(2) The total number of water molecules in a cavity is 9·4 (1·2). This is in close agreement with the values found for powder in room conditions by classical analysis (Table 1), or by thermogravimetric analysis.

To discuss the environments of Na^+ ions and water molecules, a hypothesis of the distribution inside a cavity is necessary. The solution obtained is likely to be an averaged value of a large number of possibilities. Fig. 3(*a*) shows all possible sites inside the cavity centred at ($\frac{2}{3},\frac{1}{3},\frac{1}{3}$). Fig. 3(*b*) and (*c*) are two hypotheses of ordered positions for which only $\bar{1}$ centres of symmetry are retained. Equal probabilities for these two distributions would lead to a formula unit with eight water molecules [one (1), one (2), one (3), three (4), two (5)]. The main purpose of such a hypothesis is to indicate some interatomic distances and to characterize two kinds of water molecules: some of them surround the Na^+ ions and others [one (4) and two (5) in the considered hypothesis] are mostly zeolitic ones. This could explain why the removal of water molecules occurs in two steps as observed with differential thermal analysis and thermogravimetric analysis.

It is impossible to establish the existence of hydrogen bonds from these results and we now intend to carry out a spectroscopic study of the series $M^{I}_{2}Zn_3[Fe(CN)_6]_2.xH_2O$ with M^{I} = Na, K, Cs to complete our crystallographic investigation.

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Structure of Lithium Sodium Yttrium Silicate $Na_2LiYSi_6O_{15}$

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Abstract

$Na_2LiYSi_6O_{15}$ is orthorhombic, space group *Cmca*, with cell dimensions a = 14·505 (1), b = 17·596 (1) and c = 10·375 (1) Å; Z = 8. The structure was refined by the block-diagonal least-squares method to R = 0·082 for 1501 independent reflections. The crystal structure consists of corrugated double silicate chains which have a six-tetrahedral repeat (*Sechser-Doppelkette*) in the **c** direction. Na(2) polyhedral chains and tetrahedral–octahedral chains composed of (LiO_4) and (YO_6) units link the silicate chains to form a three-dimensional structure. $Na_2LiYSi_6O_{15}$ is isostructural with synthetic $Na_2Mg_2Si_6O_{15}$ and the minerals zektzerite and emeleusite. The variation in the silicate component of these structures appears to be very small. Distortion of the tetrahedral site permits this structure type to accommodate a wide range of cations in the octahedral sites.

Introduction

Glasser & Marr (1979) reported the synthesis of $Na_2LiYSi_6O_{15}$, which from powder data was believed to be isostructural with $Na_2Mg_2Si_6O_{15}$ and with zektzerite, $NaLiZrSi_6O_{15}$ (Cradwick & Taylor, 1972; Ghose & Wang, 1978); both contain double silicate chains having a characteristic six-tetrahedral repeat known as *Sechser-Doppelkette*. The same anion is found to occur in the minerals tuhualite, $(Na,K)Fe^{2+}Fe^{3+}Si_6O_{15}.0{\cdot}5H_2O$, and emeleusite, $Na_2LiFeSi_6O_{15}$, whose structures were determined by Merlino (1969) and Neilsen & Søtofte (1978). In this work the crystal structure of $Na_2LiYSi_6O_{15}$ has been determined and its structure is compared with other isostructural phases.

Experimental

Single crystals were grown from a melt having the bulk composition (in mol%), Na_2O = 12·6, Li_2O = 6·2,

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Y_2O_3 = 6·2 and SiO_2 = 75·0. The melt was quenched to obtain a glass and this glass was crystallized at 1323 K for 72 h, yielding lath or plate-like crystals about 0·1–0·2 mm in length having low optical birefringence.

Intensity data were obtained using a Hilger & Watts Y-190 linear diffractometer (filtered Mo $K\alpha$ radiation, λ = 0·7107 Å, $\sin^2\theta \leq 0{\cdot}28$) for the layers ($h,k$,0–9). Balanced filters were employed and four count cycles were measured for each reflection, which reduced to two estimates of the intensity, yielding ultimately 1650 independent $|F_o|$, of which 1087 were classed as observed ($I \geq 3\sigma$). Absorption corrections were not applied.

