The Structure of Trisodium Hydrogensilicate Dihydrate: High-Temperature Form

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Abstract

High-temperature $Na_3HSiO_4.2H_2O$ is orthorhombic, *Pbca*, $a = 10.380$ (5), $b = 10.053$ (3), $c = 11.414$ (5) Å, $Z = 8$, $D_c = 2.209$ Mg m^{-3}, $V = 1191.1$ Å^3, λ(Mo Ka_1) = 0.7107 Å. The final $R = 0.032$ (0.039) for 664 (790) reflexions. The structure consists of chains of $[HSiO_4]^{3-}$ tetrahedra, bonded by Si–O$\cdots$H–O–Si hydrogen bonds along the *b* axis. These chains are linked to each other by the Na atoms and by hydrogen bonds from the water molecules. The three crystallographically independent Na atoms show irregular coordination with coordination numbers 6 and 7. Both crystallographically independent water molecules form two hydrogen bonds, thus linking two chains of $[HSiO_4]^{3-}$ tetrahedra.

Introduction

Three hydrate phases of trisodium hydrogensilicate are known (Schmid & Felsche, 1981*a*). The crystal structures of $Na_3HSiO_4.5H_2O$ (Smolin, Shepelev & Butikova, 1973) and the low-temperature form of $Na_3HSiO_4.2H_2O$ (Schmid, Huttner & Felsche, 1979) have been determined. $Na_3HSiO_4.2H_2O$ proved to be dimorphic with the transition point at 275 K (Schmid & Felsche, 1981*b*); in the present paper we describe the high-temperature form of this compound. The previously investigated low-temperature form (Schmid, Huttner & Felsche, 1979) is metastable at 299 K, the temperature at which it had been prepared. The transition point is at 275 K under dry-air conditions. The data were obtained by means of thermo-analytical measurements, X-ray heating powder diffraction, differential thermal analysis (DTA) and differential scanning calorimetry (DSC). These data will be published elsewhere (Schmidt & Felsche, 1981*a*).

Experimental

Crystals of the high-temperature form of $Na_3HSiO_4.2H_2O$ were obtained at 295 K as nearly hexagonal platelets under closed-system conditions from solutions containing 82.3 wt % H_2O, 13.3 wt %

Na_2O and 4.4 wt % SiO_2. (The percentages refer to the original composition of the solution.)

The compound is extremely hygroscopic; hence the crystal had to be sealed in a glass tube for the data collection. The dimensions of the crystal used were $0.1 \times 0.1 \times 0.1$ mm. The intensities were not corrected for absorption [μ(Mo Ka) = 0.591 mm^{-1}]. 790 intensities were collected on a Syntex *R*3 four-circle diffractometer at 297 K (Mo Ka_1 radiation, $\lambda = 0.7107$ Å). 664 intensities with values greater than 3.92σ were used to determine the phases by direct methods (Germain, Main & Woolfson, 1971). Subsequent refinement by full-matrix least squares using the Syntex *EXTL* structure-solving system yielded final R values of 0.032 for 664 reflexions and of 0.039 for all observed reflexions. The final atomic parameters are listed in Table 1.*

Table 1. *Final atomic parameters for the high-temperature form of* $Na_3HSiO_4.2H_2O$

The numbers in parentheses give the e.s.d.'s corresponding to the last significant digit. The H atom positions were located from difference Fourier maps without refinement.

