

Table 3. Selected bond lengths (Å) and angles (°) with *e.s.d.*'s in parentheses

H ₂ O I	
O(1)—H(1)	2 × 0.998 (3)
H(1)—O(1)—H(1)	102.0 (2)
O(3)···O(1)···O(3)	90.7 (1)
H ₂ O II	
O(2)—H(21)	1.007 (3)
O(2)—H(22)	1.007 (2)
H(21)—O(2)—H(22)	107.6 (2)
O(3)···O(2)···O(3)	115.8 (1)
OH ⁻	
O(3)—H(3)	0.948 (3)
H(3)···O(2)	2.275 (3)
Hydrogen bonding	
H(1)···O(3)	2 × 1.696 (2)
O(1)···O(3)	2 × 2.686 (2)
O(1)—H(1)···O(3)	2 × 171.0 (2)
H(21)···O(3)	1.667 (3)
O(2)···O(3)	2.668 (2)
O(2)—H(21)···O(3)	172.3 (2)
H(22)···O(3)	1.672 (2)
O(2)···O(3)	2.674 (2)
O(2)—H(22)···O(3)	173.3 (2)

References

- BAUER, O. (1903). *Z. Anorg. Chem.* **47**, 401–420; *Z. Angew. Chem.* **16**, 341–350.
- BUCHMEIER, W. & LUTZ, H. D. (1986). *Z. Anorg. Allg. Chem.* **538**, 131–142.
- CHIARI, G. & FERRARIS, G. (1982). *Acta Cryst.* **B38**, 2331–2341.
- CHIDAMBARAM, R., SEQUEIRA, A. & SIKKA, S. K. (1964). *J. Chem. Phys.* **41**, 3616–3622.
- KUSKE, P., ENGELEN, B., HENNING, J., LUTZ, H. D., FUESS, H. & GREGSON, D. (1988). *Z. Kristallogr.* **183**, 319–325.
- LEHMANN, M. S. & LARSEN, F. K. (1974). *Acta Cryst.* **A30**, 580–584.
- LUTZ, H. D. (1988). *Struct. Bonding (Berlin)*, **69**, 97–125.
- LUTZ, H. D., ECKERS, W., SCHNEIDER, G. & HAEUSELER, H. (1981). *Spectrochim. Acta Part A*, **37**, 561–567.
- LUTZ, H. D., HENNING, J. & HAEUSELER, H. (1987). *J. Mol. Struct.* **156**, 143–145.
- LUTZ, H. D., KUSKE, P. & HENNING, J. (1988). *J. Mol. Struct.* **176**, 149–157.
- LUTZ, H. D. & LANGE, N. (1989). To be published.
- SEARS, V. F. (1986). *Neutron Scattering Lengths and Cross Sections*. In *Neutron Scattering, Methods of Experimental Physics*, Vol. 23A, edited by K. SKÖLD & D. L. PRICE, pp. 521–550. New York: Academic Press.
- SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

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The Structure of Metastable Lithium Disilicate, Li₂Si₂O₅

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Abstract. Metastable lithium disilicate, Li₂Si₂O₅, *M*_r = 150.05, orthorhombic, *Pbcn*, *a* = 5.683 (4), *b* = 4.784 (5), *c* = 14.648 (13) Å, *V* = 398.2 (6) Å³, *Z* = 4, *D*_x = 2.503 Mg m⁻³, λ(Mo *K*α) = 0.71069 Å, μ = 0.77 mm⁻¹, *F*(000) = 296, *T* = 298 K, *R* = 0.063, *wR* = 0.071 for 366 independent reflections. The structure is similar to that of α-Na₂Si₂O₅ and consists of infinite silicate sheets, composed of corner-sharing SiO₄ tetrahedra, with the Li atoms situated in tetrahedral sites between the sheets.

Introduction. Ion exchange reactions potentially provide a *chimie douce* or convenient low-temperature route to new materials. The stable form of Li₂Si₂O₅ is well known (Liebau, 1961). We have prepared a

new metastable form by ion exchange of Na₂Si₂O₅. Its indexed powder pattern showed clearly that its unit cell and space group differed from that of stable Li₂Si₂O₅ and a full structural investigation was therefore undertaken. Metastable Li₂Si₂O₅ retains the silicate sheet configuration of the parent Na₂Si₂O₅ (Pant & Cruickshank, 1968) and is different from that in stable Li₂Si₂O₅.

