

## Sodium heptasilicate: A high-pressure silicate with six-membered rings of tetrahedra interconnected by SiO<sub>6</sub> octahedra: (Na<sub>8</sub>Si[Si<sub>6</sub>O<sub>18</sub>])

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### ABSTRACT

Crystals of sodium heptasilicate (Na<sub>8</sub>Si<sub>7</sub>O<sub>18</sub>) have been grown at 9 GPa, 1000 °C using the MA6/8 superpress at Edmonton. The X-ray structure was determined at room pressure ( $R = 5.8\%$ ). Sodium heptasilicate is trigonal with  $a = 7.180(1)$  Å,  $\alpha = 87.26(1)^\circ$ , space group Rbu671,  $Z = 1$ , and  $D_x = 3.009$  g/cm<sup>3</sup>. The structure contains isolated six-membered UDUDUD rings of SiO<sub>4</sub> tetrahedra interconnected by SiO<sub>6</sub> octahedra with <sup>16</sup>Si:<sup>14</sup>Si = 1:6, giving a structural formula of Na<sub>8</sub>Si[Si<sub>6</sub>O<sub>18</sub>]. The mixed <sup>14</sup>Si,<sup>16</sup>Si framework is undersaturated because only one of the non-bridging O atoms in the SiO<sub>4</sub> tetrahedron is shared with the SiO<sub>6</sub> octahedron. Six Na cations per formula unit (pfu) are in eightfold coordination with O, and two are in a distorted and compressed octahedral coordination. Sodium heptasilicate belongs to the homologous series Na<sub>2k</sub>Na<sub>2(m-k)</sub>Si<sub>m-k</sub>[Si<sub>n-m+k</sub>O<sub>2n+m</sub>], with  $k < m < n$  and  $(n - m + k) \geq (3/2)(m - k)$ . The X-ray structure is consistent with microprobe analysis data and revises the earlier characterization of this phase as ζ-Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>. The sodium heptasilicate structure does not fully relax with decompression and undergoes incipient displacive transformation ( $R\bar{3}m \rightarrow R\bar{3}$ ) with minor positional disorder of Na cations.

### INTRODUCTION

Phases in the Na<sub>2</sub>O-SiO<sub>2</sub> system at high pressure yield insights into the high-pressure crystal chemistry of silicates. They also provide model structures and analogue materials for interpreting absorption spectra of high-pressure silicate glasses and melts (Kanzaki et al. 1989, 1998; Xue et al. 1991, 1994; Xue and Stebbins 1993; Fleet and Henderson 1995a, 1995b, 1997; Fleet 1996).

The phase relations have been investigated up to 14 GPa and the crystalline products characterized by powder X-ray diffraction, <sup>29</sup>Si magic-angle-spinning nuclear magnetic resonance (MAS NMR) and vibrational spectroscopy, and X-ray structures (Kanzaki et al. 1989, 1998; Fleet and Henderson 1995a, 1995b, 1997; Fleet 1996; P.F. McMillan, M. Kanzaki, and X. Xue, personal communication). At the bulk composition Na<sub>2</sub>O·2SiO<sub>2</sub>, epsilon sodium disilicate (ε-Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>) is the solidus phase at about 4 GPa, and sodium tetrasilicate (Na<sub>2</sub>Si<sub>4</sub>O<sub>9</sub>) and melt occur with it between about 7 and 8 GPa. The high-pressure assemblages are complex mixtures of a phase reported to be a second high-pressure sodium disilicate polymorph (ζ-Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>), sodium trisilicate (Na<sub>2</sub>Si<sub>3</sub>O<sub>7</sub>) and melt. At the bulk composition Na<sub>2</sub>O·4SiO<sub>2</sub>, epsilon sodium disilicate coexists with coesite to about 5 GPa, the low-pressure limit of sodium tetrasilicate stability, and sodium trisilicate and stishovite (SiO<sub>2</sub>) are stable above 9 GPa.

The orthorhombic ( $Pbc2_1$ ,  $Z = 4$ ) structure of epsilon sodium disilicate (ε-Na<sub>2</sub>[Si<sub>2</sub>O<sub>5</sub>]) is based on a disilicate [Si<sub>2</sub>O<sub>5</sub>] sheet in the (100) plane with alternating six-membered

bered rings of UUUUDD and DDDDUU (where U is upward-pointing and D is downward-pointing) SiO<sub>4</sub> tetrahedra (Fleet and Henderson 1995a). The disilicate sheets are linked by Na cations and have a gentle undulation in *c*-axis projection. The structure resembles those of α- and β-Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> (Pant and Cruickshank 1968; Liebau 1961; Pant 1968), but differs significantly from these room-pressure structures in its relatively small Si-O<sub>br</sub>-Si (O<sub>br</sub> is bridging oxygen) bond angles. Sodium trisilicate, Na<sub>2</sub>Si[Si<sub>2</sub>O<sub>7</sub>] is monoclinic, ( $C2/c$ ,  $Z = 4$ ) and has a novel high-pressure structure with Si in both tetrahedral and octahedral coordination with O in the ratio <sup>16</sup>Si:<sup>14</sup>Si = 1:2 (Fleet and Henderson 1995b). The SiO<sub>4</sub> tetrahedra form a diorthosilicate [Si<sub>2</sub>O<sub>7</sub>] group and are linked by isolated SiO<sub>6</sub> octahedra by means of shared corners into a framework of six- and four-membered rings of silicate polyhedra. The structure of sodium tetrasilicate, Na<sub>6</sub>Si<sub>3</sub>[Si<sub>5</sub>O<sub>27</sub>], is monoclinic ( $P2_1/n$ ,  $Z = 4$ ) with Si also in both tetrahedral and octahedral coordination, but in the ratio <sup>16</sup>Si:<sup>14</sup>Si = 1:3 (Fleet 1996). The structure is complex and large, having three independent SiO<sub>6</sub> octahedra and nine independent SiO<sub>4</sub> tetrahedra. The tetrahedral silicate unit is a nine-membered ring of SiO<sub>4</sub> tetrahedra that is collapsed around and interconnected by isolated SiO<sub>6</sub> octahedra, forming a large tricluster. Layers of nine-membered rings are arranged in ABABAB... stacking sequence and alternate with layers of SiO<sub>6</sub> octahedra and NaO<sub>n</sub> polyhedra along [010], as in the wadeite-type (e.g., K<sub>2</sub>Si<sub>4</sub>O<sub>9</sub>, Swanson and Prewitt 1984) and A<sub>2</sub>Ge<sub>4</sub>O<sub>9</sub>-type (Choisnet et al. 1973) structures.

