

INORGANIC COMPOUNDS

Acta Cryst. (1995). C51, 1959–1960

Low-Temperature Form of LiGaSi₂O₆

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(Received 4 October 1994; accepted 4 April 1995)

Abstract

The structure of the low-temperature form of gallium lithium metasilicate, LiGaSi₂O₆, has been determined from diffractometer data obtained at 273 K. The title structure is similar to that of pigeonite [(Mg_{0.39}Fe_{0.52}Ca_{0.09})SiO₃].

Comment

Solid-state ⁶⁹Ga NMR spectra of the title compound, (I), indicate that there is a phase transition dependent on the temperature (Ohashi, Osawa, Sato & Onoda, 1995). Compound (I) is isostructural with (Mg_{0.39}Fe_{0.52}Ca_{0.09})SiO₃ (Morimoto & Guven, 1970) and the low-temperature forms of LiFeSi₂O₆ and LiCrSi₂O₆ (Behruzi, Hahn, Prewitt & Baldwin, 1984). Li is coordinated by seven O atoms and Ga is coordinated by six O atoms. There are two crystallographically different kinds of single silicate chain in the structure. This low-temperature form (*P*2₁/*c*) transforms to the high temperature form (*C*2/*c*) at 285 K (Sato, Osawa & Ohashi, 1994).

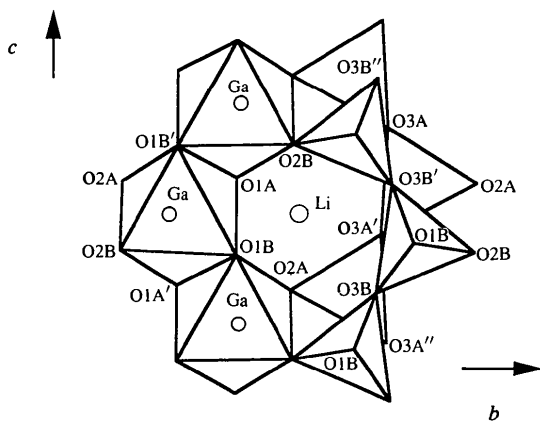


Fig. 1. Projection of the structure of LiGaSi₂O₆. The nomenclature of the O atoms is that used by Morimoto & Guven (1970).

Experimental

The title compound was prepared according to the procedure described by Ohashi, Osawa & Sato (1989).

Crystal data

LiGaSi₂O₆
M_r = 228.83
Monoclinic
*P*2₁/*c*
a = 9.5394 (4) Å
b = 8.5756 (2) Å
c = 5.2508 (3) Å
β = 110.124 (2)°
V = 403.32 (3) Å³
Z = 4
*D*_x = 3.77 Mg m⁻³

Mo *K*α radiation
λ = 0.71073 Å
Cell parameters from 22 reflections
θ = 27.7–32.0°
μ = 7.32 mm⁻¹
T = 273 K
Prism
0.28 × 0.14 × 0.13 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω/2θ scans
Absorption correction: by integration from crystal shape
*T*_{min} = 0.343, *T*_{max} = 0.439
2605 measured reflections
2605 independent reflections
2127 observed reflections
[*I* > 1.5σ(*I*)]

θ_{max} = 40°
h = 0 → 16
k = 0 → 15
l = -9 → 9
3 standard reflections monitored every 100 reflections for orientation and every 240 min for intensity decay: 1.2%

Refinement

Refinement on *F*
R = 0.041
ω*R* = 0.043
S = 1.4
2127 reflections
92 parameters
Unit weights applied
(Δ/σ)_{max} < 0.005
Δρ_{max} = 2.0 e Å⁻³
Δρ_{min} = -2.2 e Å⁻³

Extinction correction: isotropic secondary extinction
Extinction coefficient: 3.16 × 10⁻⁶
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i\cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Ga	0.25033 (3)	0.65098 (3)	0.23963 (5)	0.00407 (4)
Li	0.2479 (9)	0.0125 (9)	0.237 (1)	0.016 (1)
SiA	0.04726 (8)	0.34077 (9)	0.2683 (1)	0.0041 (1)
SiB	0.54799 (8)	0.84060 (9)	0.2525 (1)	0.0040 (1)
O1A	0.8640 (2)	0.3326 (2)	0.1534 (3)	0.0048 (3)
O2A	0.1148 (2)	0.5121 (3)	0.3132 (4)	0.0075 (4)
O3A	0.1081 (2)	0.2623 (3)	0.5688 (4)	0.0070 (3)
O1B	0.3645 (2)	0.8336 (3)	0.1340 (4)	0.0052 (3)
O2B	0.6189 (2)	1.0085 (3)	0.3431 (4)	0.0076 (4)
O3B	0.6064 (2)	0.7307 (3)	0.5210 (4)	0.0086 (4)

