

Structure of Hydroxysodalite $\text{Na}_8[\text{AlSiO}_4]_6(\text{OH})_2$, a Powder Neutron Diffraction Study at 8 K

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Abstract. $\text{Na}_8[\text{AlSiO}_4]_6(\text{OH})_2$, $M_r = 932.10$, cubic, $P\bar{4}3n$, $a = 8.7342(8) \text{ \AA}$, $V = 666.30(19) \text{ \AA}^3$, $Z = 1$, $D_x = 2.32 \text{ Mg m}^{-3}$, neutrons, $\lambda = 2.343 \text{ \AA}$, $\mu = 0.0098 \text{ mm}^{-1}$, $F(000) = 219.06$. $T = 8 \text{ K}$. The structure has been refined by the Rietveld profile analysis of powder neutron diffraction data at 8 K. Final $R_f = 0.051$, $R_p = 0.073$, $R_w = 0.166$, $R_{wp} = 0.162$. The aluminosilicate framework is completely ordered as known for the aluminosilicate sodalite phases. The O(2) atom of the hydroxyl group is located on the central 2(a) position of the sodalite cage. The two H atoms per unit cell are statistically distributed on position 8(e) of space group $P\bar{4}3n$, corresponding to the O-H bond length of 1.09 (3) \AA .

Introduction. The sodalite framework structure first described by Pauling (1930) and refined by Löns & Schulz (1967) has proved to be a versatile host lattice for a number of M^+/M^{2+} metal ions (M : Na, K, Rb, Ag, Cu, Ca, Sr, Co, Ni, ...) and corresponding X^- , XO_3^- or XO_4^- -type anions (X : Cl, Br, I, S, Se, N, P, ...) (Barrer, Cole & Sticher, 1968). So-called hydroxysodalites, $M_{6+x}^+[\text{AlSiO}_4]_6(\text{OH})_x.n\text{H}_2\text{O}$, $0 \leq x \leq 2$, $0 < n \leq 8$, contain water of different forms (OH^- , H_2O) and alkali ions, M^+ : Na^+ , K^+ , as non-framework constituents (Barrer & Vaughan, 1971). X-ray and neutron diffraction studies as well as ^1H NMR experiments on $\text{Na}_8[\text{AlSiO}_4]_6(\text{OH})_2.2\text{H}_2\text{O}$ showed different positioning of $\text{OH}^-/\text{H}_2\text{O}$ molecules with respect to the tetrahedral organization of the alkali-metal ions (Bondareva & Malinovskii, 1983; Hassan & Grundy, 1983; Galitskii, Grachushnikov, Ilyukhin & Belov, 1974).

From thorough thermoanalytical data based on distinct preparation techniques for pure phase polycrystalline samples we were recently successful in distinguishing between two separate series of phases $\text{Na}_6[\text{AlSiO}_4]_6.n\text{H}_2\text{O}$ with $0 \leq n \leq 8$ and $\text{Na}_8[\text{AlSiO}_4]_6(\text{OH})_2.n\text{H}_2\text{O}$ with $0 \leq n \leq 4$ which show limited solid-solution behaviour (Luger & Felsché, 1984; Felsché & Luger, 1986).

Within a general approach of elastic and inelastic neutron scattering experiments we shall deal with hydroxysodalite species of different $\text{OH}^-/\text{H}_2\text{O}$ constitutions in order to clarify fundamental hydrogen-controlled interactions between framework and non-framework constituents in zeolite materials. X-ray and neutron diffraction experiments recently verified hydrogen bonding between the non-framework constituents (OH_2) and framework O atoms in phases of the series $\text{Na}_6[\text{AlSiO}_4]_6.n\text{H}_2\text{O}$ only (Bärlocher, Felsché, Fischer & Luger, 1986; Felsché, Fischer & Luger, 1986*b*). No hydrogen bonding has been observed between framework and non-framework O atoms in the deuterized phase of the highest hydrate of the basic hydroxysodalite phase $\text{Na}_8[\text{AlSiO}_4]_6(\text{OD})_2.4\text{D}_2\text{O}$, however (Felsché, Fischer & Luger 1986*a*).

We report here on the 8 K neutron diffraction study of the hydroxysodalite $\text{Na}_8[\text{AlSiO}_4]_6(\text{OH})_2$, which is the anhydrous end member of the basic sodalite series.