All calculations were carried out on the Honeywell 66/80 computer of the Computing Centre at the University of Aberdeen. The programs used were those of Ahmed, Hall, Pippy & Huber (1966), modified by R. A. Howie and J. S. Knowles of the University of Aberdeen. Scattering factors for Na, Li^+, Si, O^{1-} and Y^{3+} were taken from *International Tables for X-ray Crystallography* (1974).

The values obtained by Cradwick & Taylor (1972) for $Na_2Mg_2Si_6O_{15}$ were used as starting atomic positions for the structure of $Na_2LiYSi_6O_{15}$. Preliminary structure factor calculations indicated that Li and Y of the present structure replaced Mg(1) (tetrahedral site) and Mg(2) (octahedral site) respectively in the structure of $Na_2Mg_2Si_6O_{15}$. Six cycles of block-diagonal least squares with unit weights and with all atoms allowed to vibrate isotropically yielded R = 0·15 (over all 'observed' reflections). At this stage the weighting scheme was modified to that proposed by Cruickshank: $w^{1/2} = 1/\{1 + [(|F_o| - b)/a]^2\}^{1/2}$ with a = 70 and b = 120. Six cycles of further refinement, excluding 59 reflections for which $|\Delta F|/|F_o|$ was in excess of 0·36 and with Y and Na atoms vibrating anisotropically, gave a final R factor of 0·0823 over the reflections included in the calculations (R = 0·1110 over all 'observed' reflections).

Table 1. *Atomic parameters of* $Na_2LiYSi_6O_{15}$

	x	y	z	B_{iso} (Å^2)
Na(1)	0·0000	0·4198 (6)	0·2602 (15)	4·76*
Na(2)	0·2500	0·2184 (4)	0·2500	1·86*
Li	0·2438 (25)	0·0000	0·0000	1·15 (49)
Y	0·2500	−0·0877 (1)	0·2500	0·52*
Si(1)	0·3917 (2)	0·1265 (2)	0·0244 (3)	0·09 (4)
Si(2)	0·3896 (2)	0·0790 (2)	0·3148 (3)	0·03 (4)
Si(3)	0·3921 (2)	0·1966 (1)	0·5387 (3)	0·04 (4)
O(1)	0·3795 (6)	0·2161 (5)	−0·0058 (9)	0·89 (13)
O(2)	0·3323 (6)	0·0764 (4)	−0·0700 (9)	0·53 (13)
O(3)	0·3624 (5)	0·1147 (4)	0·1750 (9)	0·50 (12)
O(4)	0·3385 (6)	0·0018 (4)	0·3435 (9)	0·51 (12)
O(5)	0·3601 (5)	0·1454 (4)	0·4142 (9)	0·43 (12)
O(6)	0·3373 (6)	0·1779 (4)	0·6649 (9)	0·90 (14)
O(7)	0·5000	0·1049 (6)	0·0007 (13)	0·71 (20)
O(8)	0·5000	0·0634 (6)	0·3192 (14)	0·71 (18)
O(9)	0·5000	0·1771 (7)	0·5645 (15)	1·08 (22)

* For these atoms $B_{iso} = \frac{4}{3}(a^2B_{11} + b^2B_{22} + c^2B_{33} + ab\cos\gamma B_{12} + ac\cos\beta B_{13} + bc\cos\alpha B_{23})$.