	x	y	z	B_{eq}/B (Å^2)*
Si	0.2452 (1)	0.0239 (1)	0.3563 (1)	0.7 (1)
O(1)	0.0978 (3)	−0.0216 (3)	0.3717 (2)	1.2 (1)
O(2)	0.3219 (3)	0.0302 (3)	0.4793 (2)	1.2 (1)
O(3)	0.2600 (3)	0.1637 (3)	0.2866 (2)	1.2 (1)
O(4)	0.3211 (3)	−0.0881 (3)	0.2709 (2)	1.3 (1)
O(5)	−0.0603 (3)	0.2022 (3)	0.3662 (2)	1.4 (1)
O(6)	0.3896 (3)	−0.1906 (3)	0.5895 (3)	1.8 (1)
Na(1)	0.1085 (2)	−0.2473 (1)	0.4379 (1)	1.4 (1)
Na(2)	0.1193 (2)	0.0565 (2)	0.5809 (1)	1.5 (1)
Na(3)	0.5393 (2)	−0.0633 (2)	0.3466 (1)	2.1 (1)
H(1)	0.3063	−0.1737	0.2769	4.0
H(2)	−0.1075	0.1740	0.3031	4.0
H(3)	−0.0183	0.2577	0.4358	4.0
H(4)	0.3419	−0.1752	0.6691	4.0
H(5)	0.3557	−0.1214	0.5481	4.0

* For non-hydrogen atoms $B_{eq} = (B_{11}B_{22}B_{33})^{1/3}$.

Structure factors were calculated with scattering factors taken from *International Tables for X-ray Crystallography* (1965, 1974). The determination of the H atom positions suffered from their strong thermal vibration at 297 K, the temperature at which the intensities had been measured. The H positions have been located from difference Fourier maps. However, we were not successful in refining their positional parameters given in Table 1.

Results and discussion

The structure of the high-temperature form of $Na_3HSiO_4.2H_2O$ consists of $[HSiO_4]^{3-}$ tetrahedra, which are arranged linearly in chains parallel to the *b* axis. The tetrahedra are joined by Si—O—H···O—Si hydrogen bonds of 2·639 Å between O(4) of the hydroxyl group of the first tetrahedron and O(3) of the next. The structure is therefore similar to that of the low-temperature form of $Na_3HSiO_4.2H_2O$, where the Si—O—H···O—Si hydrogen bond in the chain has been found to have a length of 2·917 Å, and is therefore somewhat weaker than in the high-temperature form (Schmid, Huttner & Felsche, 1979). Fig. 1 shows the unit cell.

The correlations between bond strengths and bond lengths, especially of atoms involved in hydrogen bonds, are all in good agreement with empirical data from bond-length–bond-strength curves for oxide structures (Brown & Shannon, 1973; Donnay & Donnay, 1973). Values have been calculated from universal parameters according to the expression $s = (R/R_1)^{-N_1}$, with s = bond strength, R = experimental bond length and R_1 = an empirical parameter for a given M—O bond (Brown & Shannon, 1973). It can be shown by this method that for both O atoms which are involved in the hydrogen bond between the $[HSiO_4]^{3-}$ tetrahedra, the valence sums total about 2 valence units (v.u.'s) only by taking into account the O(4)—H(1) and O(3)···H(1) bond valences derived from the Brown & Shannon correlation data. From these bond-length–bond-strength curves O(4)—H(1) and O(3)···H(1)
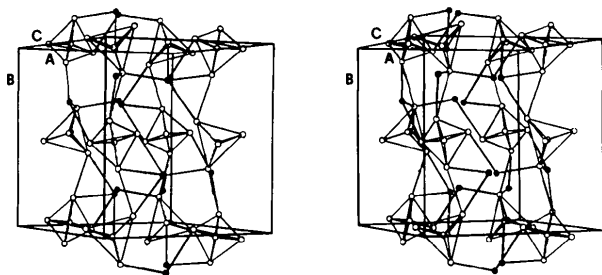

Fig. 1. Stereoscopic illustration (*ORTEP*, Johnson, 1965) of the crystal structure of the high-temperature form of $Na_3HSiO_4.2H_2O$. The figure shows hydrogen-bonded chains of $[HSiO_4]^{3-}$ tetrahedra parallel to (010) and the water molecules as black dots, hydrogen bonded to the tetrahedra.

Table 2. *The hydrogen-bonding system in the high-temperature form of* $Na_3HSiO_4.2H_2O$

E.s.d.'s in parentheses correspond to the last significant digit.

