

Na₂Al₂Ge₃O₁₀·2H₂O: an aluminogermanate with the tetranatrolite topology

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An aluminogermanate, Na₂Al₂Ge₃O₁₀·2H₂O (NaAlGe-NAT), possessing the natrolite topology has been synthesized under hydrothermal conditions at 423 K from sodium- and tetramethylammonium-containing gels. Room temperature single crystal X-ray diffraction data indicate a tetragonal unit cell with $a = 13.314(2)$ and $c = 6.819(2)$ Å, and space group $I42d$. NaAlGe-NAT displays complete disorder of aluminium and germanium in the framework, with Ge/Al = 1.5. The substitution of germanium for silicon in the framework leads to a larger unit cell volume for NaAlGe-NAT compared with Na₈Al₈Si₁₂O₄₀·8H₂O (NaAlSi-NAT) and Na₈Ga₈Si₁₂O₄₀·8H₂O (NaGaSi-NAT) framework structures. The mean rotation angle Ψ of the chains (composed of 4 = 1 secondary building units) relative to the a and b cell axes is 20.4°, compared with 21.7 and 22.9° calculated for NaGaSi-NAT and NaAlSi-NAT, respectively. Elliptical channels along the c -axis host well-ordered water molecules and sodium cations in fully occupied sites.

Introduction

Although the structural characteristics of aluminosilicate zeolites have been studied extensively, it is only relatively recently that the structural consequences of isomorphous substitution of framework silicon by germanium have begun to be explored. For example, the effects on the unit cell constants, symmetries, T–O–T angles and T–O bond lengths upon Ge substitution for Si in the topologies for ABW,¹ RHO,² FAU,³ GIS,⁴ CAN,^{5,6} LOSOD,⁷ SOD^{8–10} are reported elsewhere. In addition, theoretical studies were performed by George and co-workers, who reported the relative stability of germanium analogues for several common zeolite structures utilizing lattice energy minimization techniques.¹¹ In a recent preliminary communication,¹² the synthesis conditions for NaAlGe-NAT were also detailed. However, our attempts at structure solution from high-resolution X-ray powder diffraction data were unsuccessful due to ambiguities in symmetry and framework disorder. These difficulties were compounded by the presence of a small but significant amount of occluded tetramethylammonium hydroxide within the zeolitic cavities, which complicated structural elucidation.

Natrolite (NAT) belongs to the class of fibrous zeolites, which also includes edingtonite (EDI) and thomsonite (THO).¹³ The distinguishing feature between natrolite (orthorhombic, space group $Fdd2$) and tetranatrolite materials is the ordering within tetrahedral sites. The former material, with three independent tetrahedra, displays disorder over T2 and T3 tetrahedral sites only,^{14–16} whereas the latter shows complete disorder over all framework sites (two in this case, as the increased symmetry of the cell is accompanied by a reduction in the number of independent tetrahedra).^{17–19} With a composition close to Na₂Al₂Si₃O₁₀·2H₂O, complete order of the framework Al and Si tetrahedra was always observed in the orthorhombic space group $Fdd2$ with fully occupied Na and H₂O sites. However, in 1981 Alberti and Vezzalini noted partial Al/Si disorder within a natrolite originating from Hungary.¹⁴

In 1995 Alberti and co-workers further postulated that complete disorder cannot be reached in hydrothermal natrolites.²⁰ They stated that the “disordered (Si/Al) distribution with Si/Al ≥ 1.5 is due to unusual genetic conditions, high temperature and water pressure and, in this case, disordered paranatrolites are formed. Under air conditions paranatrolites dehydrate to a disordered phase, which we consider true ‘tetranatrolites’.” Considering the variability in both framework ordering and in the T⁴⁺ : T³⁺ ratio which is possible for the NAT topology, coupled with the paucity of synthetic natrolites reported, the unambiguous structure solution of our aluminogermanate material was desirable. Since initial attempts using powder data were inconclusive, this required the preparation of high-quality single crystals, which would thus allow accurate determination of the symmetry and degree of framework ordering for NaAlGe-NAT. In addition, the ordering of the extra-framework sodium cations and water molecules could be fully examined. This paper describes the synthesis and single crystal analysis of a sodium aluminogermanate tetranatrolite with a disordered arrangement of T atoms sites in the framework.