Table 2. Selected geometric parameters (Å, °)

SiA—O1A ⁱ	1.643 (2)	O2B···O3B ⁱⁱⁱ	2.635 (3)
SiA—O2A	1.589 (2)	O2B···O3B	2.576 (3)
SiA—O3A	1.628 (2)	O3B ⁱⁱⁱ ···O3B	2.646 (3)
SiA—O3A ⁱⁱ	1.623 (2)	O1A ^v ···O1A ^{iv}	2.983 (3)
SiB—O1B	1.645 (2)	O1A ^v ···O2A	2.857 (3)
SiB—O2B	1.592 (2)	O1A ^v ···O1B	2.607 (3)
SiB—O3B ⁱⁱⁱ	1.621 (3)	O1A ^v ···O2B ^{vii}	2.713 (3)
SiB—O3B	1.626 (2)	O1A ^{iv} ···O2A	2.757 (3)
Ga—O1A ^{iv}	2.086 (2)	O1A ^{iv} ···O1B	2.770 (3)
Ga—O1A ^v	1.980 (2)	O1A ^{iv} ···O1B ^{vi}	2.607 (3)
Ga—O1B	2.089 (2)	O2A···O1B ^{vi}	2.739 (3)
Ga—O1B ^{vi}	1.985 (2)	O2A···O2B ^{vii}	2.927 (3)
Ga—O2A	1.893 (2)	O1B···O1B ^{vi}	2.992 (3)
Ga—O2B ^{vii}	1.900 (2)	O1B···O2B ^{vii}	2.793 (3)
O1A ⁱ ···O2A	2.723 (3)	O1B ^{vi} ···O2B ^{vii}	2.900 (3)
O1A ⁱ ···O3A	2.655 (3)	Li—O1A ^{vii}	2.066 (8)
O1A ⁱ ···O3A ⁱⁱ	2.645 (3)	Li—O1B ^{viii}	2.074 (8)
O2A···O3A	2.540 (3)	Li—O2A ⁱⁱ	2.162 (6)
O2A···O3A ⁱⁱ	2.670 (3)	Li—O2B ^{ix}	2.138 (6)
O3A···O3A ⁱⁱ	2.634 (3)	Li—O3A ⁱⁱ	2.341 (7)
O1B···O2B	2.740 (3)	Li—O3B ^{xiii}	2.928 (9)
O1B···O3B ⁱⁱⁱ	2.631 (3)	Li—O3B ^{ix}	2.679 (7)
O1B···O3B	2.647 (2)		
O1A ⁱ —SiA—O2A	114.8 (1)	Ga—O1B—Ga ⁱⁱⁱ	100.2 (1)
O1A ⁱ —SiA—O3A	108.5 (1)	O1A ^v —Ga—O1A ^{iv}	94.4 (1)
O1A ⁱ —SiA—O3A ⁱⁱ	108.2 (1)	O1A ^v —Ga—O2A	95.0 (1)
O2A—SiA—O3A	104.3 (1)	O1A ^v —Ga—O1B	79.6 (1)
O2A—SiA—O3A ⁱⁱ	112.5 (1)	O1A ^v —Ga—O1B ^{vi}	172.1 (1)
O3A—SiA—O3A ⁱⁱ	108.2 (1)	O1A ^v —Ga—O2B ^{vii}	88.7 (1)
O1B—SiB—O2B	115.7 (1)	O1A ^{iv} —Ga—O2A	87.6 (1)
O1B—SiB—O3B ⁱⁱⁱ	107.3 (1)	O1A ^{iv} —Ga—O1B	83.1 (1)
O1B—SiB—O3B	108.0 (1)	O1A ^{iv} —Ga—O1B ^{vi}	79.6 (1)
O2B—SiB—O3B ⁱⁱⁱ	110.2 (1)	O1A ^{iv} —Ga—O2B ^{vii}	170.7 (1)
O2B—SiB—O3B	106.3 (1)	O2A—Ga—O1B	168.9 (1)
O3B ⁱⁱⁱ —SiB—O3B	109.1 (1)	O2A—Ga—O1B ^{vi}	89.9 (1)
SiA—O3A—SiA ^x	139.8 (1)	O2A—Ga—O2B ^{vii}	101.0 (1)
O3A···O3A ⁱⁱ ···O3A ⁱⁱ	170.8 (1)	O1B—Ga—O1B ^{vi}	94.5 (1)
Ga—O1A ^{iv} —Ga ⁱⁱⁱ	100.5 (1)	O1B—Ga—O2B ^{vii}	88.8 (1)
SiB—O3B ⁱⁱⁱ —SiB ⁱⁱⁱ	139.9 (2)	O1B ^{vi} —Ga—O2B ^{vii}	96.5 (1)
O3B ⁱⁱⁱ ···O3B···O3B ^{vi}	165.7 (1)		