O(4)—H(1)	0·877 Å*	0·98 Å†	|HSiO₄|³⁻ tetrahedron
O(3)···H(1)	1·776	1·65	
O(4)···O(3)	2·639 (4)		
O(6)···H(1)	2·680	2·22	
O(4)···O(6)	3·120 (4)		
O(5)—H(2)	0·917	1·00	$H_2O(1)$
O(3)···H(2)	1·717	1·57	
O(5)···O(3)	2·583 (4)		
O(5)—H(3)	1·064	0·95	
O(1)···H(3)	3·141	1·85	
O(5)···O(1)	2·785 (4)		
O(6)—H(4)	1·047	0·96	$H_2O(2)$
O(3)···H(4)	1·712	1·79	
O(6)···O(3)	2·747 (4)		
O(6)—H(5)	0·912	0·97	
O(2)···H(5)	1·750	1·68	
O(6)···O(2)	2·646 (4)		

O(4)—H(1)···O(3)	167°	O(6)—H(5)···O(2)	167°
O(4)—H(1)···O(6)	112		
O(5)—H(2)···O(3)	156	H(2)—O(5)—H(3)	166
O(5)—H(3)···O(1)	68	H(4)—O(6)—H(5)	99
O(6)—H(4)···O(3)	169		

* O–H distances calculated from the O and H atom positions in Table 1. H positions not refined.
† O–H distances calculated from universal bond-length–bond-strength curves of Brown & Shannon (1973).

values of 0·98 and 1·65 Å can be derived. The corresponding distances from the X-ray structure determination are 0·877 and 1·776 Å respectively. Both the derived and the X-ray values are listed in Table 2.

In the $[HSiO_4]^{3-}$ tetrahedron O(3) and O(4) are the most strongly involved in hydrogen bonding. On account of this the Si—O(4) and Si—O(3) distances are the longest in the tetrahedron, since O(4) is the hydroxyl oxygen, whereas O(3) is involved in three hydrogen bonds to O(4) and O(5) and O(6) of both water molecules. By comparison of Si—OH interatomic distances in sodium silicate hydrates, one can easily see that the shorter and therefore the stronger a Si—O—H···O—Si hydrogen bond becomes, the more the O—H bond lengthens and the Si—O bond strength decreases, whereas the Si—O bond length increases. Values found in the low-temperature form of $Na_3HSiO_4.2H_2O$ are 1·703 Å for Si—OH and 2·917 Å for Si—O—H···O—Si (Schmid, Huttner & Felsche, 1979) and 1·677 and 2·560 Å respectively for $Na_3HSiO_4.5H_2O$ (Smolin, Shepelev & Butikova, 1973). In addition to these hydrogen-bonding data, bond lengths and angles in the tetrahendron are in good agreement with values found in the $[HSiO_4]^{3-}$ tetrahedra of the low-temperature form of $Na_3HSiO_4.2H_2O$ and $Na_3HSiO_4.5H_2O$ and with

values found in the $[H_2SiO_4]^{2-}$ tetrahedra of the $Na_2H_2SiO_4 \cdot nH_2O$ sodium silicate hydrates with $n =$ 4,5,7,8. In these structures Si—O and Si—OH distances are usually found to be at about 1·6 to 1·63 Å and 1·67 to 1·71 Å respectively, and the O—Si—O and O—Si—OH angles are about 115 and 109° respectively (Jost & Hilmer, 1966; Smolin et al., 1973; Dent Glasser & Jamieson, 1976). Angles and distances in the $[HSiO_4]^{3-}$ tetrahedron are reported in Fig. 2.

It is worth mentioning that in the structure of $Na_3HSiO_4 \cdot 5H_2O$ the tetrahedra are not arranged in a linear manner along one axis as found in both forms of $Na_3HSiO_4 \cdot 2H_2O$, but are centrosymmetrically arranged in pairs, which are linked by two parallel hydrogen bonds from symmetrically equivalent O atoms.

