Synthesis and Structure of $NaZnSiO_3OH$, a New Chiral Zincosilicate Framework Material

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The structure of $NaZnSiO_3OH$, synthesized hydrothermally by reaction of Na_2ZnSiO_4 and NaOH, has been determined from single-crystal X-ray and powder neutron diffraction data (orthorhombic, space group $P2_12_12_1$, $a = 7.6872(2)$ Å, $b = 9.3899(2)$ Å, $c = 5.155(1)$ Å, $Z = 4$). The structure has a framework constructed from ZnO_4 and SiO_3OH tetrahedra with bridging and trigonal oxygen atoms. Channels formed from eight-membered rings of tetrahedra house the sodium ions and are also partially blocked by moderately strongly hydrogen bonded OH groups.

Introduction

Inorganic solids with framework structures have important applications based around their ion exchange, adsorption, and catalysis properties. The number of zeolite structures has increased rapidly over the past few decades, and well over 100 structure types have been described.[1] Similar framework structures can be built from a variety of other, nonaluminosilicate, polyhedral units, though the majority of these are tetrahedral species such as PO_4, GaO_4, GeO_4, BO_4, and ZnO_4. Recently, attention has turned to framework materials constructed from other polyhedral MO_n units; these component ions are frequently octahedra, though in a few cases other species, for example, trigonal (BO_3) or five-coordinate species, $Al(O,OH)_5$, can be employed.

In the case of four-coordinate, framework-forming species MO_4, each of the oxygen atoms normally links between two polyhedra, giving rise to so-called "tecto" type structures. For six-coordinate species, e.g., $Ti(OX)_6$, the oxygens may be shared between two or more polyhedra or may be terminal units, hydroxyl or water molecules. In some framework structures, e.g., cloverite, pendent hydroxyl groups exist on tetrahedral sites.

Silicate chemistry shows a wide range of structural units extending from discrete SiO_4^{4-} units, in materials such as Na_4SiO_4, to the three-dimensional structures of the tectosilicates, e.g., felspars, stuffed silicas, and aluminosilicate zeolites. Intermediate levels of linking of the SiO_4 units produce the metasilicates, orthosilicates, and other more complex silicate species. These silicate units can be bound in two- and three-dimensional frameworks as in, for example, the sorosilicate $ACuSi_4O_{10}$[2], which contains Si_2O_7 units linked together with CuO_4 groups to form infinite sheets. The orthosilicate species $(SiO_3OH)^{3-}$ is known in a few structures but mainly as a discrete ion, for example, as in Afwillite $Ca_3(SiO_3OH)\cdot 2H_2O$;[3] in framework-type structures it exists in Lovozerite, $Na_2ZrSi_6O_{15}(H_2O)_3(NaOH)_{0.5}$,[4] but the SiO_3OH group is very uncommon as a building block in three-dimensional structures.

Frameworks containing the zincate anion, ZnO_4^{6-}, are also relatively uncommon, probably due to the ready hydrolysis of this species. Recently, Stucky and co-workers[5] have described a number of zincophosphates where the presence of the higher charge on phosphorus helps offset the high framework charge caused by the presence of the divalent cation. Another feature of these materials is higher coordination numbers for oxygen due to the relatively weak interaction of oxygen with the divalent cation. Frameworks containing high levels of zinc based on zincosilicates are much rarer and limited mainly to the condensed cristabolite-type structures, e.g., Na_2SiZnO_4[6] and $Na_2Zn_2Si_2O_7$.[7] Generally, synthesis under nonhydrothermal or very basic conditions is required to form zincosilicates with high levels of zinc to avoid hydrolysis of the tetrahedral zincate group.

The aim of our current work is the incorporation of significant levels of zinc into materials based on linked tetrahedra in order to produce highly charged frameworks with enhanced ion exchange and catalytic properties. In this paper, we report the synthesis and structure determination of an unusual chiral framework structure containing the SiO_3OH unit with ZnO_4 tetrahedra.

