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Sodium tetrasilicate: A complex high-pressure framework silicate ($Na_6Si_3[Si_9O_{27}]$)

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ABSTRACT

Crystals of sodium tetrasilicate ($Na_2Si_4O_9$) have been grown at 6 GPa and 1000 °C to 9 GPa and 1500 °C using the MA6/8 superpress at Edmonton, and the X-ray structure was determined at room pressure ($R = 5.0\%$). High-pressure sodium tetrasilicate is monoclinic, with $a = 10.875(2)$, $b = 9.326(1)$, $c = 19.224(7)$ Å, $\beta = 90.18(2)°$, space group $P2_1/n$, and $D_x = 3.090$ g/cm^3. Si occurs in both tetrahedral and octahedral coordination, with $^{[6]}Si$:$^{[4]}Si$ = 1:3; the structural formula is $Na_6Si_3[Si_9O_{27}]$, $Z = 4$. Nine-membered rings of SiO_4 tetrahedra are collapsed around and interconnected by SiO_6 octahedra, at shared corners, giving a framework structure that is analogous to but distinct from those of $K_2Si[Si_3O_9]$ (wadeite-type) and $K_2Ge[Ge_3O_9]$ ($A_2Ge_4O_9$-type). Although all nine independent SiO_4 tetrahedra have similar nearest-neighbor stereochemistries, $^{[4]}Si$-O-$^{[4]}Si$ bond angles vary markedly (130.6–172.1°). The Na cations are displaced to one side of framework cavities in irregular polyhedra, as in other framework structures, with six to eight bonds extending to 2.9 Å. It appears that even transition-zone pressures do not dominate the stereochemical requirements of the large cations in determining the structures of the alkali and alkaline-earth aluminosilicates.

INTRODUCTION

Laboratory study of high-pressure silicates is helpful in understanding the mineralogy and physics of the Earth's interior and provides insight into the mechanisms of densification of high-pressure silicate melts (e.g., Liebau 1985; Ito and Takahashi 1987; Finger and Hazen 1991; Henderson and Fleet 1991; Xue et al. 1991, 1994; Fleet and Henderson 1995a, 1995b). Early work focused on high-pressure phases in the Mg-Si-O system (wadsleyite, ringwoodite, majorite, perovskite-type $MgSiO_3$, and stishovite) and conditioned earth scientists to anticipate only minerals of simple crystal chemistry in the Earth's deep interior. However, Finger and Hazen (1991) drew attention to the potential for complex silicate structures to exist at high pressure on the basis of the stereochemical requirements of such elements as Na, K, Ca, and Al, as well as analog structures, and concluded that: "It appears that the Earth's transition zone will display the varied mineralogy of mixed $^{[6]}Si$ and $^{[4]}Si$ silicates, including some of the most complex structures known in the mineral kingdom."

Finger and Hazen (1991) divided the fewer than 20 then-known structures with SiO_6 polyhedra into three groups: (1) structure types yielding high-pressure phases in which all Si is $^{[6]}Si$ (rutile, perovskite, ilmenite, hollandite, calcium ferrite, pyrochlore, and K_2NiF_4); (2) structure types yielding high-pressure phases with mixed $^{[4]}Si$ and $^{[6]}Si$ (majorite garnet, pyroxene, wadeite, anhydrous phase B, and phase B); and (3) structures with $^{[6]}Si$ that are stable at room pressure through a compositional control (principally silicate phosphates). The second group of structures consists predominantly of framework silicates stable at 10–20 GPa, with the framework formed from the linking of SiO_4 tetrahedral units by isolated SiO_6 octahedra at shared corners. The tetrahedral units include isolated tetrahedra, rings (principally three-membered), and chains. Recent additions to this group include two polymorphs of $BaSi_4O_9$ with structures based on tetrahedral units of three-membered Si_3O_9 rings and belonging to the benitoite ($BaTiSi_3O_9$) and barium germanate ($BaGe_4O_9$) structure types, respectively (Hazen 1994; Finger et al. 1995). The structure of sodium trisilicate ($Na_2Si[Si_2O_7]$; Fleet and Henderson 1995a) added the Si_2O_7 dimer to this series of $^{[4]}Si$-$^{[6]}Si$ framework silicate structures.

High-pressure phase relations in the Na_2O-SiO_2 system were investigated by Kanzaki et al. (1989); the crystalline phases they reported were sodium disilicate (ϵ-$Na_2Si_2O_5$) at moderate pressure and sodium trisilicate ($Na_2Si_3O_7$), sodium tetrasilicate ($Na_2Si_4O_9$), and stishovite (SiO_2) at high pressure. Santarsiero et al. (1991) reported a second high-pressure disilicate phase (ζ-$Na_2Si_2O_5$) and a partial structure for it containing $^{[6]}Si$:$^{[4]}Si$ = 1:6. Fleet and Henderson (1995a, 1995b) recently showed that epsilon sodium disilicate (ϵ-$Na_2Si_2O_5$), stable to 8 GPa, has a novel disilicate sheet structure with all Si in tetrahedral coordination, whereas sodium trisilicate ($Na_2Si[Si_2O_7]$), stable at and above 9 GPa, has a high-pressure framework structure with Si in both tetrahedral and octahedral coordination ($^{[6]}Si$:$^{[4]}Si$ = 1:2).