Experimental. Crystals of Na₂Si₂O₅ were prepared by crystallizing glass of the same composition at 1073 K for 14 h. Lumps of crystallized material were immersed in molten LiNO₃ at 573 K for 3 d after which they were removed, washed in water and dried in an oven at 473 K. From these fragments a plate-

Table 1. Atomic parameters for metastable $\text{Li}_2\text{Si}_2\text{O}_5$ E.s.d's are in parentheses. Positional parameters and B_{ij} are $\times 10^4$

		x	y	z	B_{iso} or B_{eq}^* (\AA^2)		
Li	8(d)	6043 (20)	3058 (21)	4492 (6)	1.59 (13)		
Si	8(d)	944 (3)	3062 (3)	3513 (1)	1.04		
O(1)	4(c)	0	2438 (10)	2500	1.66		
O(2)	8(d)	-751 (8)	2127 (7)	4314 (2)	1.31		
O(3)	8(d)	3466 (7)	1434 (6)	3608 (2)	1.31		
		B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
Si		139 (3)	48 (4)	10 (1)	-4 (3)	-12 (3)	-4 (8)
O(1)		270 (20)	74 (19)	10 (2)	0	-28 (10)	0
O(2)		162 (12)	100 (13)	11 (1)	16 (7)	18 (7)	-3 (23)
O(3)		180 (11)	33 (10)	15 (1)	10 (7)	-25 (7)	21 (18)

* $B_{\text{eq}} = (4/3) \sum_i B_{ij} a_i a_j$, where the correction for anisotropic thermal vibration is of the form $\exp[-(h^2 B_{11} + k^2 B_{22} + l^2 B_{33} + hk B_{12} + hl B_{13} + kl B_{23})]$.

Table 2. Selected bond lengths (\AA) and angles ($^\circ$) for metastable $\text{Li}_2\text{Si}_2\text{O}_5$

Si coordination		Li coordination	
Si—O(1)	1.605 (2)	Li—O(2)	1.971 (11)
—O(2)	1.583 (4)	—O(2 ^{iv})	1.894 (12)
—O(3)	1.638 (4)	—O(2 ^v)	2.026 (10)
—O(3 ⁱ)	1.654 (3)	—O(3)	2.104 (11)
O(1)—Si—O(2)	115.4 (2)	O(2 ^v)—Li—O(2 ⁱⁱⁱ)	107.1 (5)
—O(3)	106.4 (2)	—O(2 ^{iv})	96.6 (5)
—O(3 ⁱ)	109.1 (2)	—O(3)	103.0 (5)
O(2)—Si—O(3)	109.6 (2)	O(2 ⁱⁱⁱ)—Li—O(2 ^v)	126.3 (6)
—O(3 ⁱ)	109.6 (2)	—O(3)	119.9 (5)
O(3)—Si—O(3 ⁱ)	106.2 (2)	O(2 ^v)—Li—O(3)	99.5 (5)
O(1) coordination		O(2) coordination	
Si—O(1)	1.605 (2) $\times 2$	O(2)—Si	1.583 (4)
Si—O(1)—Si ⁱⁱ	158.6 (2)	—Li ^v	1.894 (12)
		—Li ^{vi}	2.026 (10)
		—Li ^{vii}	1.971 (11)
O(3) coordination		Si—O(2)—Li ^v	128.4 (4)
O(3)—Li	2.104 (11)	—Li ^{vi}	110.3 (4)
—Si	1.638 (4)	—Li ^{vii}	115.4 (4)
—Si ^{vii}	1.654 (3)	Li ^v —O(2)—Li ^{vi}	112.1 (5)
Li—O(3)—Si	119.1 (3)	—Li ^{vii}	97.6 (5)
—Si ^{vii}	105.7 (3)	Li ^{vi} —O(2)—Li ^{vii}	83.3 (4)
Si—O(3)—Si ^{vii}	129.4 (2)		

Symmetry operations: (i) $\frac{1}{2} - x, \frac{1}{2} + y, z$; (ii) $-x, y, \frac{1}{2} - z$; (iii) $1 + x, y, z$; (iv) $\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$; (v) $-1 + x, y, z$; (vi) $-\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$; (vii) $\frac{1}{2} - x, -\frac{1}{2} + y, z$.