Experimental Section

Synthesis. $Na_2[ZnSiO_4]$ was synthesized hydrothermally in Teflon-lined steel autoclaves from zinc oxide and sodium metasilicate pentahydrate in a 14 M sodium hydroxide solution. In a typical reaction, a temperature of 180 °C and a reaction time of 1 day was employed.

The sodium zincosilicate precursor, $Na_2[ZnSiO_4]$, was further reacted in the same autoclaves with a dilute (2 M) sodium hydroxide solution over a range of reaction times to synthesize the new phase. The highest yields were found with the following reaction conditions: $Na_2[ZnSiO_4]$ (2 g) reacted with aqueous sodium hydroxide (0.56 g in 8 mL) at 225 °C for 5 days. The reaction product was filtered, washed in distilled water, and dried at 90 °C overnight.

Under all conditions studied, a multiphase product was formed containing single crystals of the predominant $NaZnSiO_3OH$ phase and

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(1) Meier, W. M.; Olson, D. H.; Baerlocher, Ch. *Atlas of Zeolite Structure Types*; International Zeolite Assosiation: Elsevier, 1996.

(2) Hughes, E. M.; Pack, M. J.; Dann, S. E.; Weller, M. T. *An. Quim. Int. Ed*. **1997**, *93*, 233.

(3) Saito, F.; Mi, G. M.; Hanada, M. N. *J. Solid State Ion*. **1997**, *101*, 37.

(4) Ilyukhin, V. V.; Belov, N. V. *Kristallogr.* **1960**, *5*, 200.

(5) Xianhui, B.; Pingyun, F.; Thurman, G. E.; Stucky, G. D. *J. Solid State Chem*. **1998**, *136*, 210.

(6) Litvin, B. N.; Mel'nikov, O. K.; Ilyukhin, V. V.; Nikitin, A. V. *Kristallogr.* **1964**, *9*, 943.; *Sov. Phys. Crystallogr.* **1965**, *9*, 795.

(7) Amirov, S. T.; Nikitin, A. V.; Ilyukhin, V. V.; Belov, N. V. Dokl. *Akad. Nauk SSSR* **1967**, *177*, 92.; *Sov. Phys. Dokl.* **1968**, *12*, 987.

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Table 1. X-ray Crystallographic Data Collection and Refinement Parameters for $NaZnSiO_3OH$

	$NaZnSiO_3OH$
chemical formula	$HO_4NaSiZn$
fw	362.92
temperature	150 K
space group	$P2_12_12_1$ (19)
a	7.664(1) Å
b	9.370(2) Å
c	5.148(2) Å
V	369.7(1) Å^3
λ	0.7071 Å
Z	4
D_{calc}	3.260 g cm^{-3}
μ(Mo Kα)	69.44 cm^{-1}
R^a	0.0315
$R_w{}^b$	0.0392

[a] $R = \Sigma(|F_{obs}|_i - |F_{calc}|_i)/\Sigma|F_{obs}|_i$. [b] $R_w = \sqrt{[\Sigma w_i(|F_{obs}|_i - |F_{calc}|_i)^2/\Sigma w_i|F_{obs}|_i{}^2]}$.

a small level of impurity in the form of a white powder. The crystals were easily separated and washed with distilled water to remove any of the second phase.

Characterization. Initial characterization was carried out on a well-ground sample of the crystals using a Siemens D5000 powder X-ray diffractometer, producing copper $K_{\alpha1}$ radiation with wavelength $\lambda = 1.5406$ Å. Data were collected in the 2θ range 5−60° over 1 h. Further structural analysis was carried out using the following techniques. Powder neutron diffraction data were recorded on a well-ground sample of crystals using the POLARIS instrument at the Rutherford Appleton Laboratory, Oxfordshire; the sample was loaded into a 7 mm vanadium can, and a run time of 4 h at 298 K was used. As a result of the low atomic percent of hydrogen in the compound, acceptable data could be obtained on a nondeuterated sample. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were undertaken using a Polymer Laboratories PL-STA 1500 simultaneous thermal analysis machine; ^{29}Si MAS NMR spectra were collected on a Bruker AM300 spectrometer using a sample spin rate of 4500 kHz. The infrared spectrum was recorded on a Perkin-Elmer Paragon 1000 FT-IR and SEM on a JEOL JSM-6400 analytical scanning electron microscope.