Table 2. *Interatomic distances* (Å) *and angles* (°)

(i) The Na polyhedra

Na(1)–O(2) [×2]	3·13 (1)	Na(2)–O(3) [×2]	2·57 (1)
Na(1)–O(4) [×2]	2·88 (1)	Na(2)–O(5) [×2]	2·66 (1)
Na(1)–O(6) [×2]	3·02 (1)	Na(2)–O(6) [×2]	2·39 (1)
Na(1)–O(7)	2·60 (2)	Na(2)–O(1) [×2]	3·25 (1)
Na(1)–O(8)	2·49 (2)	Na(2)–O(1′) [×2]	3·36 (1)
Na(1)–O(9)	2·74 (2)		

(ii) The SiO_4 tetrahedra

Si(1)–O(1)	1·62 (1)	O(1)–Si(1)–O(2)	111·4 (5)
Si(1)–O(2)	1·57 (1)	O(1)–Si(1)–O(3)	106·4 (5)
Si(1)–O(3)	1·63 (1)	O(1)–Si(1)–O(7)	107·6 (5)
Si(1)–O(7)	1·63 (1)	O(2)–Si(1)–O(3)	112·4 (5)
		O(2)–Si(1)–O(7)	107·6 (5)
		O(3)–Si(1)–O(7)	111·4 (5)
Si(2)–O(3)	1·63 (1)	O(3)–Si(2)–O(4)	112·8 (5)
Si(2)–O(4)	1·58 (1)	O(3)–Si(2)–O(5)	103·0 (5)
Si(2)–O(5)	1·62 (1)	O(3)–Si(2)–O(8)	109·2 (5)
Si(2)–O(8)	1·63 (1)	O(4)–Si(2)–O(5)	112·2 (5)
		O(4)–Si(2)–O(8)	108·2 (5)
		O(5)–Si(2)–O(8)	111·4 (5)
Si(3)–O(5)	1·64 (1)	O(5)–Si(3)–O(6)	113·4 (5)
Si(3)–O(6)	1·57 (1)	O(5)–Si(3)–O(9)	106·6 (5)
Si(3)–O(9)	1·62 (1)	O(5)–Si(3)–O(1)	105·4 (5)
Si(3)–O(1)	1·61 (1)	O(6)–Si(3)–O(9)	107·8 (5)
		O(6)–Si(3)–O(1)	112·4 (5)
		O(9)–Si(3)–O(1)	111·0 (5)

(iii) The Y octahedron

Y–O(2) [×2]	2·22 (1)
Y–O(4) [×2]	2·25 (1)
Y–O(6) [×2]	2·21 (1)

(iv) The Li tetrahedron

Li–O(2) [×2]	2·00 (2)
Li–O(4) [×2]	2·02 (2)

At this stage a final difference map revealed no significant features other than a slight ripple in the vicinity of the Y atoms. Analysis of the agreement between $|F_o|$ and $|F_c|$ showed that layer scaling was not required and confirmed that the weighting scheme was satisfactory. The final atomic positions are given in Table 1 and selected bond lengths and angles in Tables 2 and 3.*

Description of the structure

The structure of $Na_2LiYSi_6O_{15}$ consists of folded double silicate chains with a six-tetrahedral repeat (*Sechser-Doppelkette*), very similar to the anions found in synthetic $Na_2Mg_2Si_6O_{15}$, zektzerite, and emeleusite.

The corrugated silicate chains run parallel to **c**: each chain is two tetrahedra wide in the **a** direction, giving rise to a double silicate chain. This anion may also be

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36629 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Bond distances* (Å) *and angles* (°) *in* $Na_2LiYSi_6O_{15}$

Li—O	2·00 (3), 2·02 (2)
O—Li—O (all ±1·0°)	95·7, 100·0, 107·3, 131·6
Y—O	2·215 (9), 2·225 (9), 2·251 (8)
O—Y—O (all ±0·3°)	83·2, 88·4, 89·6, 90·2, 91·3, 92·1, 95·3, 169·8, 177·9
Si(1)—O(1)—Si(3)	149·2 (6)
Si(1)—O(3)—Si(2)	147·0 (6)
Si(2)—O(5)—Si(3)	145·5 (6)
Si(1)—O(7)—Si(1′)	147·8 (0)
Si(2)—O(8)—Si(2′)	160·2 (7)
Si(3)—O(9)—Si(3′)	148·8 (8)
Li—O(2)—Y	92·0 (7)
Li—O(4)—Y	89·9 (7)

considered as a ribbon formed by fusing together three different types of four-membered tetrahedral rings. The Si—O bonds involving bridging oxygens [O(1),(3),(5),(7),(8),(9)] are longer (mean value 1·62 Å) than those to the terminal O atoms (mean value 1·57 Å). The O—Si—O angles vary from 103–112°, with a mean value of 109·4°.