Hydrogen bonding and the coordination geometry of both water molecules $H_2O(1)$ and $H_2O(2)$ are quite different from those in the low-temperature form. Both $H_2O(1)$ and $H_2O(2)$ have two close neighbouring O atoms from the tetrahedra and must therefore form two strong hydrogen bonds each. This can be proved very well by bond-length–bond-strength calculations using universal O—H and O$\cdots$O correlation parameters in the expression $s = (R/R_1)^{-N_1}$ (Brown & Shannon, 1973). O(5) from $H_2O(1)$ receives only 0·5 v.u. from three coordinated Na atoms, whereas O(6) from $H_2O(2)$

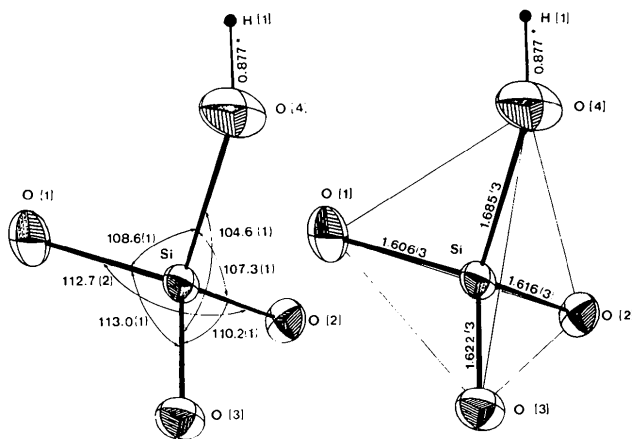Fig. 2. The $[HSiO_4]^{3-}$ tetrahedron. Interatomic distances (Å) and angles (°) are given with e.s.d.'s corresponding to the last significant digit. An asterisk indicates the proposed O—H distance calculated from the unrefined H atom positions of Table 1.
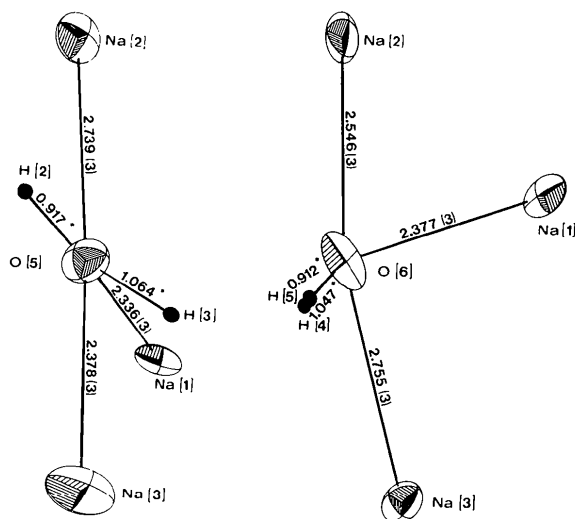