Sodium tetrasilicate was previously assumed from su-

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perficial examination to have a derivative wadeite-type structure (e.g., Fleet and Henderson 1995a). The wadeite-type structure of potassium tetrasilicate ($K_2Si[Si_3O_9]$; Swanson and Prewitt 1983) belongs to the second group of high-pressure structures of Finger and Hazen (1991) and has units of three-membered rings of SiO_4 tetrahedra linked by isolated SiO_6 octahedra at shared corners. The analog germanates $K_2Ge[Ge_3O_9]$ (Völlenkle and Wittmann 1971) and $Na_2Ge[Ge_3O_9]$ (Sakka et al. 1977) have a derivative wadeite-type structure (the $A_2Ge_4O_9$-type structure, where A = Na, K, Rb, Tl, Ag; Choisnet et al. 1973).

Sodium tetrasilicate does not occur as a stable phase in the Na_2O-SiO_2 system at room pressure (e.g., Morey 1964). However, it is present as a metastable phase, with $a = 4.9$, $b = 23.4$, and $c = 15.4$ Å, in annealed soda-silica glasses and gels (Mogensen and Christensen 1981; Neilson and Weinberg 1984; PDS file 38–20), and ertixiite, a Ca-Al–bearing sodium silicate, with $a = 5.975$ Å, $Pa3$, and $D_m = 2.35$ g/cm^3, has an ideal composition of $Na_2Si_4O_9$ (Zhang et al. 1985).

EXPERIMENTAL PROCEDURES

High-pressure sodium tetrasilicate ($Na_2Si[Si_3O_9]$) was synthesized using the MA6/8 superpress at the University of Alberta, Edmonton. This phase was encountered from 6 GPa and 1000 °C to 9 GPa and 1500 °C. The single crystal used for collection of X-ray reflection intensities was synthesized in an experiment at 6 GPa, 1000 °C, lasting 12 h (no. 1986). The charge consisted of glass of bulk composition $Na_2Si_4O_9$ 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 an N_2-H_2 gas mixture for 1 h. The product was apparently single-phase sodium silicate and was present as crystals ranging up to 0.6 mm in longest dimension. In refractive index oil, sodium tetrasilicate is colorless, weakly anisotropic, and biaxial positive ($2V \approx 15°$). Crystals grown in the presence of melt were doubly terminated pseudohexagonal prisms. Crystals grown in the subsolidus region tended to fracture on pseudohexagonal {0001}, forming tablet-shaped grains. A few grains exhibited an optical microstructure with planar features that was attributed to the effects of decompression. The EMPA composition of the crystals was determined with a JEOL 8600 superprobe at the University of Saskatchewan, giving SiO_2 = 80.3(5) wt%, Na_2O = 19.6(5) wt% (average of ten microprobe spot analyses), corresponding to a formula of $Na_{1.90}Si_4O_9$. The formula assumed for the X-ray structure analysis is $Na_2Si_4O_9$. Other experimental details, pressure-temperature phase diagrams, and structure-composition relationships in the Na_2O-SiO_2 system are discussed elsewhere.

The product crystals were investigated by X-ray precession photography. Diffraction patterns were dimensionally pseudohexagonal, with $a = 10.99$ and $c = 9.33$ Å, but reflection intensities indicated a lower symmetry. Single-crystal measurements were made at room temperature and pressure with an Enraf-Nonius CAD-4F diffractometer and graphite-monochromatized Mo$K\alpha$ X-radiation ($\lambda = 0.70926$ Å). Because of the large unit cell, a high proportion of weak reflections, and less than desirable crystal quality, measurements were required on two crystals: a large crystal (0.10 × 0.25 × 0.25 mm) from experiment 1986 for reflection intensities, and a smaller crystal (0.09 × 0.10 × 0.10 mm) from a separate experiment (1918, 9 GPa, 1300 °C, 7.5 h) for unit-cell parameters. However, the unit-cell parameters for the two crystals were identical within $\pm 2\sigma$. The crystal structure was solved using SHELXTL PC (Siemens 1993), but all other computations were performed with DATAP77 and LINEX77 (State University of New York at Buffalo). Structure refinement closely followed earlier procedures (Fleet 1992). Scattering factors for neutral atomic species and values of f' and f'' were taken, respectively, from Tables 2.2B and 2.3.1 of the *International Tables for X-ray Crystallography* (Ibers and Hamilton 1974).