The Na(1) atoms are coordinated to nine O atoms. The six Na—O bonds (2·9–3·1 Å) involving O(2), O(4) and O(6) are arranged approximately in a trigonal prism with its axis parallel to **a** while the three remaining bonds (2·5–2·7 Å) are directed to the centres of the prism faces. The Na(2) atoms, which occur within cylindrical channels formed by the corrugation of the double chains, are irregularly coordinated to ten O neighbours. Four of these bonds involving O(1) are considerably longer (3·3–3·4 Å) than the other six bonds whose mean value is 2·6 Å.

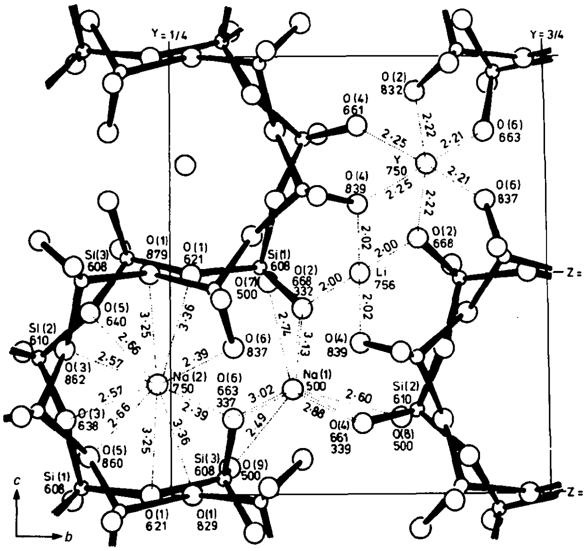

Fig. 1. Selected parts of the structure of $Na_2LiYSi_6O_{15}$ projected along **a** showing the coordination of the Li, Na, Y and Si atoms; heights are shown as 1000 X/a.

Table 4. *Coordination of* O *atoms in* $Na_2LiYSi_6O_{15}$

	Coordinated atoms	Electrostatic-valence sum
O(1)	Si(1), Si(3), Na(2), Na(2)	2·20
O(2)	Si(1), Li, Y, Na(1)	1·86
O(3)	Si(1), Si(2), Na(2)	2·10
O(4)	Si(2), Li, Y, Na(1)	1·86
O(5)	Si(2), Si(3), Na(2)	2·10
O(6)	Si(3), Y, Na(1), Na(2)	1·71
O(7)	Si(1), Si(1), Na(1)	2·11
O(8)	Si(2), Si(2), Na(1)	2·11
O(9)	Si(3), Si(3), Na(1)	2·11

Li is tetrahedrally coordinated to O at distances of 2·00–2·02 Å. Although Li—O distances in the LiO_4 tetrahedra show very little variation, O—Li—O angles show much higher deviations (95·7–131·6°) from the normal tetrahedral angles, indicating that this tetrahedron is highly distorted (Table 3). The Y atoms are octahedrally coordinated, with Y—O distances of 2·21–2·25 Å, and the octahedron is very nearly regular.

Fig. 1 shows the structure. The LiO_4 tetrahedra and YO_6 octahedra form a tetrahedral–octahedral chain parallel to, and linked with, the silicate double chain. This tetrahedral–octahedral chain is formed by sharing O(2) and O(4) by the LiO_4 tetrahedron and YO_6 octahedron.

Each octahedral–tetrahedral chain is connected to four adjacent silicate double chains and, similarly, each silicate double chain is linked to four adjacent octahedral–tetrahedral chains by sharing corners. The Na(2) polyhedral chains lying parallel to the *c* axis and formed by sharing O(1) atoms, are linked to silicate double chains as well as octahedral–tetrahedral chains, again by sharing edges and corners. The electrostatic valencies received by each O are given in Table 4. The values show that the bridging O atoms [O(1), O(3), O(5), O(7), O(8) and O(9)] are overbonded (>2·0) while the remaining O atoms [O(2), O(4) and O(6)] are underbonded (<2·0).