Fig. 3. Type O class 3 (Ferraris & Franchini-Angela, 1972) coordination polyhedra of $H_2O(1)$ and $H_2O(2)$. O—Na bond lengths (Å) are given with e.s.d.'s corresponding to the last significant digit. Asterisks indicate the proposed O—H distances and H positions calculated from the unrefined H atom parameters of Table 1. H(3) of $H_2O(1)$ is not situated in the neighbourhood of the O(5)—O(4) hydrogen bond.
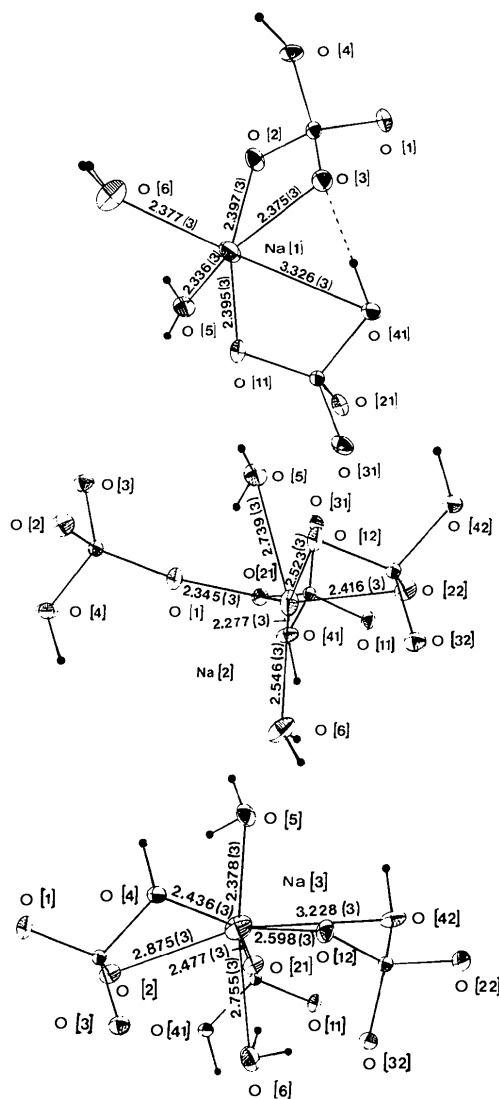

Fig. 4. O atom coordination around the three crystallographically different Na atoms. Na—O bond lengths (Å) are given with e.s.d.'s corresponding to the last significant digit.

receives 0·42 v.u. from its three near Na atoms. By addition of O–H bond strengths calculated from universal curves after Brown & Shannon (1973), both O(5) and O(6) receive full 2·05 and 1·98 v.u. respectively. From these calculated bond strengths for O–H···O hydrogen bonds, bond lengths for O–H and H···O bonds could be derived for the present water hydrogen-bonding system. These values are reported in Table 2 in comparison with distances taken from the X-ray structure analysis. The hydrogen-bond scheme can be seen in Fig. 1.

The water coordination geometry in the present structure is quite similar to that of $Na_3HSiO_4.5H_2O$ (Smolin *et al.*, 1973). $H_2O(1)$ as well as $H_2O(2)$ have type *O* class 3 coordination with three adjoining Na atoms, one in the H–O–H plane and two perpendicular to it (Ferraris & Franchini-Angela, 1972). This geometry is therefore quite different from that of the water molecules in the low-temperature form of $Na_3HSiO_4.2H_2O$ (Schmid, Huttner & Felsche, 1979). In this form one water molecule has tetrahedral type *A* class 2 coordination geometry of two H atoms and two close Na atoms (Ferraris & Franchini-Angela, 1972), whereas $H_2O(2)$ has the more widespread type *O* class 3 coordination. The water geometry and bond lengths can be seen in Fig. 3.

The three crystallographically different Na atoms, Na(1), Na(2) and Na(3), have coordination polyhedra with coordination number 6, with the exception of Na(3) which has coordination number 7 and is more distorted. Fig. 4 shows Na–O polyhedra and distances. As could be shown in the low-temperature form of $Na_3HSiO_4.2H_2O$ (Schmid, Huttner & Felsche, 1979), in the present structure one can also find two distinct spheres of coordination in the Na–O polyhedra, with long second-sphere distances in the coordination polyhedra of Na(1) and Na(3) with Na–O distances of 3·326 and 3·228 Å for Na(1) and Na(3) respectively. Second-sphere Na–O distances all occur with values longer than 3·2 Å. Na–O distances longer than 2·9 Å

do not occur in the first coordination spheres of the Na–O polyhedra in the high-temperature form of $Na_3HSiO_4.2H_2O$, thus resembling the structures of the low-temperature form of $Na_3HSiO_4.2H_2O$ and the $Na_2H_2SiO_4.nH_2O$ sodium silicate hydrates with n = 5,7,8 (Schmid, Huttner & Felsche, 1979; Williams & Dent Glasser, 1971; Dent Glasser & Jamieson, 1976; Jamieson & Dent Glasser, 1966a,b).

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