Refinement of the Crystal Structure of Lithium Polysilicate

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Abstract. Synthetic $(Li_2SiO_3)_x$, orthorhombic, $Cmc2_1$ (C_{2v}^{12}), $a_o = 9.392$ (2), $b_o = 5.397$ (2), $c_o = 4.660$ (1) Å; $D_o = 2.54$ g cm^{-3}, $D_c = 2.53$ g cm^{-3} for $Z = 4$; R (unweighted) $= 0.066$, R (weighted) $= 0.043$. $[SiO_4]$ tetrahedra form chains parallel to [001] with two tetrahedra in the identity period. Lithium is tetrahedrally coordinated, with a mean Li–O distance of 2.00 Å.

Introduction. $(Li_2SiO_3)_x$ was prepared by melting a stoichiometric mixture of Li_2CO_3 and SiO_2 at 1240 °C and subsequent slow cooling in the furnace.

The density was determined by flotation in CH_2I_2–C_6H_6 mixtures (Midgley, 1951). A needle 0.063 × 0.075 × 0.280 mm was used for data collection on an automatic Philips four-circle diffractometer with graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å) and a θ–2θ scan ($\theta_{max} = 50°$). The intensities of 1459 crystallographically independent reflexions were measured; 275 of these had $|F_o| > 3\sigma(|F_o|)$, and these were used in the subsequent refinement. The standard deviation, $\sigma(F_o)$, was estimated by

$$\sigma(F_o) = \frac{1}{2} \frac{k}{\sqrt{\mathrm{Lp}}} \left[\frac{N_T + N_{bg1} + N_{bg2} + (0.01N_{pk})^2}{N_T - N_{bg1} - N_{bg2}} \right]^{1/2}$$

(Stout & Jensen, 1968), where N_T is the total peak count and N_{bg1} and N_{bg2} are the background counts on both sides of the peak. N_{pk} is defined by $N_{pk} = N_T - N_{bg1} - N_{bg2}$. No absorption correction was applied.

Table 3. *Comparison of atomic distances in the cation–oxygen polyhedra* $[A-O_4]$ *of the isostructural compounds*

	Na$_2$SiO$_3$ McDonald (1967)	Li$_2$SiO$_3$ This paper	Na$_2$GeO$_3$ Völlenkle, Wittmann & Nowotny (1971)	Li$_2$GeO$_3$ Völlenkle & Wittmann (1968)
A–O(2)	2.40 (1)	2.17 (1)	2.35 (1)	2.19 (3)
A–O(1''')	2.30 (1)	1.94 (1)	2.31 (1)	1.91 (3)
A–O(1'')	2.28 (1)	1.94 (1)	2.28 (1)	1.93 (3)
A–O(1')	2.37 (1)	1.96 (2)	2.41 (1)	1.99 (4)
A–O(1)	2.55 (1)	2.76 (2)	2.60 (1)	2.71 (4)
O(1'')–O(1''')	3.95 (1)	3.35 (1)	3.97 (1)	3.32 (3)
O(2)–O(1'')	4.00 (1)	3.38 (1)	4.00 (1)	3.38 (2)
O(2)–O(1''')	4.08 (1)	3.42 (1)	4.01 (1)'	3.32 (3)
O(1')–O(1''')	3.53 (1)	3.12 (1)	3.56 (1)	3.14 (3)
O(1')–O(1'')	3.52 (1)	3.12 (1)	3.52 (1)	3.16 (3)
O(1')–O(2)	3.46 (1)	3.14 (1)	3.40 (2)	3.30 (3)

Table 1. *Positional and thermal parameters* (× 10^4) *with standard deviations*

Anisotropic temperature factors have the form: $T = \exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Si	0 (0)	1703 (4)	4912 (45)	13 (2)	46 (5)	17 (6)	0 (0)	0 (0)	−13 (11)
Li	1737 (9)	3449 (18)	−24 (35)	34 (7)	52 (20)	117 (22)	21 (13)	24 (24)	−33 (42)
O(1)	1446 (4)	3077 (6)	4108 (9)	15 (3)	17 (10)	130 (14)	−10 (5)	5 (6)	−8 (11)
O(2)	0 (0)	1143 (9)	8461 (11)	34 (6)	25 (16)	68 (21)	0 (0)	0 (0)	−7 (14)

Table 2. *Bond lengths* (Å) *and angles* (°)

[Si–O$_4$] tetrahedra					[Li–O$_4$] tetrahedra		
Si–O(1)	1.592 (6) (2×)	O(1)–Si–O(2)	108.4 (8) (2×)	Li–O(1')	1.955 (17)	O(1'')–O(1''')	3.347 (5)
Si–O(2)	1.681 (21) (2×)	O(1)–Si–O(2')	109.4 (7) (2×)	Li–O(1'')	1.938 (11)	O(2)–O(1'')	3.378 (4)
Si–O(2')	1.678 (10)	O(1)–Si–O(1'''')	117.1 (6)	Li–O(1''')	1.937 (11)	O(2)–O(1''')	3.416 (6)
Average	1.636 (12)	O(2)–Si–O(2')	103.4 (6)	Li–O(2)	2.170 (11)	O(1')–O(1''')	3.121 (6)
O(1)–O(1'''')	2.716 (5)	Average	109.4 (3)	Average	2.000 (7)	O(1')–O(1'')	3.120 (6)
O(1)–O(2)	2.655 (6) (2×)					O(1')–O(2)	3.140 (6)
O(1)–O(2')	2.669 (5) (2×)			Li–O(1)	2.755 (17)	Average	3.254 (2)
O(2)–O(2')	2.637 (7)	Si–O–Si	124.1 (7)				
Average	2.667 (3)						