Santarsiero et al. (1991) reported that the zeta sodium

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TABLE 1. Positional and isotropic thermal parameters ( $\text{\AA}^2$ )

Position	x	y	z	$B_{\text{eq}}^*, B$	SXK†		
					x	y	z
Na1	0.2363(5)	x	x	1.27(3)			
Na2	0.0	0.5	0.5	1.59(3)	0.0	0.5	0.0
Na3	0.5	0.0	0.0	1.50(3)	0.0	0.5	0.5
Si1	0.0	0.0	0.0	0.90(3)	0.5	0.5	0.5
Si2	0.2719(1)	0.7396(1)	0.2715(1)	1.01(2)	0.25	0.25	0.75
O1	0.2129(2)	0.5451(3)	0.2128(3)	1.60(4)	0.25	0.25	0.0
O2	0.1690(2)	0.9181(2)	0.1692(2)	1.26(4)	0.375	0.375	0.625
O3	0.2346(2)	0.7653(2)	0.4995(2)	1.49(4)	0.0	0.25	0.75

$$* B_{\text{eq}} = \frac{4}{3} \sum_j \beta_j \mathbf{a}_j \mathbf{a}_j$$

† Equivalent positions in the  $R\bar{3}m$  structure of Santarsiero et al. (1991) that are related to the present structure by translations of  $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$  on x, y, z, respectively, and symmetry operations; x, x, z for O2 are presently inferred.

disilicate phase of Kanzaki et al. (1989) was trigonal [ $R\bar{3}m$ ,  $a = 7.174(1) \text{\AA}$ ,  $\alpha = 87.24(1)^\circ$ ,  $Z = 1$ ]. Their partial structure contained octahedrally coordinated Si, with  $^{60}\text{Si};^{43}\text{Si} = 1:6$ , and all O atoms of the  $\text{SiO}_6$  octahedron were bridged to  $\text{SiO}_4$  tetrahedra. However, this structure refined to only  $R = 20\%$ , which Santarsiero et al. (1991) attributed to twinning.

The  $^{29}\text{Si}$  MAS NMR results of Kanzaki et al. (1998) are consistent with the X-ray structures of  $\epsilon\text{-Na}_2\text{Si}_2\text{O}_5$ ,  $\text{Na}_2\text{Si}[\text{Si}_2\text{O}_7]$ , and  $\text{Na}_6\text{Si}_3[\text{Si}_9\text{O}_{27}]$  in respect to  $^{60}\text{Si};^{43}\text{Si}$  ratio as well as number and possible steric environment of  $^{43}\text{Si}$  positions. They also show that  $^{60}\text{Si}$  is subordinate to  $^{43}\text{Si}$  in the zeta phase.

The structure of Santarsiero et al. (1991) for the zeta phase corresponds to a formula that is unbalanced in terms of expected atom valences (i.e.,  $\text{Na}_6\text{Si}_7\text{O}_{18}$ ; Table 1) and does not have disilicate stoichiometry. Moreover, the  $\text{SiO}_4$  tetrahedron and  $\text{SiO}_6$  octahedron are greatly distorted from ideal geometries. The limited electron microprobe (EPMA) results of Fleet and Henderson (1997) indicated a composition slightly more Na-rich than the disilicate composition. This study shows that the zeta disilicate phase of previous studies has the ideal formula  $\text{Na}_8\text{Si}_7\text{O}_{18}$ . This phase is not a polymorph of  $\text{Na}_2\text{Si}_2\text{O}_5$  composition and, henceforth, is referred to as sodium heptasilicate,  $\text{Na}_8\text{Si}_7\text{O}_{18}$  or  $\text{Na}_8\text{Si}[\text{Si}_6\text{O}_{18}]$ .