shaped crystal ($0.5 \times 0.3 \times 0.15$ mm) was selected for a single-crystal study. Nicolet P3 diffractometer. Graphite monochromator. Systematic absences: $0kl$, $k = 2n + 1$; $h0l$, $l = 2n + 1$; $hk0$, $h + k = 2n + 1$. 14 reflections ($17 < 2\theta < 18^\circ$) for refining unit-cell dimensions. ω - 2θ scan. 574 reflections measured ($0 < 2\theta < 60^\circ$), hkl , $h_{\text{max}} = 8$, $k_{\text{max}} = 6$, $l_{\text{max}} = 20$. Scan width 2.4 – 2.8° in 2θ , scan speed 5.33 – $58.6^\circ 2\theta \text{ min}^{-1}$. Two intensity reference reflections; no significant variation. Lorentz and polarization corrections applied in usual way, no absorption correction.

Crystal structure solved by Patterson function and successive Fourier syntheses; anisotropic block-diagonal least-squares refinement (on F) for non-Li atoms, isotropic form Li atoms. $w = 1/\{1 + [(|F_o| - 50)/20]^2\}$. Final $R = 0.063$, $wR = 0.071$ for 366

reflections [$I > 3\sigma(I)$]. Maximum shift/e.s.d in final least-squares cycle = 0.012 (for Li B_{iso}). Maximum and minimum peak heights in final difference synthesis: 1.42 and -0.97 e \AA^{-3} . Scattering factors for neutral atoms from *International Tables for X-ray Crystallography* (1974). NRC crystallographic programs (Ahmed, Hall, Pippy & Huber, 1966) used for all calculations. STRUPLO82 (Fischer, 1982) used for plotting all figures. Computer used: Honeywell DPS8/70 of the Computing Centre of the University of Aberdeen.

Discussion. Tables 1 and 2 report final atomic coordinates, bond distances and bond angles of the crystal structure.*

Fig. 1(a) presents a projection of the silicate sheets in metastable $\text{Li}_2\text{Si}_2\text{O}_5$ viewed along the b axis and shows clearly the corrugated sheets of SiO_4 tetrahedra running parallel to the a direction. The corners of the tetrahedra represent the O atoms of the SiO_4 tetrahedra; the Si atoms are not shown. The circles represent Li atoms. The tetrahedra lie with one face, containing three O atoms, approximately parallel to the xz plane, the fourth O atom being situated either above or below this plane. Where all four corners of the tetrahedron are shown, the fourth O atom is situated above the plane of the other three, otherwise it is situated below this plane.

The configurations of adjacent sheets in the c direction differ and are related by a c -glide plane perpendicular to b ; hence the SiO_4 tetrahedra in

* Lists of structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52367 (5 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

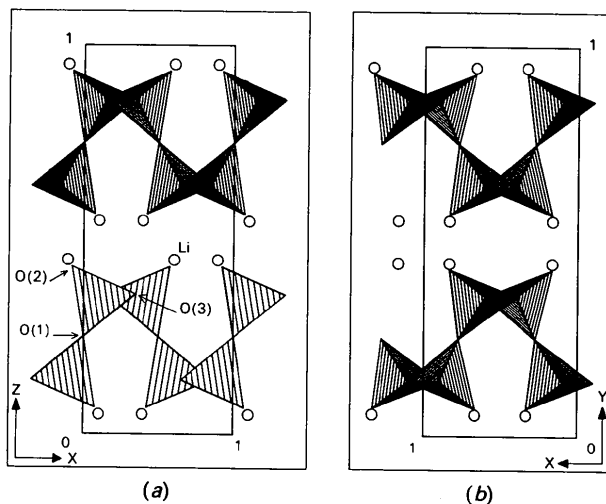


Fig. 1. (a) Projection of the structure of metastable $\text{Li}_2\text{Si}_2\text{O}_5$ along $[101]$. (b) Projection of the structure of $\text{Li}_2\text{Si}_2\text{O}_5$ along $[001]$.

adjacent sheets have the fourth O atom alternately above and below the plane of the other three and the tetrahedra in adjacent sheets appear to 'point' in opposite directions, Fig. 1(a). Li atoms are located between the sheets and are coordinated to three O atoms of one sheet and one O atom of the other. Bond distances and angles are reasonable for tetrahedrally coordinated Li and Si (Liebau, 1985; Shannon & Prewitt, 1969).