Anisotropic refinement of the crystal structure converged at R(unweighted) = 0·066 and R(weighted) = 0·043.* A list of positional and thermal parameters with estimated standard deviations is given in Table 1. Atomic distances and valence angles are shown in Tables 2 and 3.

Discussion. The structure given by Seemann (1955) with R = 26% has been confirmed and distinctly improved. [SiO$_4$] tetrahedra are corner linked to *Zweierketten* parallel to [001]. As in other silicates the Si–O bonds to the bridging oxygen, O(2), are remarkably longer than those to the terminal oxygens, O(1), in accordance with the $d_\pi-p_\pi$ bond theory of Cruickshank (1961). The value 124·1 (7)° for the Si–O–Si valence angle is rather low compared with the mean value, 137°, reported by Cameron, Sueno, Prewitt & Papike (1973) for pyroxenes.

McDonald & Cruickshank (1967) and Seemann (1955) respectively pointed out that in the isostructural (Na$_2$SiO$_3$)$_x$ the sodium ion occupies the approximate centre of a trigonal bipyramid while in (Li$_2$SiO$_3$)$_x$ the lithium ion has moved to one corner of the bipyramid, giving a [4 + 1] coordination with 2·02, 2·05, 2·11, 2·14 and 2·58 Å as Li–O distances. The values given in Table 3 reveal that the Li ions have moved even further into one half of the bipyramid, resulting in a normal tetrahedral [LiO$_4$] coordination. (Li$_2$SiO$_3$)$_x$ may be regarded as a framework of corner-linked [LiO$_4$] and [SiO$_4$] tetrahedra which is demonstrated by Fig. 1. As McDonald & Cruickshank (1967) have pointed out,

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32268 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

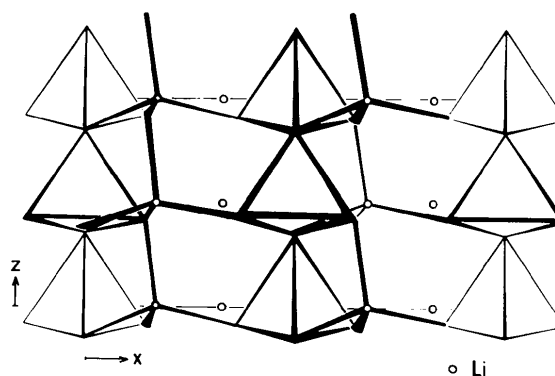Fig. 1. Projection of (Li$_2$SiO$_3$)$_x$ along [010].

the topology of this framework is identical with that of wurtzite, the hexagonal polymorph of ZnS.

References

CAMERON, M., SUENO, S., PREWITT, C. T. & PAPIKE. J. J. (1973). *Amer. Min.* **58**, 594–618.

CRUICKSHANK, D. W. J. (1961). *J. Chem. Soc.* pp. 5486–5504.

MCDONALD, W. S. & CRUICKSHANK, D. W. J. (1967). *Acta Cryst.* **22**, 37–43.

MIDGLEY, H. C. (1951). *Acta Cryst.* **4**, 565.

SEEMANN, H. (1955). *Acta Cryst.* **9**, 251–252.

STOUT, G. H. & JENSEN, L. H. (1968). *X-ray Structure Determination.* New York: Macmillan.

VÖLLENKLE, H. & WITTMANN, A. (1968). *Mh. Chem.* **99**, 244–250.

VÖLLENKLE, H., WITTMANN, A. & NOWOTNY, H. (1971). *Mh. Chem.* **102**, 964–970.

7-Chloromethylbenz[a]anthracene*

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Abstract. C$_{19}$H$_{13}$Cl, monoclinic, $P2_1/n$, a = 14·381 (7), b = 4·228 (2), c = 22·141 (7) Å, β = 95·87° (5), V = 1339 (2) Å^3, Z = 4, D_x = 1·370, D_m = 1·367 g cm^{-3} (by flotation in 1,1-dichloroethane–1,2-dibromoethane mixture), F.W. 276·77, λ(Cu K) = 1·5418 Å, μ(Cu K) = 23·2 cm^{-1}. The structure was solved by the direct phasing method and refined from 1717 diffractometer data [$I_o \geq 2.33\sigma(I)$] to R = 0·063, wR = 0·064. The ring system is essentially planar with the maximum atomic deviation ±0·05 Å. The Cl atom

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* Preliminary details of this structure were presented at the Tenth International Congress, IUCr, Amsterdam, The Netherlands, August 1975.