Powder X-ray Diffraction. The data recorded were used to establish the unit cell dimensions using the TREOR[8] computer package. The material was found to be orthorhombic, with cell parameters $a = 7.696(2)$ Å, $b = 9.403(2)$ Å, and $c = 5.168(1)$ Å. The second phase formed under the synthesis conditions was identified as $Na_2Zn_2Si_2O_7$, originally reported in 1966 by Holland and co-workers.[9]

Single-Crystal X-ray Diffraction. Data collection used a Rigaku AFC7S four-circle diffractometer equipped with an Oxford Systems open-flow cryostat operating at 150 K and using graphite-monochromated Mo Kα X-radiation ($\lambda_{max} = 0.710\,73$ Å). Data collection and refinement parameters are summarized in Table 1. No significant crystal decay or movement was observed. The structure was solved by direct methods[10] and then developed by iterative cycles of full-matrix least-squares refinement and Fourier difference syntheses, which located all non-hydrogen atoms in the asymmetric unit.[11] All atoms were refined anisotropically with the exception of oxygen atoms, which were refined isotropically. While a number of possible sites for the hydrogen atom were identified, the location of this atom could not be determined unambiguously. The Flack parameter[12] was refined (0.008(14)), and this confirmed the correct choice of enantiomorph. Final refined atomic coordinates are given in Table 2. Supplementary Information, including the asymmetric unit and derived bond lengths and angles from this data set, has been deposited.

Table 2. Final Refined Coordinates and X-ray Crystallographic Data Collection Parameters for $NaZnSiO_3OH$ (esd Given in Parentheses); Single-Crystal XRD

atom	X	Y	Z	B^a/Å^2
Zn	0.11073(7)	0.98891(6)	0.0246(1)	0.19(1)
Si	−0.0155(2)	0.6611(1)	−0.0107(3)	0.24(3)
Na	−0.2078(3)	0.8342(2)	0.4705(5)	0.67(4)
O(1)	−0.0192(5)	0.6480(4)	0.6808(7)	0.19(6)
O(2)	−0.0384(4)	0.8256(3)	0.0804(7)	0.36(7)
O(3)	0.3322(5)	0.9293(4)	−0.1337(8)	0.44(7)
O(4)	−0.3331(4)	0.9088(3)	0.8906(7)	0.16(6)

[a] $B_{eq} = 8/3\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}aa^*cc^*\cos\beta + 2U_{23}bb^*cc^*\cos\alpha)$.

Table 3. Final Refined Coordinates for $NaZnSiO_3OH$ (esd Given in Parentheses); Powder Neutron Diffraction[a]

atom	site	X	Y	Z	B/Å^2
Zn	4a	0.1121(3)	0.9885(3)	0.0224(5)	0.29(4)
Si	4a	−0.0164(5)	0.6611(3)	−0.0073(7)	0.39(5)
Na	4a	−0.2041(6)	0.8327(6)	0.4771(9)	1.32(9)
O(1)	4a	−0.0199(4)	0.6486(3)	0.6776(5)	1.03(5)
O(2)	4a	−0.0379(3)	0.8259(3)	0.0755(4)	0.65(4)
O(3)	4a	0.3326(3)	0.9290(2)	−0.1304(5)	0.33(4)
O(4)	4a	−0.3351(4)	0.9079(3)	0.8902(6)	0.84(5)
H	4a	0.2211(8)	0.3743(5)	0.5265(13)	2.11(9)

[a] Space group $P2_12_12_1$: $a = 7.6872(2)$ Å, $b = 9.3899(2)$ Å, $c = 5.1559(1)$ Å; $R_p = 2.48\%$, $R_{wp} = 1.58\%$, $\chi^2 = 1.188$.