Comparison of this structure and cell dimensions with that of the parent $\text{Na}_2\text{Si}_2\text{O}_5$ [$a = 6.409$ (2), $b = 15.422$ (4), $c = 4.896$ (2) Å (Pant & Cruickshank, 1968)] shows that whereas b and c are only a few per cent less, a is approximately 15% less in the metastable $\text{Li}_2\text{Si}_2\text{O}_5$ structure. The structural consequences are that the silicate sheets exhibit tighter corrugation in the a direction. This causes the Li coordination to be tetrahedral whereas the Na in $\text{Na}_2\text{Si}_2\text{O}_5$ is closer to five coordinate (Pant & Cruickshank, 1968).

It should also be noted that each of the three crystallographically independent O atoms has its own unique coordination with the Li and Si atoms. The bridging O atoms, O(1) and O(3), are linearly and planar trigonally coordinated respectively, whereas the terminal O atom, O(2), is tetrahedrally coordinated, Table 2.

The silicate sheet configuration in metastable $\text{Li}_2\text{Si}_2\text{O}_5$, Fig. 1(a), differs from that in stable $\text{Li}_2\text{Si}_2\text{O}_5$, Fig. 1(b), (Liebau, 1961). In the latter the tetrahedra lie, as in the metastable form, with one face containing three O atoms approximately parallel to the xy plane. The difference, however, lies in the position of

the fourth O atom, which is always situated above the plane of the other three. Thus the tetrahedra 'point' in the same direction; the silicate sheets are in the same orientation and are simply related by C-centring.

This significant difference in the geometry of the silicate sheets in the stable and metastable forms of $\text{Li}_2\text{Si}_2\text{O}_5$ is reflected in the kinetic stability of the metastable form which shows no evidence of decomposition or transformation to the stable form at temperatures below 673 K.

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References

- AHMED, F. R., HALL, S. R., PIPPY, M. E. & HUBER, C. P. (1966). *NRC Crystallographic Programs for the IBM 360 System*. National Research Council of Canada, Ottawa, Canada.
- FISCHER, R. X. (1982). *STRUPLO82. A Fortran Program for the Graphical Display of Crystal Structures*. Univ. of Mainz, Federal Republic of Germany.
- International Tables for X-ray Crystallography* (1974). Vol. IV, 2nd ed., pp. 202–203. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- LIEBAU, F. (1961). *Acta Cryst.* **14**, 389–395.
- LIEBAU, F. (1985). *Structural Chemistry of Silicates. Structure, Bonding and Classification*. Berlin, Heidelberg, New York, Tokyo: Springer-Verlag.
- PANT, A. K. & CRUICKSHANK, D. W. J. (1968). *Acta Cryst.* **B24**, 13–19.
- SHANNON, R. D. & PREWITT, C. T. (1969). *Acta Cryst.* **B25**, 925–945.

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Structure du Sulfure de Thulium et de Zinc ZnTm_2S_4

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Abstract. $M_r = 531.49$, orthorhombic, $Pnma$, $a = 13.308$ (5), $b = 7.769$ (3), $c = 6.285$ (2) Å, $V = 649.8$ (7) Å³, $Z = 4$, D_m (293 K) = 5.3 (1), $D_x = 5.42$ (3) Mg m⁻³, $\text{Mo } K\alpha$, $\lambda = 0.71069$ Å, $\mu = 32.9$ mm⁻¹, $F(000) = 232$, $T = 293$ K, $R = 0.0393$ for 573 observed reflections. ZnTm_2S_4 has the olivine structure. The Tm^{III} atoms have an octahedral coordination (Tm—S: 2.671 to 2.744 Å) and the Zn^{II}

atoms a tetrahedral coordination (Zn—S: 2.294 to 2.388 Å). Distortions of the coordination octahedra and tetrahedra are discussed.

Introduction. Les composés de formule ZnB_2S_4 présentent une structure de type spinelle direct pour $B = \text{Cr}^{3+}$ ou Sc^{3+} (Raccach, Bouchard & Wold, 1966; Tressler, Hummel & Stubican, 1968), et une structure