

## Localization of Water in Hexasodium Hexakis(aluminosilicate)–Deuterium Oxide (1/8), $\text{Na}_6[\text{AlSiO}_4]_6 \cdot 8\text{D}_2\text{O}$ . A Neutron Powder Diffraction Rietveld Profile Analysis at 10 K

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**Abstract.**  $M_r = 1012.55$ , cubic,  $P\bar{4}3n$ ,  $a = 8.8160$  (4) Å,  $V = 685.2$  Å<sup>3</sup>,  $Z = 1$ ,  $D_x = 2.45$  Mg m<sup>-3</sup>,  $\lambda = 1.863$  Å,  $\mu = 0.014$  mm<sup>-1</sup>,  $F(000) = 360.32$ ,  $T = 10$  K. The structure has been refined by the Rietveld profile analysis of powder neutron diffraction data at 10 K. Final  $R_f = 8.84$ ,  $R_p = 15.62$ ,  $R_{wp} = 17.17\%$ . The aluminosilicate framework is completely ordered as known for the aluminosilicate sodalite phases. The six Na ions are statistically distributed on the 8(e) position of space group  $P\bar{4}3n$  and show octahedral coordination to the O atoms [ $3 \times \text{Na}-\text{O}(1) = 2.47$  (1),  $3 \times \text{Na}-\text{O}(2) = 2.44$  (1) Å]. The eight hydrate water O(2) atoms coordinate to the Na ions, thus forming a ditetrahedral arrangement [ $\text{Na}_3\text{O}_4$ ]<sup>3+</sup> per sodalite cage. Both of the crystallographically independent D atoms show positional disorder [O(2)–D(1) = 1.07 (4), O(2)–D(2) = 1.05 (3) Å, D(1)–O(2)–D(2) = 113 (2)°] but only one of the hydrate D atoms exhibits substantial hydrogen bonding to the framework O atoms [D(1)–O(1) = 1.94 (4) Å]. These findings are contrary to the behaviour of the water molecules in the basic sodalites  $\text{Na}_8[\text{AlSiO}_4]_6(\text{OH})_2 \cdot n\text{H}_2\text{O}$ ,  $0 \leq n \leq 4$ , which show no hydrogen bonding to the framework O atoms.

**Introduction.** Borchert & Keidel (1947) first reported a 'sodium poor' sodalite of composition  $\text{Na}_6[\text{AlSiO}_4]_6 \cdot 8\text{H}_2\text{O}$ . This compound was later named zeolite Zh (Zhdanov, Buntar & Egorova, 1964) corresponding to the considerable exchange and absorption properties. Some arbitrary structural data were given (Shishakova & Dubinin, 1965). The structure should show close resemblance to that of the mineral sodalite  $\text{Na}_8[\text{AlSiO}_4]_6\text{Cl}_2$  (Pauling, 1930; Löns & Schulz, 1967). Barrer & White (1952) and Barrer, Cole & Sticher (1968) revealed the solid-solution character of the hydrosodalites (hydroxysodalites) with limits of composition  $\text{Na}_{8-x}[\text{AlSiO}_4]_6(\text{OH})_{2-x} \cdot n\text{H}_2\text{O}$ ,  $0 \leq x \leq 2$ ,  $0 \leq n \leq 8$ .

We recently reported the surprising antagonistic volume/hydrate water concentration effect in the two end-member series of the hydrosodalites (Luger &