Table 4. Selected Derived Bond Lengths (Å); Powder Neutron Diffraction

Zn−O(1)	1.956(4)	Si−O(1)	1.629(4)
Zn−O(2)	1.932(3)	Si−O(2)	1.613(4)
Zn−O(3)	1.951(3)	Si−O(3)	1.602(4)
Zn−O(3)	1.996(4)	Si−O(4)	1.651(5)
Na−O(1)	2.462(6)	Na−O(3)	3.052 (6)
Na−O(1)	2.562(6)	Na−O(4)	2.459(6)
Na−O(2)	2.434(6)	Na−O(4)	2.494(6)
H−O(4)	1.026(8)	O(4)H···O(2)	1.571(7)

Powder Neutron Diffraction. Single-crystal X-ray diffraction indicated the presence of a hydroxide group attached to the tetrahedral silicon atoms; however, the low X-ray scattering cross section of hydrogen made it impossible to accurately locate within the structure using this method. Powder neutron diffraction data were therefore recorded with the aim of determining the hydrogen atom coordinates. The data were refined with the GSAS[13] computer package using the structure obtained from the single-crystal X-ray diffraction as the starting model. The framework and sodium ions refined with only slight adjustment to the atom positions and cell dimensions. A difference Fourier map was then used to locate the hydrogen atom present in the structure. An area of negative scattering ($b_H = -3.34$ fm) was clearly visible at a distance of about 1 Å from the terminal oxygen (O4); these coordinates were entered into the structure as a hydrogen atom. The position of this final atom was refined through several cycles. The final stage of the refinement incorporated all the atoms' positional and thermal parameters together with a full analysis of the background and peak shape functions. The refinement converged yielding good R factors and a χ^2 of 1.188; the final atomic coordinates are detailed in Table 3, with important derived bond distances and angles being shown in Tables 4 and 5. The refined atomic coordinates were in all cases close to those found in single-crystal X-ray diffraction study. The final refinement profile fit is shown in Figure 1.

Thermal Analysis. A single weight loss of 5.0% was seen at 450 °C accompanied by an endothermic transition; see Figure 2. This is consistent with the decomposition of the hydroxide group and loss of half a water molecule per formula unit from the material (calculated weight 4.96%). Powder neutron diffraction data recorded above this

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(8) Werner, P. E. *Z. Kristallogr.* **1964**, *120*, 375.
(9) Holland, A. E.; Segnit, E. R. *Aust. J. Chem.* **1966**, *19*, 905.
(10) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467.
(11) *TEXSAN*, *Crystal Structure Analysis Package*; Molecular Structure Corporation: Houston, TX, 1992.
(12) Lack, H. D. *Acta Crystallogr., Sect. A* **1983**, *39*, 876.
(13) Larson, A. C.; Von Dreele, R. B. *GSAS General Structure Analysis System MS-H805*; Los Alamos, NM87545, 1990.

Table 5. Selected Derived Bond Angles (deg); Powder Neutron Diffraction

O(1)−Zn−O(2)	117.8(2)
O(1)−Zn−O(3)	108.8(2)
O(1)−Zn−O(3)	104.6(2)
O(2)−Zn−O(3)	110.5(2)
O(2)−Zn−O(3)	107.9(2)
O(3)−Zn−O(3)	106.7(1)
O(1)−Si−O(2)	109.3(3)
O(1)−Si−O(3)	113.1(3)
O(2)−Si−O(3)	108.3(2)
Zn−O(1)−Si	126.0(2)
Zn−O(2)−Si	131.2(2)
Zn−O(3)−Zn	115.9(2)
Si−O(4)−H	116.6(4)
O(5)−H−O(7)	174.5(6)