High-pressure sodium tetrasilicate is monoclinic, with $a = 10.875(2)$, $b = 9.326(1)$, $c = 19.224(7)$ Å, $\beta = 90.18(2)°$, $V = 1949.5$ Å^3, space group $P2_1/n$ (no. 14), $Z = 4$, and $D_x = 3.090$ g/cm^3. A total of 13103 reflections with indices h, $\pm k$, $\pm l$ to $2\theta = 60°$ were measured in the ω-scan mode. Transmission factors varied from 0.794 for $4\bar{2}9$ to 0.918 for 300 (crystal volume = 4.30×10^{-3} mm^3, $\mu = 10.8$ cm^{-1}). There were 5660 unique reflections, with 622 considered unobserved on the basis of $I < 3\sigma_I$. All reflections systematically absent in space group $P2_1/n$ had zero intensity with $I < 3\sigma_I$. Structure refinement in $P2_1/n$ initially converged to $R = 0.090$, $R_w = 0.093$, with anisotropic displacement parameters for Si and Na and isotropic displacement parameters for O, and refinement with anisotropic displacement parameters for all atoms failed to converge. Comparison of observed and calculated structure factors for reflection pairs hkl and $hk\bar{l}$ suggested that the crystal (from experiment 1986) was twinned by 180° rotation about c [normal to pseudohexagonal $(01\bar{1}0)$] or reflection on (001). The twinning may be related to the planar structure noted above, but this aspect was not investigated further. The observed structure factors were corrected for the twin contribution following the procedure of Fleet and Burns (1990) and Fleet and Pan (1995). The twin volume [8.1(1)%] was determined by iteration in the final stages of structure refinement. Refinement in $P2_1/n$ converged to $R = 0.050$, $R_w = 0.036$ [for reflections with $I \geq 3\sigma_I$, $S = 1.683$, $g = 0.03(2) \times 10^{-4}$, $\Delta\rho = -0.86$ e/Å^3 near Si1 to 0.72 e/Å^3 near Na1]. Final parameters are given in Tables 1 and 2, and observed and calculated structure factors in Table 3.[1] The anomalously low value of B_{11} for O7 (Table 2) is attributed to limitations in the procedure for unfolding the twinned reflection intensities.

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[1] A copy of Table 3 may be ordered as Document AM-96-624 from the Business Office, Mineralogical Society of America, 1015 Eighteenth Street NW, Suite 601, Washington, DC 20036, U.S.A. Please remit $5.00 in advance for the microfiche.

Table 1. Positional and isotropic displacement parameters (Å^2)

Position	*x*	*y*	*z*	B_{eq}*
Na1	0.9383(1)	0.0513(2)	0.2955(1)	1.59(3)
Na2	0.9274(1)	0.4768(2)	0.2722(1)	1.67(3)
Na3	0.4367(1)	0.0447(2)	0.3863(1)	1.70(3)
Na4	0.3948(1)	0.0263(2)	0.0773(1)	1.41(3)
Na5	0.4833(1)	0.4635(2)	0.3842(1)	1.78(3)
Na6	0.3304(1)	0.4582(2)	0.0726(1)	1.51(3)
Si1	0.71897(8)	0.00508(10)	0.41306(4)	0.53(1)
Si2	0.27224(7)	0.00272(10)	0.24171(4)	0.50(1)
Si3	0.78255(8)	0.49927(10)	0.42084(4)	0.52(1)
Si4	0.94002(7)	0.22798(10)	0.45674(4)	0.38(1)
Si5	0.56746(7)	0.27450(10)	0.10670(4)	0.41(1)
Si6	0.44151(7)	0.27507(10)	0.24580(4)	0.44(1)
Si7	0.71925(7)	0.26456(10)	0.30325(4)	0.40(1)
Si8	0.87596(7)	0.24314(10)	0.16051(4)	0.37(1)
Si9	0.15079(7)	0.24210(10)	0.15532(4)	0.40(1)
Si10	0.59627(7)	0.26068(10)	0.49017(4)	0.39(1)
Si11	0.30679(7)	0.26137(10)	0.48260(4)	0.42(1)
Si12	0.16298(7)	0.24081(11)	0.34665(4)	0.45(1)
O1	0.9020(2)	0.3930(3)	0.4583(1)	0.74(4)
O2	0.5008(2)	0.3087(3)	0.0327(1)	0.94(4)
O3	0.8965(2)	0.3967(3)	0.1260(1)	0.85(4)
O4	0.4568(2)	0.3128(3)	0.1629(1)	0.71(4)
O5	0.2835(2)	0.2417(3)	0.3980(1)	1.03(4)
O6	0.7808(2)	0.3919(3)	0.3456(1)	0.90(4)
O7	0.4507(2)	0.3097(3)	0.4876(1)	0.72(4)
O8	0.1906(2)	0.3964(3)	0.1832(1)	0.80(4)
O9	0.3548(2)	0.3930(3)	0.2791(1)	0.65(4)
O10	0.0156(2)	0.1915(3)	0.1837(1)	0.89(4)
O11	0.8065(2)	0.2535(3)	0.2348(1)	1.23(4)
O12	0.6702(2)	0.3900(3)	0.1240(1)	0.80(4)
O13	0.0436(2)	0.1941(3)	0.3958(1)	0.82(4)
O14	0.7244(2)	0.1074(3)	0.3339(1)	0.94(4)
O15	0.8331(2)	0.1144(3)	0.4511(1)	0.75(4)
O16	0.1309(2)	0.3934(3)	0.3130(1)	0.74(4)
O17	0.6649(2)	0.3938(3)	0.4575(1)	0.96(4)
O18	0.5777(2)	0.3093(3)	0.2813(1)	0.95(4)
O19	0.2148(2)	0.3876(3)	0.5045(1)	0.86(4)
O20	0.1756(2)	0.1106(3)	0.2943(1)	0.83(4)
O21	0.2430(2)	0.1108(3)	0.1673(1)	0.71(4)
O22	0.4068(2)	0.1116(3)	0.2616(1)	0.64(4)
O23	0.1415(2)	0.2678(3)	0.0707(1)	1.05(4)
O24	0.8309(2)	0.1132(3)	0.1152(1)	0.95(4)
O25	0.5983(2)	0.1088(3)	0.1183(1)	0.70(4)
O26	0.2835(2)	0.1017(3)	0.5101(1)	0.83(4)
O27	0.6020(2)	0.1154(3)	0.4471(1)	0.83(4)

* $B_{eq} = \frac{4}{3} \sum_i \sum_j \beta_{ij} a_i a_j$.