Felsche, 1984; Felsche & Luger, 1986a). The basic hydrosodalites  $\text{Na}_8[\text{AlSiO}_4]_6(\text{OH})_2 \cdot n\text{H}_2\text{O}$ ,  $0 \leq n \leq 4$ , show contraction of the  $\text{TO}_4$  framework upon dehydration, whereas the non-basic sodalities  $\text{Na}_6[\text{AlSiO}_4]_6 \cdot n\text{H}_2\text{O}$ ,  $0 \leq n \leq 8$ , expand considerably with release of water molecules [ $-\Delta m(8\text{H}_2\text{O}) \sim +\Delta V(9.6\%)$ ] (Felsche & Luger, 1986b; Baerlocher, Felsche & Luger, 1986). In a thorough reinvestigation by scattering and spectroscopic methods we provide comprehensive data on the different bonding of the non-framework constituents (Na, O, H) and their corresponding interactions with the sodalite framework. We account for the model character of this system for the more complex zeolites *A* and *X/Y* in order to distinguish between  $\alpha$ - and  $\beta$ -cage properties. We have already shown the special features of the structures of:  $\text{Na}_8[\text{AlSiO}_4]_6(\text{OH})_2 \cdot 4\text{H}_2\text{O}$  (neutron, 10 K) (Felsche, Fischer & Luger, 1987);  $\text{Na}_8[\text{AlSiO}_4]_6(\text{OH})_2$  (neutron, 8/295 K) (Luger, Felsche & Fischer, 1987);  $\text{Na}_8[\text{AlSiO}_4]_6(\text{OH})_2$  (quasielastic neutron 2–600 K) (Buehrer, Luger & Felsche, 1985; Buehrer, Felsche & Luger, 1987);  $\text{Na}_6[\text{AlSiO}_4]_6 \cdot n\text{H}_2\text{O}$ ,  $n = 8$ ,  $n = 0$  (X-ray, 295/695 K) (Baerlocher, Felsche & Luger, 1986) by scattering data and <sup>1</sup>H/<sup>23</sup>Na MAS-NMR spectroscopy (Buhl, Felsche, Foerster & Luger, 1986).

The neutron Rietveld structure analysis of the most water-rich hydrate phase of the non-basic series,  $\text{Na}_6[\text{AlSiO}_4]_6 \cdot 8\text{D}_2\text{O}$ , is given here.

**Experimental.** All experimental data are listed in Table 1. Hydrosodalite samples of composition  $\text{Na}_6[\text{AlSiO}_4]_6 \cdot 8\text{D}_2\text{O}$  were obtained from given pure-phase batches of hydrosodalites of composition  $\text{Na}_8[\text{AlSiO}_4]_6(\text{OH})_2 \cdot 4\text{H}_2\text{O}$  by additional leaching of NaOH by D<sub>2</sub>O in an autoclave at 403 K. The products have been examined by thermoanalytical methods. For thermoanalytical data consult Felsche & Luger (1986a,b). Neutron diffraction experiments were carried out on the multichannel diffractometer at the reactor Saphir in the EIR, CH-Würenlingen. Starting parameters in the refinement of Si, Al, O and Na atoms

were from the recent X-ray structure determination of Na<sub>6</sub>[AlSiO<sub>4</sub>]<sub>6</sub>·8H<sub>2</sub>O (Baerlocher, Felsche & Luger, 1986). The positions of the D atoms were selected from the difference Fourier maps. Several cycles of subsequent refinement of the peak profiles and atomic parameters finally yielded the agreement of observed and calculated intensities as shown in Fig. 1. Computer program used was the Rietveld version of Werner, Salomé, Malmros & Thomas (1979), *b* values from Koester, Rauch, Herkens & Schroeder (1981).

Table 1. *Experimental data*

Sample container	Cylindrical vanadium container, 8 mm diameter, He-gas atmosphere
Radiation	Neutrons (wavelength $\lambda = 1.1863 \text{ \AA}$ )
$\mu R$	0.113
Reactor	Saphir, EIR CH-Würenlingen
Monochromator	(002) planes of graphite
Filter	Pyrolytic graphite, thickness 6 cm
Cooling	Closed-cycle He refrigerator
Pattern $2\theta$ range ( $^{\circ}2\theta$ )	3–130.7
Step-scan increment ( $^{\circ}2\theta$ )	0.1
Coherent scattering length (fm)	Al = 3.49, Si = 4.15, O = 5.81, Na = 3.63, D = 6.674
Number of contributing reflections	252
Background	Linear interpolation between points of no contribution from reflections
Preferred orientation	None
Number of cycles	6
Number of parameters	23
Definitions	
$R_I = 100 \sum  I_i(\text{obs}) - (1/c)I_i(\text{calc})  / \sum I_i(\text{obs})$	
$R_P = 100 \sum  Y_i(\text{obs}) - (1/c)Y_i(\text{calc})  / \sum Y_i(\text{obs})$	
$R_{wp} = 100 [ \sum w_i  Y_i(\text{obs}) - (1/c)Y_i(\text{calc}) ^2 / \sum w_i  Y_i(\text{obs}) ^2 ]^{1/2}$	
Final <i>R</i> values	$R_I = 8.84$ , $R_P = 15.62$ , $R_{wp} = 17.17$
Max. $\Delta/\sigma$	<0.1