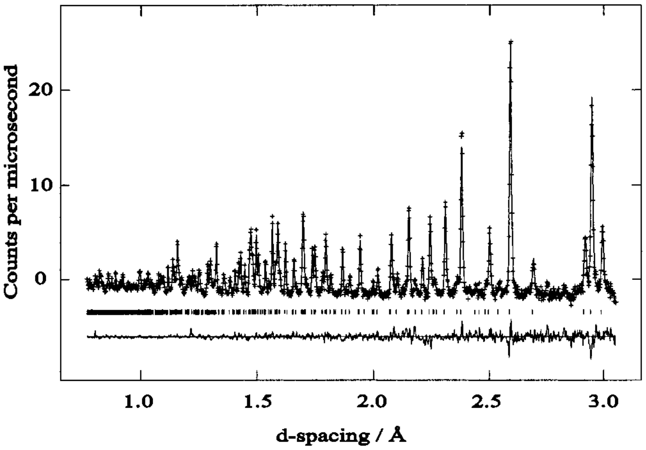

Figure 1. Final fit achieved to the powder neutron diffraction data. Crosses are observed data, the upper continuous line shows the calculated profile, and the lower continuous line shows the difference. Tick marks show reflection positions.

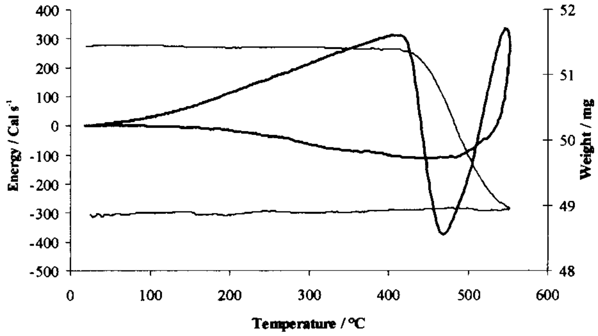

Figure 2. Thermogravimetric/differential thermal analysis data for the decomposition of $NaZnSiO_3OH$.

transition temperature showed a few broad reflections indicating that the framework had collapsed to yield a poorly crystalline product.

Discussion

The structure of $NaZnSiO_3OH$ consists of an array of ZnO_4 and SiO_3OH tetrahedra; see Figure 3. These form eight-membered rings along the crystallographic *c* direction. The sodium ions are sited in these channels with five close contacts and one longer contact to the framework oxygens. The framework contains one oxygen site O(3), which is three coordinate to two zinc atoms and one silicon atom; see Figure 4. This higher coordinate site is not unexpected, given that an oxygen atom shared only between two framework zinc atoms is markedly underbonded with just two O−Zn interactions of around 1.95 Å. In stuffed silicas of the type A_2ZnSiO_4, interactions between the framework oxygen and the alkali metal cations help offset the underbonding of oxygen connected to zinc. Bond valence calculations on the four oxygen atoms give reasonable values between 1.82 and 2.03 Å. The framework also contains a short interaction between the tetrahedral atoms, a nonbonded zinc−silicon distance of 3.069(4) Å exists.

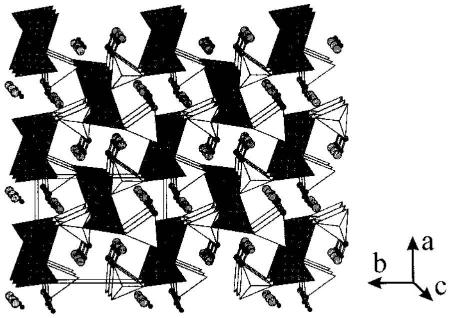

Figure 3. Structure of $NaZnSiO_3OH$ viewed along the *c* direction. Tetrahedra: ZnO_4 (dark gray), SiO_3OH (mid gray). Atoms: sodium (medium gray), hydrogen (black).

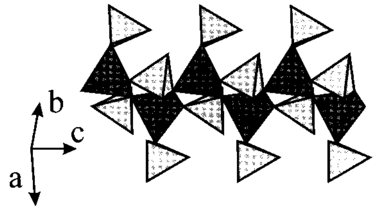

Figure 4. Linking of the polyhedral units along the *c* direction. ZnO_4 are large black tetrahedra, and SiO_3OH are small gray tetrahedra.

