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Low-Density Form of $NaGaSi_2O_6$

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Abstract

The structure of the title compound, gallium sodium silicate, is similar to that of jadeite ($NaAlSi_2O_6$). Comparison of the new crystal-structure refinement for $NaGaSi_2O_6$ with published refinements for eleven $NaM^{3+}Si_2O_6$ pyroxenes suggests that there are two different electronic states, Ga(α) and Ga(β), for the octahedral Ga^{3+} ion. Ga(α) occurs in the Mn–Fe–Ga(α) series and Ga(β) in the Al–Ga(β)–In series.

Comment

The structure of the title compound is isostructural with $NaAlSi_2O_6$, $NaCrSi_2O_6$ and $NaFeSi_2O_6$ (Clark, Appleman & Papike, 1969), $NaScSi_2O_6$ (Hawthorne & Grundy, 1973), $NaInSi_2O_6$ (Hawthorne & Grundy, 1974), $NaTiSi_2O_6$ (Ohashi, Fujita & Osawa, 1982), Na Ga(α)Si_2O_6 (Ohashi, Fujita & Osawa, 1983) $NaMnSi_2O_6$ (Ohashi, Osawa & Tsukimura, 1987) and $NaVSi_2O_6$ (Ohashi, Osawa & Sato, 1994).

The cell parameters of the Na Ga(α)Si_2O_6 pyroxene are: a = 9.557 (5), b = 8.679 (4), c = 5.260 (1) Å, β = 107.68 (2)° and V = 415.7 (3) Å^3 (Ohashi *et al.*, 1983). The calculated density (D_x) is 3.91 Mg m^{-3} and is higher than that (D_x = 3.89 Mg m^{-3}) of the Na Ga(β)Si_2O_6 pyroxene studied here. The atomic z coordinate for O1 [z = 0.1312 (7)] of the Na Ga(α)Si_2O_6 pyroxene differs from that of the Na Ga(β)Si_2O_6 pyroxene.

The O1—Si—O2 angle is the largest O—Si—O angle in the $NaM^{3+}Si_2O_6$ pyroxenes. This may be due in part to the greater repulsion between the more negatively charged non-bridging O atoms. As shown in Fig. 2, the O1—Si—O2 angles correlate with the differences d_{br-nbr} in such a way that they follow three different trends: the Sc–Ti–V–Cr series, the Mn–Fe–Ga(α) series and the Al–Ga(β)–In series, where d_{br-nbr} = ⟨Si—O_{br}⟩ − ⟨Si—O_{nbr}⟩ (br = bridging, nbr = non-bridging), ⟨Si—O_{br}⟩ = 1/2(Si—O3*A*1 + Si—O3*A*2)

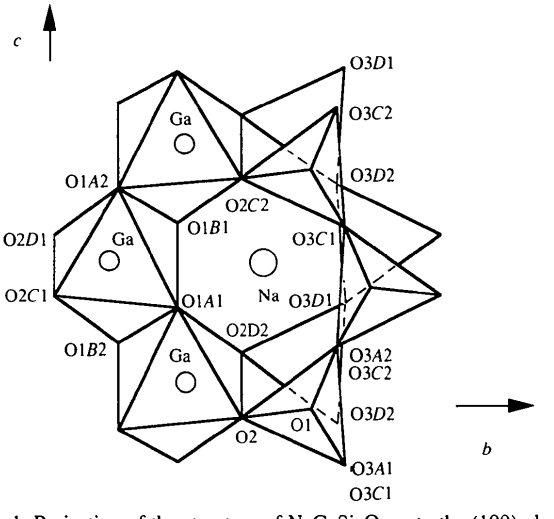

Fig. 1. Projection of the structure of $NaGaSi_2O_6$ onto the (100) plane. Atom labelling follows that used by Clark *et al.* (1969).

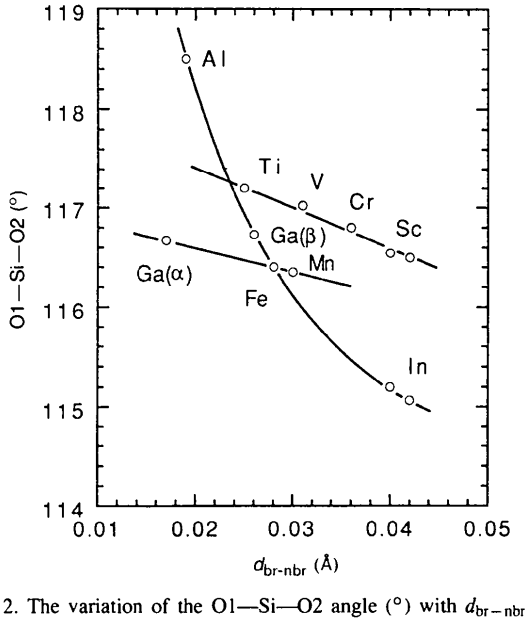

Fig. 2. The variation of the O1—Si—O2 angle (°) with d_{br-nbr} (Å) for the $NaM^{3+}Si_2O_6$ pyroxenes. Data are from Ohashi *et al.* (1994).

and $\langle Si—O_{nbr}\rangle$ = 1/2(Si—O1 + Si—O2). These trends suggest that there are two different electronic states for the octahedral Ga^{3+} ion.

Experimental

The title compound was prepared by solid-state reaction using belt-type high-pressure apparatus. A mixture of crystalline $Na_2Si_2O_5$, Ga_2O_3 and SiO_2 was sealed in a platinum capsule and maintained at 1770 K and 6 GPa for 5 h.