**Discussion.** Atomic parameters and isotropic thermal parameters are given in Table 2, atomic distances and angles are listed in Table 3.\* The configuration of the non-framework constituents Na, O(2), D(1), D(2) is given in Fig. 2. The six Na ions per unit cell are statistically distributed on the 8(*e*) position of space group *P*43*n*, yielding a bond distance to the framework O atoms of Na–O(1) = 2.47 (1) Å. The water O(2) atoms are located on the 8(*e*) position of the cubic unit cell, yielding a tetrahedral configuration within the sodalite cage. The refinement of the O(2) position yields an O(1)···O(2) distance of 2.986 (8) Å, short enough to be hydrogen bridged. Compare this with the X-ray data, which show an O(1)···O(2) contact of 2.956 (8) Å (Baerlocher, Felsche & Luger, 1986). In fact, the D(1) atoms, which are statistically distributed on the 24(*i*) position of space group *P*43*n*, yield bond lengths of O(1)–D(1) = 1.94 (4) and O(2)–D(1) = 1.07 (4) Å, respectively. Significantly, the hydrogen bonding is not linear, O(2)–D(1)–O(1) = 165 (2)°. The other half of the D atoms, D(2), shows also positional disorder with statistical distribution of the eight D(2) atoms on the 24(*i*) position, yielding bond lengths of D(2)–O(2) = 1.05 (3) and D(2)–O(1) = 2.35 (4) Å, respectively. The latter value excludes the possibility of hydrogen bonding from D(2) to the framework O(1) atom.

\* Lists of structure factors and observed and calculated data points for Fig. 1 have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43694 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

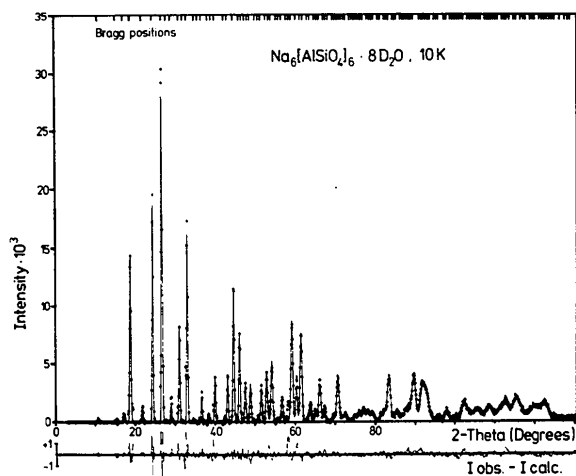


Fig. 1. Observed (dots) and calculated (solid line) neutron powder profiles of the Na<sub>6</sub>[AlSiO<sub>4</sub>]<sub>6</sub>·8D<sub>2</sub>O sample at temperature of 10 K. Significance of differences  $I_{\text{obs}} - I_{\text{calc}}$  is shown at the bottom. Bragg positions are indicated at the top of the diagram.

Table 2. *Atomic positional parameters and isotropic thermal parameters (Å<sup>2</sup>) with e.s.d.'s in parentheses*

	Occupancy	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
Al	1.0	6( <i>c</i> )	$\frac{1}{4}$	0	$\frac{1}{2}$	0.18 (2)
Si	1.0	6( <i>d</i> )	$\frac{1}{4}$	$\frac{1}{2}$	0	0.18 (2)
O(1)	1.0	24( <i>i</i> )	0.1363 (5)	0.1455 (7)	0.4313 (3)	0.18 (2)
O(2)	1.0	8( <i>e</i> )	0.3773 (6)	0.3773 (6)	0.3773 (6)	1.7 (2)
D(1)	0.33	24( <i>i</i> )	0.286 (5)	0.379 (2)	0.298 (5)	4.0 (5)
D(2)	0.33	24( <i>i</i> )	0.373 (5)	0.440 (4)	0.276 (4)	11 (1)
Na	0.75	8( <i>e</i> )	0.151 (1)	0.151 (1)	0.151 (1)	2.1 (2)