Crystallization of $NaZnSiO_3OH$ in the noncentrosymmetric space group $P2_12_12_1$ produces a chiral structure and, as such, is one of a growing number of frameworks of this type. Other chiral frameworks, which have been described recently, are those of *d*-$Co(en)_3[H_3Ga_2P_4O_{16}]$,[14] tetrahedral cobalt phosphates,[15] a decavanadium(V) cluster,[16] $NaZnPO_4{\cdot}H_2O$,[17] and an extended nickel framework.[18] In these systems, the chirality results from the adoption of one of the enatiomorphic space group pairs (e.g., $P4_332$ or $P4_132$) or the crystallization in a space group with no improper rotations. $NaZnSiO_3OH$ belongs to the later class and the refinement of the Flach parameter to a value very close to zero confirms that the crystal studied in the single-crystal X-ray work was a single enantiomorph.

The SiO_3OH tetrahedra are reasonably regular, though the Si−O(4)H bond is significantly longer than the other three distances. The OH group points into the main eight-membered ring and the hydrogen forms a moderately strong hydrogen bond to oxygen on the opposite side of the channel; the hydrogen atom lies slightly off the O−O direction (O−H···O = 173.4°), typical behavior for this type of interaction. The observed OH stretching frequency of 2900 cm^{-1} is also consistent with a moderately strong hydrogen bond with a decrease of 700 cm^{-1} from the free OH value 3600 cm^{-1}.[19]

The ^{29}Si MAS NMR resonance frequency occurred at −66.30 ppm referenced to TMS. Previous ^{29}Si NMR resonance data on tectozincosilicates show that the SiO_4 group in these materials

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(14) Stadler, S. M.; Wilkinson, A. P. *Chem. Mater.* **1997**, *9* (10), 2168.

(15) Feng, P. Y.; Bu, X. H.; Tolbert, S. H.; Stucky, G. D. *J. Am. Chem. Soc.* **1997**, *119* (10), 2497.

(16) Oyaizu, K.; Tsuchida, E. *J. Am. Chem. Soc.* **1998**, *120* (1), 237.

(17) Harrison, W. T. A.; Gier, T. E.; Stucky, G. D.; Broach, R. W.; Bedard, R. A. *Chem. Mater.* **1996**, *8*, 145.

(18) Kepert, C. J.; Rosseinsky, M. J. *Chem. Commun.* **1998**, *1*, 31.

(19) Pimentel, G. C.; McClellan, A. L. *The Hydrogen Bond*; W. H. Freeman and company: San Francisco/London, 1960.

is generally found in the region 65−95 ppm.[20] The value found for $NaZnSiO_3OH$, lying at the bottom end of this range, is consistent with the orthosilicate-type SiO_3OH unit, with weaker deshielding of ^{29}Si by next nearest neighbor H^+ as compared with Zn^{2+}.

The presence of the SiO_3OH in a framework structure is uncommon, though it can be considered to form a building block of the Uranophane structure $Ca(UO_2)_2(SiO_3OH)_2(H_2O)_5$,[21] where the orthosilicate groups bridge between the uranyl units. The pyramidal SiO_3OH^{3-} group may therefore be considered as an additional unit from which to construct framework structures, and attempts to construct different materials containing this species are in progress. The channel-like structure of $NaZnSiO_3OH$ may mean that exchange of the sodium ions or the protons may be possible and investigation of such behavior is also currently being undertaken.

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Supporting Information Available: Listings of single-crystal X-ray diffraction refinement parameters, derived bond lengths and angles, anisotropic thermal parameters, and the asymmetric unit. This material is available free of charge via the Internet at http://pubs.acs.org.

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(20) Camblor, M. A.; Davis, M. E. *J. Phys. Chem.* **1994**, *98*, 13151.
(21) Viswanathan, K.; Harneit, O. *Am. Miner.* **1986**, *71*, 1489.