Table 2. Anisotropic displacement parameters (×10^2 Å^2) and bond valence

Position	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	*s*
Na1	161(6)	115(6)	201(7)	24(5)	−4(5)	12(5)	0.96
Na2	166(6)	137(6)	197(7)	−75(5)	56(5)	−36(5)	1.00
Na3	108(5)	152(7)	250(7)	31(5)	−69(5)	−101(6)	1.08
Na4	198(6)	134(6)	90(5)	−51(5)	−27(4)	10(4)	0.96
Na5	214(6)	135(6)	184(6)	−8(5)	−37(5)	60(5)	0.86
Na6	166(6)	156(7)	131(6)	52(5)	−13(4)	−21(5)	0.93
Si1	65(3)	40(3)	54(3)	−1(3)	−19(2)	−2(3)	4.02
Si2	60(3)	30(3)	60(3)	4(3)	−1(2)	−2(3)	3.86
Si3	55(3)	38(3)	61(3)	1(3)	−4(2)	4(3)	3.98
Si4	28(3)	65(3)	22(3)	−5(3)	3(2)	2(3)	4.17
Si5	32(3)	64(3)	26(3)	−5(3)	3(2)	0(3)	4.16
Si6	38(3)	62(3)	31(3)	3(3)	2(2)	0(3)	4.11
Si7	33(3)	59(3)	28(3)	5(3)	10(2)	−2(3)	4.18
Si8	38(3)	50(3)	23(3)	−2(3)	8(2)	2(3)	4.25
Si9	37(3)	48(3)	36(3)	−1(3)	−4(2)	−1(3)	4.09
Si10	36(3)	52(3)	28(3)	0(3)	−5(2)	−1(3)	4.23
Si11	31(3)	64(3)	31(3)	2(3)	0(2)	3(3)	4.12
Si12	44(3)	66(3)	25(3)	0(3)	−1(2)	−2(3)	4.10
O1	110(8)	62(9)	51(8)	13(7)	−20(6)	−1(7)	2.05
O2	124(9)	134(10)	24(8)	11(8)	−20(6)	−9(8)	2.16
O3	92(8)	43(9)	121(9)	14(7)	−12(7)	22(8)	2.01
O4	41(7)	107(10)	64(8)	4(7)	27(6)	10(8)	2.13
O5	94(8)	182(11)	33(7)	14(9)	3(6)	−4(8)	2.06
O6	115(9)	73(9)	81(9)	−24(8)	19(7)	−19(8)	2.08
O7	13(7)	109(10)	94(8)	0(7)	21(6)	−1(8)	2.11
O8	121(9)	44(9)	75(9)	−7(7)	−24(7)	−19(8)	2.03
O9	55(8)	83(9)	57(8)	22(7)	−3(6)	1(8)	1.96
O10	48(8)	164(11)	54(8)	0(7)	−25(6)	30(8)	2.17
O11	131(8)	195(11)	42(8)	19(9)	13(6)	1(9)	2.27
O12	87(8)	87(10)	64(8)	−29(7)	−13(6)	10(8)	1.98
O13	65(8)	109(10)	72(8)	−6(7)	28(6)	−3(8)	2.05
O14	133(9)	77(10)	72(9)	8(8)	−9(7)	14(8)	1.99
O15	54(8)	72(9)	100(9)	−21(7)	−13(6)	−3(8)	2.02
O16	77(8)	32(9)	113(9)	−8(7)	13(7)	16(7)	2.02
O17	85(8)	74(10)	127(10)	−7(7)	4(7)	26(8)	1.99
O18	70(8)	130(10)	85(9)	−7(8)	−15(6)	−4(8)	2.07
O19	95(8)	75(9)	88(9)	30(7)	−7(7)	−33(8)	1.94
O20	89(9)	61(9)	100(9)	5(7)	18(7)	−14(8)	1.92
O21	78(8)	77(9)	56(8)	0(7)	11(7)	20(8)	1.90
O22	81(8)	43(9)	67(9)	2(7)	−20(6)	−6(7)	2.06
O23	118(8)	157(11)	41(8)	18(7)	−5(6)	−11(7)	2.07
O24	59(8)	86(10)	140(10)	−12(7)	−2(7)	−43(8)	2.02
O25	73(8)	74(9)	62(8)	12(7)	5(6)	−11(7)	2.02
O26	91(8)	61(9)	97(9)	−4(7)	−8(7)	15(8)	1.92
O27	93(8)	66(9)	88(9)	5(7)	−15(7)	−28(8)	2.08

Note: Anisotropic displacement factors have the form $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + \cdots + 2B_{23}klb^*c^*\cos\alpha^*)]$, and bond valence is after Brown (1981).