### EXPERIMENTAL PROCEDURES

High-pressure sodium heptasilicate ( $\text{Na}_8\text{Si}[\text{Si}_6\text{O}_{18}]$ ) was synthesized using the MA6/8 superpress at the University of Alberta, Edmonton. The single crystal used for collection of X-ray reflection intensities was synthesized at 9 GPa, 1000 °C, 24 h run time (no. 1889; Fleet and Henderson 1997). The starting composition consisted of glass of bulk composition  $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$  that was contained in a sealed platinum capsule and dried at about 380 °C for 2 h before welding. The pressure assembly (without the sample capsule) was fired at 1000 °C in a  $\text{N}_2\text{-H}_2$  gas mixture for 1 h. The products consisted of sodium heptasilicate and  $\text{Na}_2\text{Si}[\text{Si}_2\text{O}_7]$ . Sodium heptasilicate occurred as massive aggregates of small ( $<50 \mu\text{m}$ ) colorless sugary grains that were of low birefringence, uniaxial, and neg-

ative optic sign. Sodium heptasilicate crystals were commonly twinned; some with a simple contact twin but others exhibited complex fine-scale lamellae. In addition, crystals from subsolidus experiments tended to be sheared, but the visible effects of decompression were minimized for crystals grown in the presence of melt.

Sodium heptasilicate was analysed using the JEOL 8600 superprobe at the University of Saskatchewan, but this EPMA investigation was not extensive, largely because the data were collected with the assumption that the phase was of ideal  $\text{Na}_2\text{Si}_2\text{O}_5$  composition. However, 4 EPMA spot analyses for experiment no. 1916 (8 GPa, 1200 °C; Fleet and Henderson 1997) yielded  $\text{SiO}_2 = 63.9(7) \text{ wt\%}$ ,  $\text{Na}_2\text{O} = 35.1(10) \text{ wt\%}$ . The EPMA calibration employed consistently underestimated  $\text{Na}_2\text{O}$  contents in each of the three previous studies on high-pressure sodium silicates; the EPMA formula being  $\text{Na}_{1.95}\text{Si}_2\text{O}_5$  for epsilon sodium disilicate (Fleet and Henderson 1995a),  $\text{Na}_{1.92}\text{Si}_{3.02}\text{O}_7$  for  $\text{Na}_2\text{Si}[\text{Si}_2\text{O}_7]$  (Fleet and Henderson 1995b) and  $\text{Na}_{1.90}\text{Si}_4\text{O}_9$  for  $\text{Na}_6\text{Si}_3[\text{Si}_9\text{O}_{27}]$  (Fleet 1996). Therefore, normalizing to the EPMA results for epsilon sodium disilicate in experiment no. 1831 (4 GPa, 900 °C; Fleet and Henderson 1997), which were  $\text{SiO}_2 = 67.3(9) \text{ wt\%}$ ,  $\text{Na}_2\text{O} = 32.3(2) \text{ wt\%}$ , the above analysis for sodium heptasilicate implies  $\text{SiO}_2 = 62.8 \text{ wt\%}$ ,  $\text{Na}_2\text{O} = 37.2 \text{ wt\%}$ , which compares favorably with the ideal composition of  $\text{Na}_8\text{Si}_7\text{O}_{18}$  (i.e.,  $\text{SiO}_2 = 62.9 \text{ wt\%}$ ,  $\text{Na}_2\text{O} = 37.1 \text{ wt\%}$ ).

Single-crystal measurements were made at room temperature and pressure with an Nonius MACH3 Kappa-CCD diffractometer and graphite-monochromatized  $\text{MoK}\alpha$  X-radiation ( $\lambda = 0.70926 \text{\AA}$ ) at Nonius BV, Delft, The Netherlands. The crystal of sodium heptasilicate was triangular prismatic (dimensions =  $0.05 \times 0.08 \times 0.10 \text{ mm}$ ; volume =  $0.19 \times 10^{-3} \text{ mm}^3$ ). It was optically clear and untwinned. The crystal structure was solved using SHELXTL PC (Siemens 1993), and all other computations were carried out with DATAP77 and LINEX77 (State University of New York at Buffalo). Structure refinement closely followed earlier procedures (Fleet 1992; Fleet 1996). Scattering factors for neutral atomic species and values of  $f'$  and  $f''$  were taken, respectively, from

**TABLE 2.** Anisotropic thermal parameters ( $\times 10^2 \text{ \AA}^2$ ) and bond valence

Position	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$	$s^*$
Na1	127(3)						1.37
Na2	180(7)	139(7)	158(7)	-20(5)	-25(5)	17(5)	1.03
Na3	111(7)	116(7)	221(7)	6(5)	-15(5)	-10(5)	1.32
Si1	90(3)						3.58
Si2	95(3)	104(3)	102(3)	-5(2)	-2(2)	-4(2)	4.07
O1	182(9)	136(8)	167(9)	-16(6)	-54(7)	-11(6)	2.03
O2	136(8)	133(8)	107(8)	1(6)	-22(6)	5(6)	2.01
O3	172(9)	163(9)	108(8)	20(7)	6(6)	-4(6)	2.27

Note: Anisotropic temperature factors have the form  $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + \dots + 2B_{23}klb^*c^*\cos\alpha^*)]$ .

\*Bond valence is after Brown (1981).

Tables 2.2A and 2.3.1 of the *International Tables for X-ray Crystallography* (Ibers and Hamilton 1974).