Crystal data

$NaGaSi_2O_6$
M_r = 244.88
Monoclinic
$C2/c$
a = 9.5573 (5) Å
b = 8.7019 (2) Å
c = 5.2705 (3) Å
β = 107.637 (2)°
V = 417.73 (4) Å^3
Z = 4
D_x = 3.89 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.7107 Å
Cell parameters from 22 reflections
θ = 13.8–16.3°
μ = 7.17 mm^{-1}
T = 296 K
Prism
0.09 × 0.04 × 0.04 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: by integration from crystal shape
T_{min} = 0.673, T_{max} = 0.771
728 measured reflections
728 independent reflections
649 observed reflections [$I > 1.5\sigma(I)$]
θ_{max} = 31.5°
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 12$
$l = -7 \rightarrow 7$
3 standard reflections monitored every 100 reflections for orientation and every 240 min for intensity
intensity decay: none

Refinement

Refinement on F
R = 0.018
wR = 0.029
S = 1.3
649 reflections
48 parameters
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max} < 0.005$
$\Delta\rho_{max}$ = 0.480 e Å^{-3}
$\Delta\rho_{min}$ = −0.657 e Å^{-3}
Extinction correction: isotropic secondary
Extinction coefficient: 1.83 × 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* (Å^2)

$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
Na	0	0.3005 (1)	1/4	0.0125 (3)
Ga	0	0.90189 (3)	1/4	0.00471 (5)
Si	0.29116 (5)	0.09116 (5)	0.2322 (1)	0.0043 (1)
O1	0.1120 (2)	0.0779 (1)	0.1334 (3)	0.0057 (3)
O2	0.3587 (2)	0.2588 (2)	0.3018 (3)	0.0076 (3)
O3	0.3527 (1)	0.0097 (2)	0.0076 (2)	0.0068 (3)

Table 2. *Selected geometric parameters* (Å, °)

Si tetrahedron		Ga octahedron		
Si—O1	1.636 (1)	Ga^{ii}—O1$A1$, $B1^{iii}$		2.066 (1)
Si—O2	1.592 (1)	Ga^{ii}—O1$A2^{i}$, $B2^{iv}$		1.987 (1)
Si—O3$A1$	1.634 (2)	Ga^{ii}—O2$C1^{v}$, $D1^{vi}$		1.917 (1)
Si—O3$A2^{i}$	1.646 (1)	Mean of 6		1.990
Mean of 4	1.627			
O1···O2	2.748 (2)	O1$A1$···O1$B1^{iii}$		2.773 (2)
O1···O3$A1$	2.647 (2)	O2$C1^{vi}$···O2$D1^{vi}$		2.914 (2)
O1···O3$A2^{i}$	2.649 (2)	O1$A1$···O2$C1^{v}$	×2	2.802 (2)
O2···O3$A1$	2.655 (2)	O1$A1$···O1$A2^{i}$	×2	2.964 (2)
O2···O3$A2^{i}$	2.584 (2)	O1$A2^{i}$···O2$C1^{v}$	×2	2.783 (2)
O3$A1$···O3$A2^{i}$	2.641 (2)	O1$A2^{i}$···O2$D1^{vi}$	×2	2.894 (2)
Si···Si^{i}	3.0760 (7)	O1$A1$···O1$B2^{iv}$	×2	2.565 (2)
		Ga^{ii}···Ga^{vii}		3.1401 (2)
O1—Si—O2	116.73 (7)	O1$A1$—Ga^{ii}—O1$B1^{iii}$		84.30 (6)
O1—Si—O3$A1$	108.11 (7)	O1$A1$—Ga^{ii}—O2$C1^{v}$	×2	89.32 (6)
O1—Si—O3$A2^{i}$	107.66 (7)	O1$A1$—Ga^{ii}—O1$A2^{i}$	×2	93.95 (5)
O2—Si—O3$A1$	110.76 (8)	O1$A1$—Ga^{ii}—O1$B2^{iv}$	×2	78.47 (5)
O2—Si—O3$A2^{i}$	105.89 (7)	O1$A2^{i}$—Ga^{ii}—O2$C1^{v}$	×2	90.94 (5)
O3$A1$—Si—O3$A2^{i}$	107.25 (7)	O1$A2^{i}$—Ga^{ii}—O2$D1^{vi}$	×2	95.65 (5)
		O2$C1^{v}$—Ga^{ii}—O2$D1^{vi}$		98.96 (6)
Na antiprism				
Na—O1$A1$, $B1^{iii}$	2.382 (2)	Si—O3—Si^{xiv}		139.40 (8)
Na—O2$C2^{viii}$, $D2^{ix}$	2.395 (1)	Ga^{ii}—O1—Ga^{vii}		101.53 (5)
Na—O3$C1^{x}$, $D1^{xi}$	2.417 (2)	O3^{i}···O3···O3^{xiv}		172.64 (8)
Na—O3$C2^{xii}$, $D2^{xiii}$	2.777 (2)			
Mean of 8	2.493			

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

Data were collected using Enraf–Nonius (1989) *CAD-4 Software*. The structure determination was initiated with the atomic parameters of $NaAlSi_2O_6$ given by Clark *et al.* (1969). All calculations were performed with the *SDP* program system (B. A. Frenz & Associates Inc., 1982).

Lists of structure factors and anisotropic displacement parameters have been deposited with the IUCr (Reference: OH1083). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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