DISCUSSION

The structure of sodium tetrasilicate ($Na_2Si_4O_9$) accommodates Si in both tetrahedral and octahedral coordination ($^{[6]}Si$:$^{[4]}Si$ = 1:3; Figs. 1 and 2) and belongs to the second group of high-pressure structures in the classification of Finger and Hazen (1991). However, the structure is not derived from either the wadeite- ($KZr[Si_3O_9]$) or $A_2Ge_4O_9$-type structures, as anticipated by most, if not all, previous studies. In fact, high-pressure sodium tetrasilicate has a unique and very large (45-atom) structure, with three independent octahedral positions for Si and nine independent tetrahedral positions (Table 1), giving a formula of $Na_6Si_3[Si_9O_{27}]$, $Z = 4$. The three-membered rings of SiO_4 tetrahedra that characterize the wadeite- and $A_2Ge_4O_9$-type structures are not present. Instead, the SiO_4 tetrahedra form a nine-membered (Si_9O_{27}) ring in the (010) plane that is collapsed around and interconnected by isolated SiO_6 octahedra at shared corners to form a framework of mixed SiO_4 tetrahedra and SiO_6 octahedra. More specifically, the nine-membered rings are gathered into large triclusters of $^{[4]}Si$-$^{[4]}Si$-$^{[4]}Si$-$^{[4]}Si$-$^{[6]}Si$ rings by nonbridging O3, O12, and O26 on $Si1O_6$ and O19, O24, and O25 on $Si3O_6$ (Fig. 1; Table 4), and interconnected by O14, O15, and O27 on $Si1O_6$, O8, O9, O16, O20, O21, O22 on $Si2O_6$, and O1, O6, and O17 on $Si3O_6$. The layers of nine-membered rings are arranged in ABABA . . . stacking sequence along [010] (Fig. 2b). Also, the SiO_6 octahedra are interspersed with unoccupied trigonal prisms forming columns along [010], with alternating $Si1O_6$ and $Si3O_6$ in one column and $Si2O_6$ alone in another. In transverse section (Fig. 2a), layers of tetrahedral rings alternate with layers of SiO_6 octahedra and Na polyhedra.

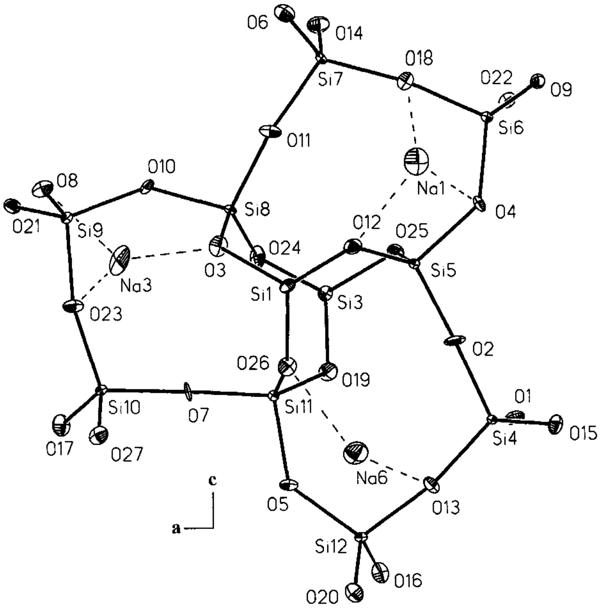

FIGURE 1. Nine-membered rings of independent SiO_4 tetrahedra in the structure of $Na_6Si_3[Si_9O_{27}]$ gathered by O3, O12, and O26 of the $Si1O_6$ octahedron and O19, O24, and O25 of the $Si3O_6$ octahedron. Note that the vibrational ellipsoids were determined at room temperature and pressure.

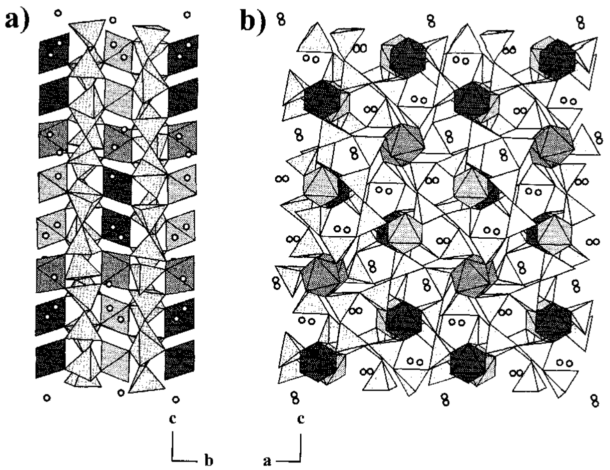

FIGURE 2. Polyhedral representations of the structure of $Na_6Si_3[Si_9O_{27}]$ viewed along [100] (**a**) and [010] (**b**). Shading of octahedra is light for $Si1O_6$, moderate for $Si2O_6$, and heavy for $Si3O_6$. Open circles are Na positions. Note that the layers of collapsed nine-membered rings of SiO_4 tetrahedra are in ABABA . . . packing along [010]. Also, octahedra, interspersed with unoccupied trigonal prisms, form columns along [010], with alternating $Si1O_6$ and $Si3O_6$ in one column and $Si2O_6$ alone in another.