High-pressure sodium heptasilicate, investigated at room temperature and pressure, is trigonal (rhombohedral) with  $a = 7.180(1) \text{ \AA}$ ,  $\alpha = 87.26(2)\%$ ,  $V = 368.92 \text{ \AA}^3$ , [ $a = 9.908(1)$ ,  $c = 13.017(1) \text{ \AA}$ ,  $V = 1106.75 \text{ \AA}^3$ ] space group  $R\bar{3}$  (No. 148),  $Z = 1$ , and  $D_x = 3.009 \text{ g/cm}^3$ . Using 90 CCD film packs, 4181 reflections were recorded and reduced to 603 non-equivalent reflections with rhombohedral symmetry, Laue class 3, to  $2\theta \approx 56^\circ$  ( $0.75 \text{ \AA}$ ). An on-line absorption correction was made ( $\mu = 10.0 \text{ cm}^{-1}$ ).  $R_{\text{int}}$  was 0.079 and  $R^2_{\text{int}}$  was 0.046 for all reflections but the agreement between equivalent reflections deteriorated significantly with increasing  $2\theta$  (decreasing  $d_{hkl}$ -spacing); e.g.,  $R^2_{\text{int}}$  was 0.025 for reflections with  $d_{hkl} > 1.61 \text{ \AA}$  and 0.255 for reflections with  $d_{hkl} < 0.78 \text{ \AA}$ . Of the 603 unique reflections, 43 were considered unobserved on the basis of  $I < 3\sigma_I$ . Using SHELXTL PC, a centrosymmetric space group was indicated, and the combined figure of merit (CFOM) was 6.04 for space group  $R\bar{3}$ , compared with 9.06 for space group  $R\bar{3}m$ . Structure refinement in  $R\bar{3}$  converged to  $R = 0.058$ ,  $R_w = 0.035$  [for reflections with  $I \geq 3\sigma_I$ ,  $S = 0.580$ ,  $g = 0.0050(4) \times 10^{-4}$ ,  $\Delta\rho = -0.60 \text{ e/\AA}^3$  at  $x = 0.36$ ,  $y = 0.32$ ,  $z = 0.78$  to  $0.69 \text{ e/\AA}^3$  at  $x, y, z = 0.39$ ] with isotropic thermal parameters for Si1 and Na1, and  $x$  of Na1 refined by iteration. Final parameters are given in Tables 1 and 2, and observed and calculated structure factors in Table 3.<sup>1</sup>

## DISCUSSION

The structure of high-pressure sodium heptasilicate is built from isolated six-membered UDUDUD rings of  $\text{SiO}_4$  tetrahedra interconnected by  $\text{SiO}_6$  octahedra (Figs. 1 and 2). The  $\text{SiO}_4$  tetrahedra and  $\text{SiO}_6$  octahedra are present in the ratio  $^{16}\text{Si}:^{14}\text{Si} = 1:6$ . The Na cations are accommodated in medium- and medium-large-sized cavity positions, with 6 pfu (Na2, Na3) in eightfold coordination with O and 2 pfu (Na1) in a distorted and compressed octahedral coordination.

<sup>1</sup> For a copy of Table 3, Document AM-98-008, contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. Deposit items may also be available on the *American Mineralogist* web site at <http://www.minsocam.org>.

The present structure analysis supports the EPMA evidence that the high-pressure phase previously labeled  $\zeta$ - $\text{Na}_2\text{Si}_2\text{O}_5$  (Kanzaki et al. 1989) is more  $\text{Na}_2\text{O}$ -rich than the disilicate composition. The actual formula of this phase is  $\text{Na}_8\text{Si}_7\text{O}_{18}$  and the structural formula is  $\text{Na}_8\text{Si}[\text{Si}_6\text{O}_{18}]$ . Recognizing that the spectrum in Figure 5b of Kanzaki et al. (1998) was obtained by using a composite sodium heptasilicate ( $\text{Na}_8\text{Si}[\text{Si}_6\text{O}_{18}]$ ) + sodium trisilicate ( $\text{Na}_2\text{Si}[\text{Si}_2\text{O}_6]$ ) sample (P.F. McMillan, M. Kanzaki, and X. Xue personal communication 1997), this study now confirms the agreement between the  $^{29}\text{Si}$  MAS NMR results and X-ray structure of sodium heptasilicate. The  $^{29}\text{Si}$  MAS NMR technique used by Kanzaki et al. (1998) is indeed a sensitive probe for  $^{16}\text{Si}:^{14}\text{Si}$  ratio in small amounts of experimental products. Also, the present description of the structural topology, with  $[\text{Si}_6\text{O}_{18}]^{12}$  rings parallel to (111) (normal to hexagonal  $c$  axis; Fig. 1b), is consistent with the negative optic sign of this phase.

With the exception of the Na1 position, the present structure is basically that of Santarsiero et al. (1991); see Table 1. The earlier structure was incomplete and ill-defined to the extent that the ideal composition and basic structural topology (isolated six-membered rings) were not recognized. Starting with the schematic positions reproduced in Table 1, the Santarsiero et al. (1991) structure does refine to the present structure using the present reflection data, even though the initial residual index ( $R$ ) is very high (52%). The crystal used in the earlier study was either twinned or not of good diffraction quality. Santarsiero et al. (1991) suggested that their crystal was twinned with 50% obverse and 50% reverse rhombohedral orientation. However, with twin domains that are incoherent to X-ray diffraction, this twin system results in reflections with mixed obverse ( $-h + k + l = 3n$ ; hexagonal lattice) and reverse ( $h - k + l = 3n$ ) rhombohedral indices.