Table 3. *Selected bond distances (Å) and angles (°)*

Al–O(1)	1.737 (5)	Si–O(1)	1.630 (5)
O(1)–Al–O(1 <sup>iv</sup> )	109.5 (2)	O(1)–Si–O(1 <sup>iv</sup> )	108.6 (2)
O(1 <sup>iv</sup> )–Al–O(1 <sup>iv</sup> )	109.5 (2)	O(1 <sup>iv</sup> )–Si–O(1 <sup>iv</sup> )	111.2 (3)
Na–O(1)	2.47 (1)	Na–D(1)	2.50 (2)
Na–O(2)	2.44 (1)	Na–D(2)	2.66 (4)
Na–Na	3.77 (1)		
O(1)–D(1)	1.94 (4)	O(2)–D(1)	1.07 (4)
O(1)–D(2)	2.35 (4)	O(2)–D(2)	1.05 (3)
D(1)–O(2)–D(2)	113 (2)	O(1)–D(1)–O(2)	165 (2)

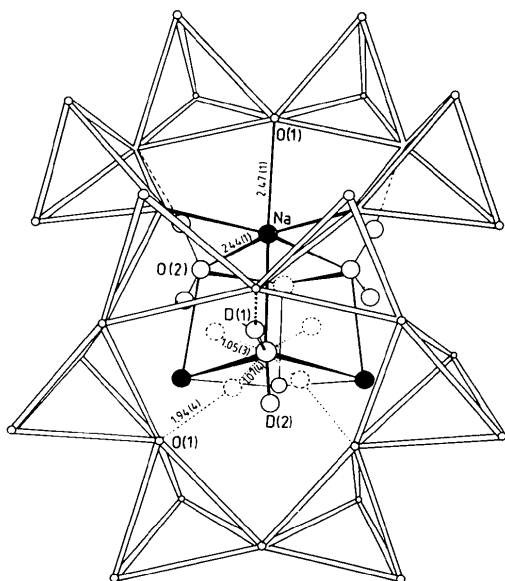


Fig. 2. Configuration of the non-framework constituents Na, O(2), D(1) and D(2) within the sodalite cage of the structure of  $(\text{Na}_3\text{Q})_2[\text{AlSiO}_4]_6 \cdot 8\text{D}_2\text{O}$ . Only two six-membered rings of the aluminosilicate framework are shown, Si and Al atoms omitted for clarity. Dashed lines show the hydrogen bonding between one of the H atoms of the hydrate water [D(1)—O(1) = 1.94 (4) Å] and the framework O atoms. It is this hydrogen bond which makes this structure different from the hydrates of the basic hydrosodalite phases  $\text{Na}_8[\text{AlSiO}_4]_6(\text{OH})_x \cdot n\text{H}_2\text{O}$  ( $0 \leq x \leq 2$ ;  $0 < n \leq 4$ ), which give no evidence for hydrogen bonding from corresponding diffraction studies. Dashed circles indicate positional disorder of symmetry-equivalent D(1) and D(2) atoms.

Because of the large value of the temperature factor of the D(2) atom, the enlarged angle D(1)—O(2)—D(2) = 113 (2)° and the contact distances of the H atoms and the Na ions, there is some evidence for

positional disorder or considerable dynamical behaviour of the D(2) atoms with respect to the remaining non-framework constituents. For verification of these findings special NMR and quasielastic neutron scattering experiments are now being carried out.

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## Structure of Caesium Hydrogenselenate

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**Abstract.**  $\text{CsHSeO}_4$ ,  $M_r = 276.9$ , monoclinic,  $P2_1/c$ ,  $a = 7.977(4)$ ,  $b = 8.409(4)$ ,  $c = 7.803(6)$  Å,  $\beta = 111.37(5)^\circ$ ,  $V = 487.4$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 3.77$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 15.6$  mm<sup>-1</sup>,  $F(000) =$

488,  $T = 299(1)$  K, final  $R = 0.047$  and  $wR = 0.062$  for 1020 non-zero reflexions. The crystal is not isomorphous with any other  $\text{MHSeO}_4$  or  $\text{MHSO}_4$  crystal. The separated chains of asymmetric hydrogen bonds run parallel to the  $c$  axis. The O...O distance utilized in the hydrogen bonding is 2.603 (15) Å.

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