The stereochemical features of Si, Na, and O are equivalent to those in the sodium silicate structures determined recently ($Na_2Si[Si_2O_7]$ and ϵ-$Na_2Si_2O_5$; Fleet and Henderson 1995a, 1995b).

Bonds from Si to nonbridging O atoms are short (1.571–1.602 Å; Table 4), as expected for silicates of low-field-strength cations, but these shorter bonds are compensated by longer bonds to bridging O atoms (1.620–1.667 Å). The tetrahedrally coordinated Si atoms are overbonded (bond strength 4.09–4.25; Table 2), whereas octahedrally coordinated Si atoms are marginally underbonded (3.86–4.02). An interesting feature of this structure is the very wide variation in $^{[4]}$Si-O-$^{[4]}$Si bond angles (130.6–172.1°; ⟨148.4°⟩; Table 4), which encompasses much of the range in bridging O-atom bond angles for the diverse silicate structures surveyed by Liebau (1985). The range in Si-O-Si bond angles made by nonbridging O atoms ($^{[4]}$Si-O-$^{[6]}$Si) is similarly quite wide (126.0–160.4°; ⟨140.9°⟩).

The $^{[6]}$Si-O bond distances range from 1.758 to 1.821 Å (mean values of 1.774–1.790 Å) and again encompass the values in the literature for $^{[6]}$Si-O in other structures (1.778 Å in $K_2Si_4O_9$, Swanson and Prewitt 1983; 1.775 Å in stishovite, Baur and Khan 1971; 1.792 Å in perovskite-type $MgSiO_3$, Ross and Hazen 1990; 1.789 Å in $Na_2Si[Si_3O_7]$, Fleet and Henderson 1995a) as well as the mean value of 1.768 Å for all hexaoxosilicon compounds surveyed by Liebau (1985).

The Na cations are displaced closer to one proximal (010) layer of SiO_4 tetrahedral rings than the other (Fig. 2a), as are the large cations in wadeite- and $A_2Ge_4O_9$-type structures (e.g., Choisnet et al. 1973). All NaO_n polyhedra are irregular, with six to eight bonds extending to 2.9 Å. As always seems to be the case where Na is an extraframework cation (e.g., Merlino 1984; Fleet and Henderson 1995a, 1995b), the Na cations are displaced to one side of the framework cavities in the sodium tetrasilicate structure (Figs. 1 and 2).

Bridging O atoms tend to be slightly overbonded, particularly O11 (2.27), and nonbridging O atoms are either saturated or slightly underbonded. As expected (e.g., Downs et al. 1990; Fleet and Henderson 1995a, 1995b), the major axis of the vibrational ellipsoid of the bridging O atom is transverse to the Si-O bonding plane (Fig. 1).

The structure-composition relations of the monovalent cation tetrasilicates and tetragermanates may be rationalized from consideration of the spatial accommodation of the large extraframework cation (effective ionic radii: $^{[7]}$Na 1.12, $^{[8]}$K 1.51, $^{[8]}$Rb 1.61, $^{[8]}$Cs 1.74, $^{[7]}$Ag 1.22, $^{[8]}$Tl 1.59 Å; Shannon 1976). The very large monovalent cations (K, Rb, Cs, Tl) prefer cavity positions offering eight to 12 bonds with O. K commonly bonds to nine O atoms in silicate frameworks; e.g., in an ideal stuffed tridymite structure, contra-rotation of adjacent TO_4 tetrahedra in six-membered rings positions three sets of three O atoms close to the K cation, above, below, and in the equatorial plane (e.g., Merlino 1984; Barbier and Fleet 1988). The Na cation is too small for these large framework cavities. Usually, the introduction of Na results in distortion of the framework to yield an oval-shaped cavity with Na displaced to one end and bonded to fewer O atoms. A