Problems also exist with the present structure refinement. The isotropic thermal parameters for the Si and O atoms were considerably larger than expected for silicates in general and high-pressure sodium silicates in particular (cf. Fleet and Henderson 1995a, 1995b; Fleet 1996) and refinement of the positional parameter for Na1 would not converge. The present structure is very close to  $R\bar{3}m$  symmetry; in fact, only Si2 has  $x$  and  $y$  parameters departing significantly ( $\pm 1\sigma$ ) from this higher-symmetry space group. In addition, the refined structure included a small fraction of Na in a fourth medium-large cation position (Na4) at  $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$  (equipoint 1b). The occupancy of Na4 was 0.0078(9), corresponding to 0.047(5) Na cations pfu, and this was most satisfactorily accounted for by loss of Na from Na3. Alternatively, this weak residual electron density could indicate domains of the basic structure with an origin at  $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ , but this explanation was not supported by residual electron density near  $\frac{3}{4}, \frac{1}{4}, \frac{3}{4}$ , corresponding to Si2, and weaker residual peaks corresponding to the Na and O structural positions. The Na4 position is at the center of the six-membered ring of  $\text{SiO}_4$  tetrahedra and coplanar with the bridging O atoms (O3). It represents a

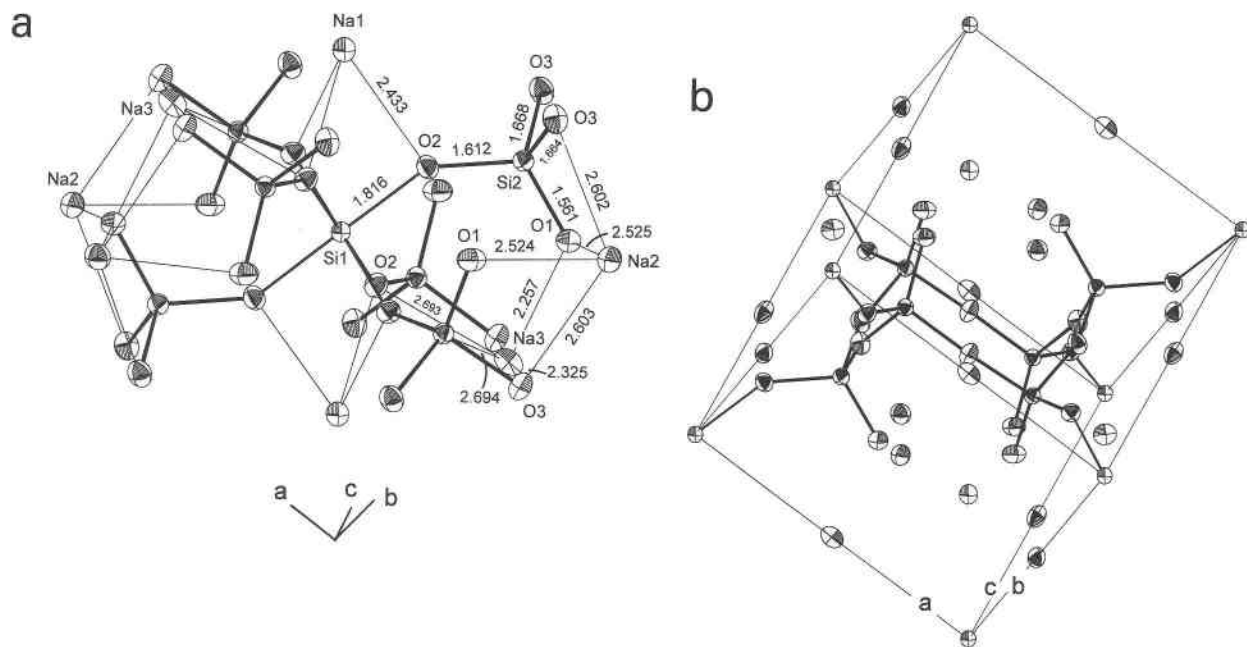


FIGURE 1. Details of the structure of sodium heptasilicate ( $\text{Na}_8\text{Si}[\text{Si}_6\text{O}_{18}]$ ) at room temperature and pressure: (a) environment of the  $\text{SiO}_6$  octahedron and bond distances (Å); (b) six-membered ring of  $\text{SiO}_4$  tetrahedra.