Discussion

Amongst silicates having the Si:O ratio 6:15, both chain and ring anions ($Si_{12}O_{30}$) appear to offer stable configurations. Despite much inquiry regarding the balance of forces which dictate whether chains or rings are stable for a particular composition (or, indeed, if either configuration is stable) it has proven difficult to assess the stability of different anion configurations quantitatively. The problem is further complicated if the comparison is extended to include single chains, $(SiO_3)_\infty$, and rings (i) because a great variety of chain configurations occur and (ii) because of the existence of many types of metasilicate rings, *e.g.* Si_3O_9, Si_4O_{12}, Si_6O_{18}, $Si_{12}O_{36}$.

One peculiarity of the *Sechser-Doppelkette* unit is that, unlike other metasilicate units, it does persist essentially unchanged in a wide variety of structures containing ions of different charges in octahedral sites, *e.g.* M^{2+}, M^{3+} and M^{4+}, as well as different numbers of charge-balancing cations. Thus, in the series $Na_2LiM^{3+}Si_6O_{15}$, stable phase formation occurs for octahedral ions as small as Fe^{3+} (0·66 Å) and as large as Sm^{3+} (0·96 Å). The present structure determination was undertaken because Y (0·90 Å) is amongst the largest trivalent ions which can be substituted in melt-grown crystals.

In the compounds $Na_2Mg_2Si_6O_{15}$, $Na_2LiFeSi_6O_{15}$, $NaLiZrSi_6O_{15}$ and $Na_2LiYSi_6O_{15}$ the following features are observed. In the unit cells of these compounds the *c* axis, which is parallel to the direction of propagation of the silicate double chains and is thus a rough measure of the degree to which the chains are folded, lies in the relatively narrow range 10·072–10·375 Å. Also, the Si—O—Si angles are similar in all four. Thus the silicate chain constitutes a stable and relatively inflexible building unit. Again, in all cases there is marked distortion of the bond angles at the tetrahedral site. We conclude, therefore, that this distortion enables the structure to accommodate a wide range of cations on the octahedral sites without necessitating changes to the *Sechser-Doppelkette* unit.

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The Structure of Sodium Strontium Phosphate Nonahydrate

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Abstract

The crystal structure of $SrNaPO_4.9H_2O$ has been determined by single-crystal X-ray diffraction. The crystals are cubic, $a = 10{\cdot}544\ (2)$ Å, space group $P2_13$, with $Z = 4$, $\rho_m = 2{\cdot}11$, $\rho_c = 2{\cdot}083$ g cm^{-3}. The structure was refined by full-matrix least-squares techniques to $R = 0{\cdot}025$ and $R_w = 0{\cdot}026$ for the 323 reflections used in the refinement. All cations and anions are completely surrounded by water molecules. All nine water molecules are coordinated to the same Sr^{2+} ion, forming a tricapped trigonal prism. The Na^+ ion is coordinated to six water molecules, forming a distorted octahedron. Extensive edge-sharing of $Sr(H_2O)_9$ and $Na(H_2O)_6$ polyhedra exists. The environment of the PO_4^{3-} ion consists of 15 water molecules all of which are probably hydrogen bonded to PO_4 oxygens. However, there is considerable disordering of the phosphate O atoms, somewhat similar to those of SO_4 groups in alums.

Introduction

A large number of struvite-type compounds and their structural relationships have been reported (Dickens & Brown, 1972; Mathew, Kingsbury, Takagi & Brown, 1982; Takagi, Mathew & Brown, 1982). A common feature of these struvite-type compounds (represented by the general formula $M^{2+}N^+XO_4.nH_2O$ where $n = 6$ to 8 and X = As or P) is that the ionic radius of the monovalent cation is larger than that of the divalent