Symmetry codes: (i) $x - 1, y, z$; (ii) $x, \frac{1}{2} - y, z - \frac{1}{2}$; (iii) $x, \frac{3}{2} - y, z - \frac{1}{2}$; (iv) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$; (v) $1 - x, 1 - y, -z$; (vi) $x, \frac{3}{2} - y, \frac{1}{2} + z$; (vii) $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$; (viii) $x, y - 1, z$; (ix) $1 - x, 1 - y, 1 - z$; (x) $x, \frac{1}{2} - y, \frac{1}{2} + z$; (xi) $x, y, z - 1$.

The structure was solved by direct methods with *MULTAN11/82* (Main *et al.*, 1982). All calculations were performed with the *SDP* program system (B. A. Frenz & Associates Inc., 1985).

Lists of structure factors and anisotropic displacement parameters have been deposited with the IUCr (Reference: OH1080). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1995). **C51**, 1960–1962

TaOI₂: Eine zentrosymmetrische Variante der NbOI₂-Struktur

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(Eingegangen am 16. Januar 1995; angenommen am 15. März 1995)

Abstract

The crystal structure of tantalum(IV) oxide diiodide was determined by single-crystal X-ray diffraction. TaOI₂ contains sheets of distorted TaO₂I₄ octahedra which share *trans* I–I edges and *trans* O corners (centrosymmetric MoOCl₂ type). The Ta atoms are displaced from the centres of the octahedra forming Ta···Ta pairs [3.100(2) Å]. The structure is closely related to the structure of NbOI₂, which was reported as the non-centrosymmetric NbOCl₂ type.

Kommentar

TaOI₂ kristallisiert im MoOCl₂-Typ (Schäfer & Schnering, 1964). Die Ta-Atome sind verzerrt oktaedrisch von je zwei *trans*-ständigen O-Atomen und vier I-Atomen in der Oktaederbasis umgeben. Über die I-Atome sind diese Oktaeder zu linearen Strängen verbunden. Die Verzerrung der Oktaeder resultiert aus dem paarweisen Zusammenrücken der Ta-Atome [$d(\text{Ta—Ta}) = 3,100(2) \text{ \AA}$], so daß genauer von Ketten aus *trans*-kantenverknüpften Ta₂O₄I₆-Doppeloktaedern gesprochen werden muß. Die gleichzeitige Eckenverknüpfung der Oktaeder über gemeinsame O-Atome führt zu Schichten, die zusammenfassend als $\frac{2}{\infty}[\text{Ta}_2\text{O}_4/2\text{I}_2\text{I}_4/2]$ formuliert werden können. Die Oberfläche einer solchen Schicht besteht aus einem leicht gewellten, angenähert quadratischen Netz von I-Atomen. Die Stapelung der Schichten entlang der kristallographischen *a*-Achse erfolgt in der Weise, daß die Iodatome der benachbarten Schicht über den Mittelpunkten dieser Quadrate liegen.

Der strukturelle Aufbau von TaOI₂ (Raumgruppe *C2/m*) lehnt sich eng die im NbOCl₂-Typ kristallisierenden Nioboxiddihalogenide (Schäfer & Schnering, 1964) an. In einer detaillierteren Arbeit über die Struktur von NbOI₂ (Rijnsdorp & Jellinek, 1978)