Refinement of the Structure of 'Sodium Gadolinium Silicate', NaGdSiO$_4$.xNaOH ($x \simeq 0 \cdot 2$)

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Abstract. NaGdSiO$_4$.0·213NaOH, $M_r = 280 \cdot 8$, tetragonal, $I\bar{4}$, $a = 11 \cdot 748$ (6), $c = 5 \cdot 450$ (3) Å, $U = 752 \cdot 2$ Å^3, $Z = 8$, $D_c = 4 \cdot 96$ g cm^{-3}, μ(Mo $K\alpha$) = $171 \cdot 5$ cm^{-1}; final $R = 0 \cdot 028$ for 1176 reflections. The Gd atom has distorted eightfold coordination; of the two Na atoms one is seven coordinate and the other ten coordinate; the Si atom is tetrahedral. The Na$^+$ and OH$^-$ ions partially occupy the $4(e)$ and $2(a)$ sites respectively.

Introduction. In a study of some sodium rare-earth silicates Shannon, Gier, Foris, Nelen & Appleman (1980) found that crystal symmetry and space-group extinction conditions for 'NaGdSiO$_4$' were consistent with data represented by Avetisyan, Chichagov & Belov (1971), but that a positive second-harmonic-generation test (SHG) implied a non-centrosymmetric space group, $I4$ or $I\bar{4}$, rather than the centrosymmetric space group, $I4/m$, that Avetisyan *et al.* (1971) used to refine the structure of 'NaGdSiO$_4$'. Because of this discrepancy we have redetermined the structure of 'NaGdSiO$_4$'.

Laue symmetry, systematic absences $h + k + l = 2n + 1$, and a positive SHG test limit the possible space groups to $I4$ and $I\bar{4}$. $I\bar{4}$ gave a satisfactory result for the structure refinement. A tetragonal prismatic crystal with approximate dimensions $0 \cdot 04 \times 0 \cdot 04 \times 0 \cdot 12$ mm was used for intensity collection. The ω–2θ scan technique was used to measure, on a Philips automatic four-circle diffractometer, with graphite-monochromated Mo $K\alpha$ radiation, intensities up to $2\theta = 80°$. The scan speed was $0 \cdot 02°$ s^{-1} in ω and the scan width was calculated from $(1 \cdot 44 + 0 \cdot 3 \tan \theta)°$. Intensities were corrected for the Lorentz–polarization factor and absorption corrections were applied using *SHELX* 76 (Sheldrick, 1976). 1176 independent reflections with $|F| > 6\sigma(|F|)$ were used for the structure determination.

The attempted solution in $I4$ failed. Solution in $I\bar{4}$ was achieved when the Gd atom was slightly displaced from zero in the $8(h)$ position of $I4/m$; that is into the $8(g)$ position of $I\bar{4}$ ($R = 0 \cdot 158$). A difference Fourier synthesis based on this Gd position revealed the Si, Na and O atoms required for the formulation NaGdSiO$_4$

Table 1. *Fractional atomic coordinates* ($\times 10^5$ *for* Gd, $\times 10^4$ *for others*) *and equivalent isotropic thermal parameters* (Å^2 $\times 10^4$)

	x	y	z	Number of atoms per unit cell	Site	U_{eq}*
Gd	18429 (2)	11682 (2)	2157 (5)	8	8(g)	57 (1)
Si	1022 (1)	2465 (1)	4900 (4)	8	8(g)	59 (6)
Na(1)	896 (3)	3943 (3)	−74 (8)	8	8(g)	161 (14)
Na(2)	0	0	4304 (27)	1·7	4(e)	232 (72)
O(1)	335 (5)	2069 (6)	2449 (10)	8	8(g)	120 (22)
O(2)	1077 (4)	3849 (4)	5155 (12)	8	8(g)	116 (19)
O(3)	482 (5)	1894 (5)	7351 (10)	8	8(g)	114 (22)
O(4)	2324 (4)	2017 (4)	4418 (10)	8	8(g)	83 (17)
O(5)	0	0	0	1·7	2(a)	90 (35)

* $U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$.

($R = 0 \cdot 061$). At this stage there were two peaks of significance left in the difference Fourier map. An examination of their associated coordination polyhedra (Table 2) led to the assignment of one peak as Na$^+$ [Na(2)] [position $4(e)$, with a maximum occupation factor of $0 \cdot 5$ as the result of the close proximity of these atom sites] and the other to OH$^-$ [O(5)], rather than H$_2$O to maintain a charge balance. Subsequent refinement of the site-occupation factor for these two atoms led to the final formulation, for the total cell content, of Na$_8$Gd$_8$Si$_8$O$_{32}$. 1·7 NaOH. Final refinement with anisotropic thermal parameters gave $R = 0 \cdot 028$ [$R_w = 0 \cdot 027$, $w = 1/\sigma^2(F)$]. Atomic scattering factors for neutral atoms and dispersion correction factors were taken from *International Tables for X-ray Crystallography* (1974). Final positional and equivalent isotropic thermal parameters are listed in Table 1.*

Discussion. Fig. 1 shows the unit cell viewed almost parallel to **c**. Interatomic distances are listed in Table 2.

