite

The 1-pulse  $^{29}\text{Si}$  spectrum of krauskopfite shows one peak and in addition the signal due to an impurity. The two Si sites cannot be distinguished well in this spectrum [0001]. The  $^1\text{H}$ - $^{29}\text{Si}$  cross polarization (CP) MAS NMR spectra for krauskopfite, a silicate with Oh group – Fig. 10a – show two peaks at -80.3 and -84.1 ppm [0001]. Each peak in the CP spectra shows an increase in intensity to a maximum with increasing contact time, and then a decrease – Fig. 10b. The rise of integrated intensities versus contact time, at short contact times, is sensitive to the cross-polarization time constants,  $\tau_{\text{SiH}}$ . The damping on the curve is dictated by proton spin relaxation times in the rotating frame,  $\tau_{1\rho}(\text{H})$ . The cross polarization rate  $\tau_{\text{SiH}}^{-1}$  is related to the square of the Si-H heteronuclear dipolar coupling, which in turn depends on the sum of  $r_{\text{SiH}}^{-6}$  over all Si-H distances for a given Si site. Thus, the protons that are closest to the Si, transfer magnetization faster and  $\tau_{\text{SiH}}$  will be dominated by the shortest distance. The experimental data, on a number of minerals, show a positive correlation between  $r_{\text{SiH}}$  and  $\tau_{\text{SiH}}$ . A rough inverse correlation was shown between  $\tau_{1\rho}(\text{H})$  values and large bulk H density, as expected from other studies showing that an increase in proton concentration is linked to a shorter  $\tau_{1\rho}(\text{H})$  [81S1].

### 8.1.4.7.5 Optical properties

#### Inesite

The IR absorption spectra of inesite were studied [68R1]. Based on the IR absorption spectra it was concluded that inesite contains single silicate chains with five-tetrahedral repeat

The refractive indices for some minerals are listed in Table 7.