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

Na1-O4^b	2.623(3)	Na4-O1^c	2.410(2)
Na1-O10	2.655(2)	Na4-O16^b	2.462(3)
Na1-O11	2.638(3)	Na4-O19^b	2.356(2)
Na1-O12^b	2.462(2)	Na4-O21	2.521(2)
Na1-O13	2.605(2)	Na4-O25	2.470(2)
Na1-O14	2.498(2)	Mean	2.475
Na1-O18^b	2.703(3)	Na5-O7	2.478(2)
Na1-O20	2.638(2)	Na5-O9	2.539(2)
Mean	2.603	Na5-O10^b	2.495(3)
Na2-O6	2.276(2)	Na5-O17	2.508(2)
Na2-O11	2.564(3)	Na5-O18	2.655(2)
Na2-O14^b	2.889(2)	Na5-O24^b	2.456(2)
Na2-O16	2.471(2)	Mean	2.522
Na2-O22^b	2.293(2)	Na6-O2	2.445(2)
Na2-O25^b	2.456(2)	Na6-O4	2.594(2)
Mean	2.492	Na6-O8	2.680(2)
Na3-O3^b	2.292(2)	Na6-O13^b	2.661(3)
Na3-O5	2.490(3)	Na6-O15^c	2.433(2)
Na3-O8^b	2.367(2)	Na6-O23	2.715(2)
Na3-O22	2.497(2)	Na6-O26^b	2.417(2)
Na3-O23^b	2.842(3)	Mean	2.564
Na3-O27	2.240(2)	Si1-O3^b	1.777(2)
Mean	2.455	Si1-O12^b	1.766(2)
Na4-O1^b	2.628(2)	Si1-O14	1.797(2)
Si1-O15	1.763(2)	Si5-O25	1.597(3)
Si1-O26^a	1.781(2)	Mean	1.617
Si1-O27	1.763(2)	Si6-O4	1.640(2)
Mean	1.774	Si6-O9	1.585(2)
Si2-O8^b	1.796(2)	Si6-O18	1.660(1)
Si2-O9^b	1.764(2)	Si6-O22	1.600(2)
Si2-O16^b	1.805(2)	Mean	1.621
Si2-O20	1.774(2)	Si7-O6	1.587(2)
Si2-O21	1.777(2)	Si7-O11	1.628(2)
Si2-O22	1.821(2)	Si7-O14	1.581(3)
Mean	1.790	Si7-O18	1.649(1)
Si3-O1	1.784(2)	Mean	1.611
Si3-O6	1.758(2)	Si8-O3	1.594(2)
Si3-O17	1.762(2)	Si8-O10	1.653(1)
Si3-O19^a	1.782(2)	Si8-O11	1.620(2)
Si3-O24^b	1.768(2)	Si8-O24	1.571(2)
Si3-O25^b	1.815(2)	Mean	1.609
Mean	1.778	Si9-O8	1.595(2)
Si4-O1	1.594(3)	Si9-O10	1.639(1)
Si4-O2^c	1.637(2)	Si9-O21	1.599(2)
Si4-O13	1.657(2)	Si9-O23	1.647(2)
Si4-O15	1.577(2)	Mean	1.620
Mean	1.616	Si10-O7	1.648(1)
Si5-O2	1.626(2)	Si10-O17	1.580(2)
Si5-O4	1.659(2)	Si10-O23^c	1.645(2)
Si5-O12	1.586(2)	Si10-O27	1.589(2)
Mean	1.616	O8b-Si2-O9^b	92.1(1)
Si11-O5	1.656(2)	O8b-Si2-O16^b	91.5(1)
Si11-O7	1.631(1)	O8b-Si2-O20	89.3(1)
Si11-O19	1.602(2)	O8b-Si2-O21	177.2(1)
Si11-O26	1.601(3)	O8b-Si2-O22	87.7(1)
Mean	1.623	O9b-Si2-O16^b	89.9(1)
Si12-O5	1.638(1)	O9b-Si2-O20	89.6(1)
Si12-O13	1.667(2)	O9b-Si2-O21	90.5(1)
Si12-O16	1.602(2)	O9b-Si2-O22	178.0(1)
Si12-O20	1.583(2)	O16b-Si2-O20	179.1(1)
Mean	1.622	O16b-Si2-O21	87.4(1)
O3b-Si1-O12^b	88.0(1)	O16b-Si2-O22	88.1(1)
O3b-Si1-O15	179.2(1)	O20-Si2-O21	91.8(1)
O3b-Si1-O14	88.2(1)	O20-Si2-O22	92.4(1)
O3b-Si1-O26^a	91.2(1)	O21-Si2-O22	89.7(1)
O3b-Si1-O27	88.8(1)	O1-Si3-O6	91.3(1)
O12b-Si1-O14	87.5(1)	O1-Si3-O17	93.3(1)
O12b-Si1-O15	92.2(1)	O1-Si3-O19^a	89.6(1)
O12b-Si1-O26^a	90.4(1)	O1-Si3-O24^b	176.8(1)
O12b-Si1-O27	176.8(1)	O1-Si3-O25^b	87.7(1)
O14-Si1-O15	91.1(1)	O6-Si3-O17	90.3(1)
O14-Si1-O26^a	177.8(1)	O6-Si3-O19^a	178.4(1)
O14-Si1-O27	91.7(1)	O6-Si3-O24^b	90.8(1)
O15-Si1-O26^a	89.5(1)	O6-Si3-O25^b	89.2(1)
O15-Si1-O27	90.9(1)	O17-Si3-O19^a	91.1(1)
O26-Si1-O27	90.4(1)	O17-Si3-O24^b	89.1(1)
O17-Si3-O25^b	178.9(1)	O11-Si7-O18	110.8(1)