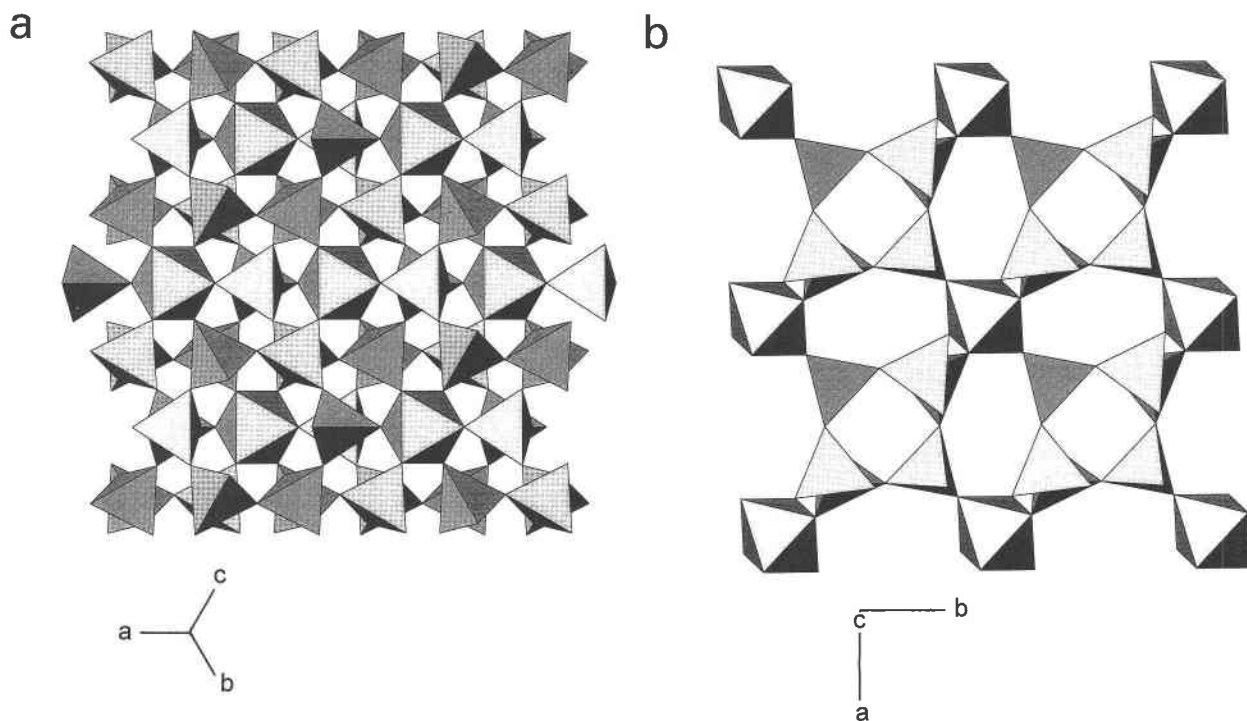


FIGURE 2. Polyhedral representation of the structure of sodium heptasilicate ( $\text{Na}_8\text{Si}[\text{Si}_6\text{O}_{18}]$ ), showing six-membered rings of  $\text{SiO}_4$  tetrahedra interconnected by  $\text{SiO}_6$  octahedra: (a) viewed in direction of [111] (hexagonal  $c$  axis); (b) viewed parallel to (001) and revealing alternating layers of  $\text{SiO}_6$  octahedra and six-membered ring units.

TABLE 4. Selected bond distances (Å) and angles (°)

Na1-O1	×3	2.214(4)		
Na1-O2	×3	2.433(5)	Si2-O1	1.561(2)
Mean		2.324	Si2-O2	1.612(2)
Na2-O1	×2	2.525(1)	Si2-O3	1.664(2)
Na2-O1*	×2	2.524(1)	Si2-O3†	1.668(2)
Na2-O3	×2	2.602(1)	Mean	1.626
Na2-O3‡	×2	2.603(1)	O2d-Si1-O2§	×6 86.4(1)
Mean		2.564	O2d-Si1-O2†	×6 93.6(1)
Na3-O1*	×2	2.257(1)	O1-Si2-O2	115.7(1)
Na3-O2¶	×2	2.693(2)	O1-Si2-O3	111.7(1)
Na3-O2§	×2	2.694(1)	O1-Si2-O3†	111.9(1)
Na3-O3¶	×2	2.325(1)	O2-Si2-O3	106.2(1)
Mean		2.492	O2-Si2-O3†	106.4(1)
Si1-O2¶	×6	1.816(1)	O3-Si2-O3†	104.2(1)

\* z, x, y.

† -z, -x, -y.

‡ -y, -z, -x.

§ y - 1, z, x.

¶ x, y - 1, z.

large cavity in the sodium heptasilicate structure; Na4 forms six bonds to O3 at 2.63 Å and has three distant non-bridging O atoms (O1) above and below (Figs. 1b and 2a).

These problems in the structure refinement point to limitations in the diffraction quality of the crystal investigated, which could arise from damage during decompression (cf. Fleet and Henderson 1995a), retrogression, or alteration (e.g., room-temperature and room-pressure hydration; Fleet and Henderson 1997). It seems probable that sodium heptasilicate has the structure with  $R\bar{3}m$  symmetry under the pressure and temperature conditions of synthesis, but undergoes a displacive transformation to  $R\bar{3}$  symmetry during quenching and decompression. The evidence for the lower symmetry in the room-temperature and room-pressure structure is not an artifact of the structure refinement. Numerous  $hkil, h\bar{k}l$  reflection pairs differ by more than  $\pm 1\sigma$  in observed structure factors, and the Si2  $x$  and  $y$  positional parameters and most anisotropic thermal parameters strongly indicate  $R\bar{3}$  symmetry. The structure of sodium heptasilicate is suggested to relax on quenching and decompression; transformation to a lower symmetry structure is incipient, with a small fraction of Na3 cations moving into the Na4 position. The anisotropic thermal parameters and residual electron density in the present refinement did not indicate any evidence for symmetry lower than  $R\bar{3}$ .

The  $^{16}\text{Si-O}$  bond distance of 1.816 Å (Table 4) is greater than those in  $\text{Na}_2\text{Si}[\text{Si}_2\text{O}_7]$  (1.789 Å; Fleet and Henderson 1995b) and  $\text{Na}_6\text{Si}_3[\text{Si}_9\text{O}_{27}]$  (1.774–1.790 Å; Fleet 1996) but lies within the range for corner-shared polyhedra of 1.758–1.863 Å in the structures surveyed by Finger and Hazen (1991). With the exception of the volume of the octahedron (7.94 Å<sup>3</sup>), other parameters for the  $\text{SiO}_6$  octahedron and  $\text{SiO}_4$  tetrahedra, including quadratic elongation (1.0037, 1.0045, respectively), bond length distortion (0, 0.000711), bond angle variance (14, 19), and volume of the tetrahedron (2.19 Å<sup>3</sup>), are generally similar to values in  $\text{Na}_2\text{Si}[\text{Si}_2\text{O}_7]$  and  $\text{Na}_6\text{Si}_3[\text{Si}_9\text{O}_{27}]$  (Fleet and Henderson 1997).