The structure comprises Gd ('eight'-coordinate) polyhedra sharing corners with three, and edges with two, Si tetrahedra. The eighth coordination site is occupied by the oxygen from the OH$^-$ ion; this site is

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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 36446 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
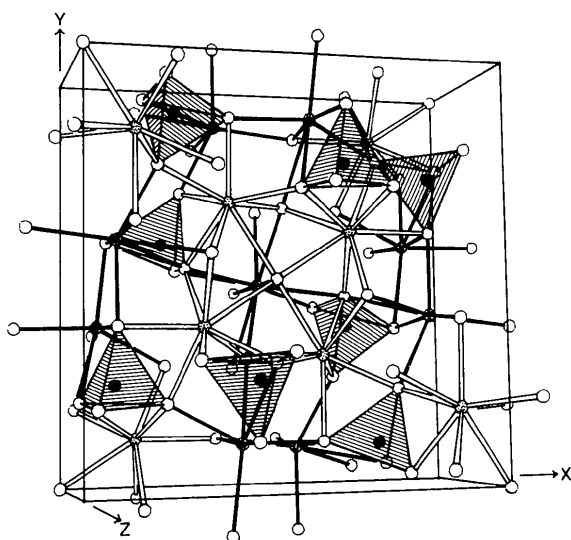
Fig. 1. View of the unit cell. The silicon tetrahedra (Si full circles) have been shaded, the sodium polyhedra (Na cross-hatched) full lined, and gadolinium polyhedra (Gd speckled) thick open-lined. Ellipsoids are isotropic of arbitrary size.

Table 2. *Bond lengths* (Å)

Gd–O(1)	2·302 (6)	Gd–O(1)	2·395 (6)
–O(3)	2·349 (6)	–O(2)	2·444 (5)
–O(4)	2·385 (5)	–O(4)	2·561 (5)
–O(3)	2·392 (6)	–O(5)	2·5661 (3)
Si–O(3)	1·624 (6)		
–O(1)	1·628 (6)		
–O(2)	1·633 (5)		
–O(4)	1·639 (5)		
Na(1)–O(4)	2·392 (6)	Na(2)–O(5)	2·346 (15)
–O(2)	2·406 (6)	–O(3) × 2	2·467 (8)
–O(2)	2·525 (6)	–O(1) × 2	2·662 (8)
–O(2)	2·611 (8)	–O(3) × 2	2·834 (11)
–O(1)	2·678 (7)	–O(1) × 2	3·033 (11)
–O(3)	2·829 (7)	–O(5)	3·105 (15)
–O(2)	2·860 (8)		
O(5)–Na(2) × 2	2·346 (15)		
–Gd × 4	2·5661 (3)		

only 85% occupied. The coordination polyhedron about the Gd atom is more regular than that reported by Avetisyan *et al.* (1971) (bond lengths vary between 2·30 and 2·57 Å), and each shares two faces with two, and corners with three, Gd polyhedra.

The Si atoms are in regular tetrahedral sites, Si–O bond lengths ranging between 1·62 and 1·64 Å, O–O lengths between 2·57 and 2·70 Å and interatomic angles between 103·8 (3) and 112·0 (3)°.

Na(1) has seven O atoms at distances <2·860 Å, the next-nearest neighbour being Si at 3·111 (4) Å. The coordination polyhedron is best described as a distorted pentagonal bipyramid; these polyhedra form edge-shared groups of four related by 4 point symmetry, and share edges generating columns parallel to **c**.

Na(2), which is associated with the OH⁻ ion in the tunnel formed by the Gd polyhedra, has a coordination polyhedron formed by eight O atoms at distances between 2·467 and 3·033 Å and hydroxyl O atoms at 2·346 and 3·104 Å. Both Na(2) and the hydroxyl sites are only partially occupied and it should be noted that the crystals were grown hydrothermally in the presence of a 50% sodium hydroxide solution (Shannon *et al.*, 1980).

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Hexachlorozinn(IV)säure-Decahydrat

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Abstract. H₂SnCl₆.10H₂O, monoclinic, $P2_1/n$, a = 8·973 (2), b = 7·248 (2), c = 13·942 (3) Å, β = 92·43 (1)°, U = 905·9 (4) Å³, Z = 2, D_x = 1·883 (1) Mg m⁻³, lattice parameters and X-ray intensities measured at 170 (±5) K on a diffractometer, Mo $K\alpha$ radiation, R value 0·022 for 2291 reflexions. $SnCl_6^{2-}$ ions of almost regular octahedral shape (site symmetry $\bar{1}$) occupy the corners and the centre of the unit cell.