Experimental. Hydroxysodalite samples $\text{Na}_8[\text{AlSiO}_4]_6(\text{OH})_2$ have been obtained from given pure phase batches of the hydroxysodalite hydrate $\text{Na}_8[\text{AlSiO}_4]_6(\text{OH})_2.n\text{H}_2\text{O}$, $n = 3(8:2:3)$.* Thermogravimetrically controlled annealing at 863 K for 3 h under dry N_2 atmosphere yielded corresponding samples of composition $\text{Na}_8[\text{AlSiO}_4]_6(\text{OH})_2(8:2:0)$ * (Luger & Felsché, 1984). Care had to be taken against subsequent attack of (8:2:0)* samples by moisture or carbon dioxide from the atmosphere. Any manipulations of samples, e.g. in analytical procedures or for transfer to further equipment, had to be carried out under air-exclusion conditions. Owing to high-temperature annealing (863 K) of the starting product $\text{Na}_8[\text{AlSiO}_4]_6(\text{OH})_2.3\text{H}_2\text{O}$ a small amount (~5%) of the decomposition product $(\text{Na}_2\text{O})_{0.16}\text{Na}[\text{AlSiO}_4]$ appeared to contribute to the diffraction pattern of the sample used.

* Molar ratios of non-framework constituents are given as an abbreviation.

Table 1. *Experimental data*

Sample container	Cylindrical vanadium container. 10 mm diameter, He gas atmosphere
Radiation	Neutrons [wavelength $\lambda = 2.343$ (2) Å]
μR	0.098
Reactor	Saphir, EIR CH-Würenlingen
Monochromator	(002) planes of graphite
Filter	Pyrolytic graphite, thickness 6 cm
Soller slits	Horizontal divergence $\alpha_1 = 20$, $\alpha_2 = 30^\circ$
Cooling	Closed-cycle He refrigerator
Pattern 2θ range ($^\circ 2\theta$)	6.05–139.7
Step-scan increment ($^\circ 2\theta$)	0.15
Coherent scattering lengths (fm)	Al = 3.49, Si = 4.15, O = 5.81, H = -3.44, Na = 3.63
Number of contributing reflections	42
structure 1	12
structure 2	
Background	Linear interpolation between points of no contribution from reflections
Preferred orientation	None
Number of cycles	6
Number of parameters	19
Definitions	
$R_I = \sum I_i(\text{obs}) - (1/c)I_i(\text{calc}) / \sum I_i(\text{obs})$	
$R_F = \sum I_i(\text{obs}) ^{1/2} - I_i(\text{calc}) ^{1/2} / \sum I_i(\text{obs}) ^{1/2}$	
$R_p = \sum Y_i(\text{obs}) - (1/c)Y_i(\text{calc}) / \sum Y_i(\text{obs})$	
$R_{wp} = [\sum w_i Y_i(\text{obs}) - (1/c)Y_i(\text{calc}) ^2 / \sum w_i Y_i(\text{obs}) ^2]^{1/2}$	
$Y_i =$	
Largest correlation matrix element	0.74
Max. A/σ	<0.01
Computer program used	Rietveld, version of Werner, Salomé & Malmros (1979)

The refinement yielded the final $R_I = 0.057$, $R_F = 0.073$ for the hydroxysodalite and $R_p = 0.166$, $R_{wp} = 0.162$ for the profile. The α -carnegieite-type phase $(\text{Na}_2\text{O})_{0.16}\text{Na}[\text{AlSiO}_4]$ (Klingenberg & Felsche, 1986) has been refined with space group $F43m$ and the final parameters Si (0, 0, 0), Al ($\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$), O (x , x , x), $x = 0.178$, Na ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) and $a = 7.261$ Å. The refinement of this phase yielded $x = 0.176$ (4), $a = 7.264$ (4) Å and final $R_I = 0.317$ and $R_F = 0.231$. (For details see Table 1.)