TABLE 4.—*Continued*

O19a-Si3-O24^b	88.3(1)	O14-Si7-O18	111.3(1)
O19a-Si3-O25^b	89.5(1)	O3-Si8-O10	104.1(1)
O24b-Si3-O25^b	89.9(1)	O3-Si8-O11	112.3(1)
O1-Si4-O2^c	106.8(1)	O3-Si8-O24	120.4(1)
O1-Si4-O13	112.0(1)	O10-Si8-O11	102.1(1)
O1-Si4-O15	117.3(1)	O10-Si8-O24	102.1(1)
O2c-Si4-O13	108.5(1)	O11-Si8-O24	112.9(1)
O2c-Si4-O15	102.6(1)	O8-Si9-O10	113.0(1)
O13-Si4-O15	109.0(1)	O8-Si9-O21	118.2(1)
O2-Si5-O4	101.9(1)	O8-Si9-O23	102.5(1)
O2-Si5-O12	111.2(1)	O10-Si9-O21	107.1(1)
O2-Si5-O25	113.9(1)	O10-Si9-O23	108.5(1)
O4-Si5-O12	103.3(1)	O21-Si9-O23	106.9(1)
O4-Si5-O25	105.6(1)	O7-Si10-O17	103.0(1)
O12-Si5-O25	118.7(1)	O7-Si10-O23^c	110.9(1)
O4-Si6-O9	107.8(1)	O7-Si10-O27	105.1(1)
O4-Si6-O18	105.4(1)	O17-Si10-O23^c	111.2(1)
O4-Si6-O22	114.4(1)	O17-Si10-O27	116.3(1)
O9-Si6-O18	103.4(1)	O23c-Si10-O27	109.9(1)
O9-Si6-O22	116.3(1)	O5-Si11-O7	103.5(1)
O18-Si6-O22	108.4(1)	O5-Si11-O19	104.2(1)
O6-Si7-O11	102.5(1)	O5-Si11-O26	101.4(1)
O6-Si7-O14	119.2(1)	O7-Si11-O19	112.4(1)
O6-Si7-O18	109.5(1)	O7-Si11-O26	113.0(1)
O11-Si7-O14	102.9(1)	O19-Si11-O26	119.8(1)
O5-Si12-O13	106.5(1)	Si1b-O12-Si5	144.0(2)
O5-Si12-O16	114.3(1)	Si4-O13-Si12	152.0(2)
O5-Si12-O20	108.4(1)	Si1-O14-Si7	143.8(2)
O13-Si12-O16	107.0(1)	Si1-O15-Si4	159.3(2)
O13-Si12-O20	103.2(1)	Si2b-O16-Si12	127.6(1)
O16-Si12-O20	116.4(1)	Si3-O17-Si10	160.4(2)
Si3-O1-Si4	135.8(2)	Si6-O18-Si7	152.6(2)
Si4c-O2-Si5	156.5(2)	Si3a-O19-Si11	129.6(1)
Si1b-O3-Si8	126.0(1)	Si2-O20-Si12	148.2(2)
Si5-O4-Si6	131.5(1)	Si2-O21-Si9	131.4(1)
Si11-O5-Si12	135.4(1)	Si2-O22-Si6	132.9(1)
Si3-O6-Si7	148.4(1)	Si9-O23-Si10^c	157.4(2)
Si10-O7-Si11	147.8(2)	Si3b-O24-Si8	153.8(1)
Si2b-O8-Si9	145.9(1)	Si3b-O25-Si5	129.5(1)
Si2b-O9-Si6	141.0(2)	Si1a-O26-Si11	142.8(2)
Si8-O10-Si9	130.6(2)	Si1-O27-Si10	136.1(1)
Si7-O11-Si8	172.1(2)		

Note: a = −*x*, −*y*, −*z*; b = ½ − *x*, ½ + *y*, ½ − *z*; c = ½ + *x*, ½ − *y*, ½ + *z*.

good example is provided by the nepheline structure (ideal composition $K_2Na_6[Al_8Si_8O_{32}]$), with K in the large A-site cavities and Na in the smaller oval cavities (e.g., Merlino 1984; Gregorkiewitz 1984). Review of monovalent cation gallo-aluminosilicates and germanates shows that, indeed, accommodation of the large extraframework cation is the most important factor controlling structure type. This was emphasized by the structure-composition relations in the $NaAlGeO_4$-$KAlGeO_4$ system (Barbier and Fleet 1988).

In the wadeite-type structure, the three-membered Si_3O_9 rings are too rigid to permit the distortion required to accommodate the Na cation. The more open germanate ring apparently permits some distortion, giving the twisted Ge_3O_9 ring of the $A_2Ge_4O_9$-type structure that accommodates the smaller Ag cation and, apparently, Na as well. Hence, sodium tetrasilicate adopts a framework configuration with the pliable five-membered $^{[4]}$Si-$^{[4]}$Si-$^{[4]}$Si-$^{[4]}$Si-$^{[6]}$Si rings.

Further discussion of this series of structures requires confirmation of the assignment of $A_2Ge_4O_9$-type structures for sodium tetragermanate. The structure determination of Sakka et al. (1977) was based on just 17 powder reflections, and at least six of these reflections are in poor agreement with observed and calculated intensities. Other crystallographic features (unit-cell parameters, crystal morphology, etc.) give an ambiguous indication of structure type.

Finally, this report on the sodium tetrasilicate structure is timely confirmation of Finger and Hazen's (1991) prediction of complex crystal chemistry for high-pressure framework silicates. Clearly, even transition-zone pressures do not dominate the stereochemical requirements of the large cations in determining the structures of the alkali and alkaline-earth aluminosilicates.

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