Some relatively short Na-O bonds exist in sodium heptasilicate; e.g., Na1-O1 = 2.214 Å and Na3-O1 = 2.257 Å (Table 4). Fleet and Henderson (1997) noted that  $\text{NaO}_n$  polyhedra do not appear to be compressed in  $\text{Na}_2\text{Si}[\text{Si}_2\text{O}_7]$  and  $\text{Na}_6\text{Si}_3[\text{Si}_9\text{O}_{27}]$  relative to low-pressure structures; i.e., the high-pressure structures determined at room pressure were fully relaxed. The sodium heptasilicate structure does not appear to decompress to the same extent. In fact, the compressed  $\text{NaO}_6$  octahedron may be the first evidence of a partially pressure-quenched cation polyhedron in a high-pressure alkali silicate structure. The failure of this structure to fully relax during decompression, with incipient displacive transformation, explains the poor diffraction quality of the crystals investigated to date.

Triclinic  $\text{CaSi}_2\text{O}_5$  (which has a derivative titanite structure with  $^{16}\text{Si}$ ,  $^{15}\text{Si}$  and  $^{14}\text{Si}$ ; Angel et al. 1996; Kudoh and Kanzaki 1996) undergoes displacive transformation to monoclinic  $\text{CaSi}_2\text{O}_5$  (titanite-type structure with  $^{16}\text{Si}$  and  $^{14}\text{Si}$ ) at about 0.2 GPa in a diamond-anvil cell (Angel 1997). Because the triclinic phase with the interesting and unusual fivefold-coordinated Si has been reported only from synthesis with the multi-anvil press, Angel (1997) suggests that its formation is promoted by non-hydrostatic stresses during decompression. Although the  $\text{NaO}_n$  polyhedra in sodium heptasilicate may have been extensively modified during decompression, no evidence supports association of the incipient displacive transformation with significant reorganization of the mixed  $^{14}\text{Si}, ^{16}\text{Si}$  framework.

Bond valence sums for some atoms in the sodium heptasilicate structure depart significantly from ideal values (Table 2). The low value for octahedral Si1 and the high value for the bridging O3 atom continue trends evident in the structures of  $\text{Na}_2\text{Si}[\text{Si}_2\text{O}_7]$  and  $\text{Na}_6\text{Si}_3[\text{Si}_9\text{O}_{27}]$  (Fleet and Henderson 1995b; Fleet 1996). The high bond valences for Na1 and Na3 reflect short Na-O bond distances and point to limitations in the calculation of bond valence in high-pressure structures that are not fully relaxed using coefficients calculated for low-pressure structures.

In their classification of high-pressure structures, Finger and Hazen (1991) distinguished a group of structures comprised predominantly of framework silicates stable at 10 to 20 GPa, with the framework formed from the linking of  $\text{SiO}_4$  tetrahedral units by isolated  $\text{SiO}_6$  octahedra by shared corners. The alkali and alkaline earth silicates with mixed  $^{14}\text{Si}, ^{16}\text{Si}$  frameworks belong to a distinct class of these high-pressure silicate structures (Hazen et al. 1996). The tetrahedral groups now recognized range through isolated tetrahedron ( $\text{CaSi}_2\text{O}_5$  structures: triclinic  $\text{Ca}_2\text{SiSi}[\text{SiO}_4]_2\text{O}_2$  and monoclinic  $\text{CaSi}[\text{SiO}_4]_2\text{O}$ ), diorthosilicate dimer ( $\text{Na}_2\text{Si}[\text{Si}_2\text{O}_7]$ -sodium trisilicate), rings (three-membered:  $\text{K}_2\text{Si}[\text{Si}_3\text{O}_9]$ -wadeite structure,  $\text{BaSi}[\text{Si}_3\text{O}_9]$ -benitoite structure,  $\text{BaSi}[\text{Si}_3\text{O}_9]$ -barium germanate structure; six-membered,  $\text{Na}_8\text{Si}[\text{Si}_6\text{O}_{18}]$ -sodium heptasilicate; and nine-membered:  $\text{Na}_6\text{Si}_3[\text{Si}_9\text{O}_{27}]$ -sodium tetrasilicate), and a sheet ( $\text{Na}_{1.8}\text{Ca}_{1.1}\text{Si}[\text{Si}_5\text{O}_{14}]$ , Gasparik et al. 1995). Hazen et al. (1996) suggest that many related structures

remain to be discovered, noting that Rb, Cs, Sr, and Ba silicate compositions have not been extensively investigated at high pressure.