Discussion. Atomic parameters and isotropic thermal parameters are given in Table 2, atomic distances and angles in Table 3. The agreement between the observed and the calculated profiles is shown in Fig. 1.*

The configuration of the non-framework constituents Na, O(2) and H in the sodalite framework is given in Fig. 2. The Na atoms are located on the eightfold 8(e) position in the cubic unit cell of space-group symmetry $P43n$. The Na atoms of the tetrahedral Na configuration show close contacts to three O atoms of the six-membered rings of the cubo-octahedral TO_4 -framework structure [$\text{Na}-\text{O}(1) = 2.349$ (9) Å]. The centre 2(a) position is occupied by the non-framework oxygen O(2) of the formal hydroxyl grouping (see below), whereas it is occupied by an H atom of the

* Lists of structure factors, observed and calculated data points for Fig. 1 and extended lists of chemical bonding data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43269 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Atomic positional parameters and isotropic thermal parameters (\AA^2) with e.s.d.'s in parentheses*

Occu- pancy	Site	x	y	z	B
Al	1-0 6(c)	$\frac{1}{4}$	$\frac{1}{4}$	0	0.59 (9)
Si	1-0 6(d)	$\frac{1}{4}$	0	$\frac{1}{4}$	0.59 (9)
O(1)	1-0 24(f)	0.1370 (8)	0.4265 (5)	0.1458 (8)	0.59 (9)
O(2)	1-0 2(a)	0	0	0	1.9 (5)
Na	1-0 8(e)	0.1587 (9)	0.1587 (9)	0.1587 (9)	1.2 (3)
H	0.25 8(e)	-0.072 (4)	-0.072 (4)	-0.072 (4)	2 (1)

Table 3. *Selected bond distances (\AA) and angles ($^\circ$) with e.s.d.'s in parentheses*

SiO₄ tetrahedra			
Si-O(1)	1.635 (6)	O(1)-Si-O(1)	108.1 (3)
O(1)-O(1)	2.646 (6)		112.4 (3)
	2.716 (6)		
AlO₄ tetrahedra			
Al-O(1)	1.734 (6)	O(1)-Al-O(1)	108.9 (3)
O(1)-O(1)	2.822 (6)		110.6 (3)
	2.852 (6)	Si-O(1)-Al	132.9 (3)
Sodium coordination			
Na-O(1)	2.349 (9)		
Na-O(2)	2.401 (8)		
Hydrogen coordination			
H-O(2)	1.09 (3)		
H-Na	2.28 (3)		

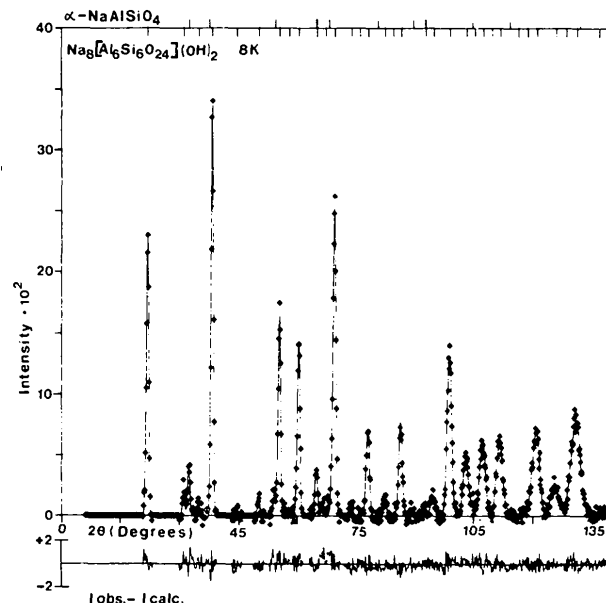


Fig. 1. Observed (dots) and calculated (solid line) neutron powder diffraction profile of the $\text{Na}_8[\text{AlSi}_6\text{O}_{24}](\text{OH})_2$ sample at 8 K. Significance of differences $I_{\text{obs}} - I_{\text{calc}}$ is shown at the bottom. Contributions of the cubic Na_2O -rich carnegieite-type phase $(\text{Na}_2\text{O})_{0.16}\text{NaAlSiO}_4$ are indicated at the top, where Bragg positions corresponding to α - NaAlSiO_4 are given.

hydrated hydroxyl group $[O_{1+n}H_{1+2n}]^-$ in the parent hydrosodalite species $Na_8[AlSiO_4]_6(OH)_2 \cdot 4H_2O$ (Felsche, Fischer & Luger, 1986a). However, Hassan & Grundy (1983) suggested the centre 2(a) position to be empty in the basic sodalite of intermediate composition $Na_8[AlSiO_4]_6(OH)_2 \cdot 2H_2O$ (single-crystal X-ray structure analysis at 298 K). Bondareva & Malinovskii (1983) confirm the positional disorder from the statistical distribution of the OH/OH₂ constituents of the dihydrate $Na_8[AlSiO_4]_6(OH)_2 \cdot 2H_2O$ in the orthorhombic low-temperature phase, which shows up below 150 K at a reversible phase transition. In the case of our hydrosodalite sample of $Na_8[AlSiO_4]_6(OH)_2$ no phase transition has been observed down to temperatures of 8 K.

From the centring of the sodalite cage by the O atom a close resemblance is given with the mineral sodalite $Na_8[AlSiO_4]_6Cl_2$ which shows the Cl atom on position 2(a) of the same space-group symmetry, unambiguously (Löns & Schulz, 1967). Thus the presence of the one H atom per sodalite cage makes the essential difference between the two structures. The H atom coordinates the central O(2) atom statistically in a tetrahedron as shown in Fig. 2. Detailed interpretation of the bonding of the H atom is strongly affected by the extent of the relative contributions of positional disorder and of the thermal motion of the H atom in this 8 K study. Taken strictly at face value the distances of

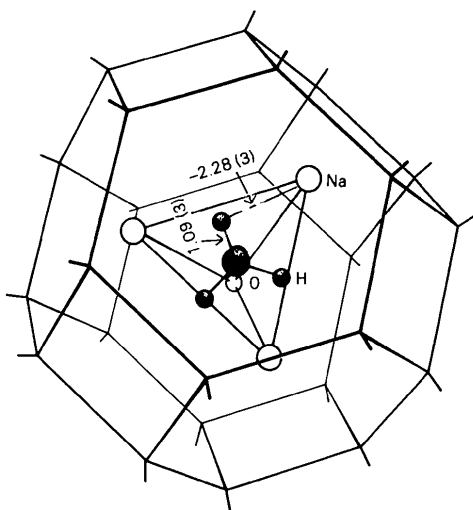


Fig. 2. Configuration of the non-framework constituents Na, O, H in the framework structure of $Na_8[AlSiO_4]_6(OH)_2$. The atom O(2) of the hydroxyl group is unambiguously located on the centre of the cubo-octahedral cage of the $[AlSiO_4]^-$ framework. The H atom shows positional disorder. It is statistically distributed on the vertices of the smaller tetrahedron, thus contacting the O atom [$H-O(2) = 1.09(3) \text{ \AA}$] and three out of four Na atoms of the Na_4 tetrahedron as well [$H-Na = 2.28(3) \text{ \AA}$]. One sodalite cage with $T-O-T = 180^\circ$ bridging angles is shown for clarity.

$O-H = 1.09(3)$ and $Na-H = 2.28(3) \text{ \AA}$ provide some ambiguity with regard to the real nature of the bonding between the H atom and the central O(2) atom and also the three out of four Na atoms which coordinate the H atom in a trigonal pyramid.

Data for the inelastic and quasi-elastic neutron scattering experiment of the same and the deuterized samples of hydroxysodalite covering the extended range of temperatures $2 \text{ K} < T < 1000 \text{ K}$ will help to overcome the problem of distinguishing between dynamical and static-statistical properties of the H atom in this phase. Thus special ordering of the H atoms would amount to a reduction of the space-group symmetry below cubic! (Bührer, Felsche & Luger, 1987).

Spectroscopic data for the corresponding high-temperature *in situ* IR and magic-angle spinning (MAS) 1H NMR experiments at 298 K provide some preliminary evidence of the very distinct nature of the chemical bond to the H atom in the given matrix of the sodalite cage. The diminishing of the 3640 cm^{-1} stretching mode of the hydroxysodalite sample of composition $Na_8[AlSiO_4]_6(OH)_2$ and the chemical shift of -6.5 p.p.m. indicate substantial decoupling of the O-H contact. Values of the chemical shift of 3.5 and -1.0 p.p.m. are found in the 1H -MAS-NMR spectrum of the parent phase for regular hydroxyl groupings for comparison (Felsche & Luger, 1986; Buhl, Felsche, Förster & Luger, 1986).

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