Whereas the two other high-pressure sodium silicate phases with octahedrally coordinated Si ( $\text{Na}_2\text{Si}[\text{Si}_2\text{O}_7]$  and  $\text{Na}_6\text{Si}_3[\text{Si}_9\text{O}_{27}]$ ) have  $\text{SiO}_2$ -rich compositions and saturated  $^{14}\text{Si}$ ,  $^{16}\text{Si}$  frameworks (i.e., all of the O atoms are shared by Si polyhedra), only one of the non-bridging O atoms (O2) in the  $\text{SiO}_4$  tetrahedron in the structure of sodium heptasilicate is shared with the  $\text{SiO}_6$  octahedron; the other non-bridging O atom (O1) is bonded instead only to Na atoms (Na1,  $2\times\text{Na}2$  and Na3), as well as Si2 (Fig. 1; Table 4). The proportion of  $^{16}\text{Si}$  to  $^{14}\text{Si}$  in sodium heptasilicate is insufficient to saturate all of the tetrahedral O atoms. The structure of sodium heptasilicate is thus intermediate between the medium-pressure structure of  $\epsilon$ - $\text{Na}_2\text{Si}_2\text{O}_5$ , which has sheets of six-membered rings cross-linked by  $\text{NaO}_n$  polyhedra, and the high-pressure saturated  $^{14}\text{Si}$ ,  $^{16}\text{Si}$  framework structures of  $\text{Na}_2\text{Si}[\text{Si}_2\text{O}_7]$  and  $\text{Na}_6\text{Si}_3[\text{Si}_9\text{O}_{27}]$ . Another comparative feature of note is that the alternating interconnected six-membered rings of UUUUDD and DDDDUU  $\text{SiO}_4$  tetrahedra are collapsed in  $\epsilon$ - $\text{Na}_2\text{Si}_2\text{O}_5$  but the isolated UDUDUD ring in sodium heptasilicate is fully extended (Fig. 2a). As occurs in the structures of  $\text{Na}_2\text{Si}[\text{Si}_2\text{O}_7]$ ,  $\text{Na}_6\text{Si}_3[\text{Si}_9\text{O}_{27}]$ , wadeite-type, and  $\text{A}_2\text{Ge}_4\text{O}_9$ -type (e.g., Choynet et al. 1973; Fleet and Henderson 1997; see also Fig. 1 of Hazen et al. 1996), the structural elements are layered in the structure of sodium heptasilicate. Layers of six-membered  $\text{SiO}_4$  tetrahedral rings and  $\text{NaO}_n$  polyhedra alternate with layers of  $\text{SiO}_6$  octahedra and  $\text{NaO}_n$  polyhedra, viewed parallel to  $\{001\}$  planes (Fig. 2b).

Fleet and Henderson (1997) noted that possible corner-shared framework structures are limited by the bond valence requirements of the non-bridging O atoms in the  $\text{Na}_2\text{O-SiO}_2$  system; with the single optimum coordination environment for a non-bridging O atom shared with a  $\text{SiO}_6$  octahedron being  $^{14}\text{Si} + ^{16}\text{Si} + 2\times\text{Na}$ . Thus, the optimum proportion of  $\text{Na}^{16}\text{Si}$  is 2:1, and formulae for compositions  $m\text{Na}_2\text{O}-n\text{SiO}_2$  belong to the homologous series  $\text{Na}_{2m}\text{Si}_m[\text{Si}_{n-m}\text{O}_{2n+m}]$ , with  $m < n$ . It was suggested that the two known structures ( $\text{Na}_2\text{Si}[\text{Si}_2\text{O}_7]$  and  $\text{Na}_6\text{Si}_3[\text{Si}_9\text{O}_{27}]$ ) might be the only representatives of this structure-composition series. The sodium heptasilicate structure shows that this homologous series is only restrictive for saturated  $^{14}\text{Si}$ ,  $^{16}\text{Si}$  frameworks of the more  $\text{SiO}_2$ -rich compositions. The sodium heptasilicate structure belongs to a more general family of possible structures in the modified homologous series  $\text{Na}_k\text{Na}_{2(m-k)}\text{Si}_{m-k}[\text{Si}_{n-m+k}\text{O}_{2n+m}]$ , with  $k < m < n$  and  $(n - m + k) \geq (3/2)(m - k)$ . In sodium heptasilicate,  $k = 3$ ,  $m = 4$ , and  $n = 7$ , and the condition  $(n - m + k) \geq (3/2)(m - k)$  is required because possible structures in the homologous series are limited to those with all O atoms associated with  $\text{SiO}_4$  tetrahedra. As noted previously, because  $\text{Na}_2\text{Si}[\text{Si}_2\text{O}_7]$  and stishovite appear in the  $\text{SiO}_2$ -rich portion of the system at 9 to 10 GPa, the possibilities for undiscovered structures of  $\text{SiO}_2$ -rich com-

positions appear quite limited. However, other mixed  $^{14}\text{Si}$ ,  $^{16}\text{Si}$  framework structures could exist in the central portion of the  $\text{Na}_2\text{O-SiO}_2$  system at higher pressures.

The composition  $\text{Na}_2\text{Si}_2\text{O}_5$  does not belong in the homologous series of Fleet and Henderson (1997) or the present study because creation of  $^{16}\text{Si}$  generates O atoms not linked to any tetrahedron (e.g.,  $\text{Na}_2\text{Si}[\text{SiO}_4]\text{O}$ ). All evidence to date suggests that such placement of O tends to be avoided in mixed  $^{14}\text{Si}$ ,  $^{16}\text{Si}$  framework structures of alkali silicates at high pressures (10–20 GPa). This observation could explain the absence of a high-pressure phase of sodium disilicate composition, which exhibits complex polymorphism at low pressure, in the 10 to 20 GPa high-pressure range. As noted in Fleet and Henderson (1997), a significant increase in the proportion of  $^{16}\text{Si}$  in mixed  $^{14}\text{Si}$ ,  $^{16}\text{Si}$  frameworks must generate O atoms not linked to tetrahedra. Thus, a disilicate phase could reappear in the  $\text{Na}_2\text{O-SiO}_2$  system at even higher pressures.

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