Experimental

Synthesis

Table 1 presents the various synthetic conditions used for attempted preparations of crystalline NaAlGe-NAT and summarizes the products obtained. As is apparent from Table 1, a variety of structure directing agents (SDAs) can be employed in conjunction with sodium cations for the synthesis of NaAlGe-NAT. In a typical procedure, 1.16 g H₂O, 0.02 g NaOH and 2.0 g tetramethylammonium (TMA) hydroxide (25% w/w aqueous solution) were mixed together in a polypropylene bottle and stirred for 1 h with the slow addition of 0.1 g Al₂O₃ (Catapal, Vista), followed by the addition of 0.25 g GeO₂ (Alfa). The mixture was then heated at 150 °C for 4 d in a Teflon pouch contained within a hermetically sealed stainless steel bomb. After cooling to room temperature, the product was recovered by filtration,

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Table 1 Summary of gel compositions and reaction products

Sample	Gel composition	Temp./°C	Time/h	Products
A	(4–4.5)R ₁ : (1–1.5)Na ₂ O: Al ₂ O ₃ : (8–10)GeO ₂ : (300–320)H ₂ O	95	24	NAT ^a
B	R ₁ : Na ₂ O: Al ₂ O ₃ : 2GeO ₂ : 200H ₂ O	110	120	NAT
C	4R ₁ : Na ₂ O: Al ₂ O ₃ : 5GeO ₂ : 300H ₂ O	110	120	NAT
D	6R ₁ : Na ₂ O: 1.5Al ₂ O ₃ : 5GeO ₂ : 315H ₂ O	150	100	JBW ^b +SOD ^b
E	6R ₁ : 1.3Na ₂ O: 1.5Al ₂ O ₃ : 5GeO ₂ : 280H ₂ O	150	100	SOD
F	6R ₁ : 0.5Na ₂ O: 1.5Al ₂ O ₃ : 5GeO ₂ : 305H ₂ O	150	100	NAT
G	(4–6)R ₁ : (0.5–1)Na ₂ O: (1–1.5)Al ₂ O ₃ : (2–5)GeO ₂ : 300H ₂ O	175	100–200	SOD
H	2R ₂ : Na ₂ O: Al ₂ O ₃ : 2GeO ₂ : 200H ₂ O	110	120	NAT
I	6R ₂ : Na ₂ O: Al ₂ O ₃ : 2GeO ₂ : 200H ₂ O	110	120	NAT _{m1} +GIS _{m2} ^b
J	R ₃ : Na ₂ O: Al ₂ O ₃ : 2GeO ₂ : 200H ₂ O	110	120	NAT+GIS
K	3R ₃ : Na ₂ O: Al ₂ O ₃ : 2GeO ₂ : 200H ₂ O	110	120	GIS+NAT _{tr}
L	R ₄ : Na ₂ O: Al ₂ O ₃ : 2GeO ₂ : 200H ₂ O	110	120	NAT+SOD
M	3R ₄ : Na ₂ O: Al ₂ O ₃ : 2GeO ₂ : 200H ₂ O	110	120	SOD

R₁=Tetramethylammonium oxide [(TMA)₂O]; R₂=1,4-diazabicyclo[2,2,2]octane (DABCO); R₃=tetraethylammonium oxide [(TEA)₂O]; R₄=tetrapropylammonium oxide [(TPA)₂O]. m1 Major product; m2 minor product; tr obtained in trace amounts only. ^aObtained as crystalline powder. ^bAlGe equivalents of zeolites with JBW, SOD and GIS topology.

washed with deionized water and dried at room temperature. The resultant translucent octahedral crystals were initially examined by powder X-ray diffraction, using a Scintag PAD-X diffractometer, to establish phase identity and purity. Further structural characterization was achieved *via* single crystal X-ray diffraction.

Single-crystal X-ray studies

A suitable crystal (0.2 × 0.2 × 0.1 mm) was carefully selected under a polarizing microscope and was glued to a thin glass fiber with epoxy resin. This was mounted on a Bruker Smart-CCD diffractometer equipped with a normal-focus sealed-tube X-ray source (Mo-K α radiation, $\lambda = 0.71073$ Å) operating at 50 kV and 30 mA. A hemisphere of intensity data was collected at room temperature in 1660 frames with ϕ scans (width of 0.30° and exposure time of 10 s per frame) in the 2θ range 4.32 to 56.58°. The structure was solved by direct methods followed by successive Fourier difference syntheses, with all calculations performed using SHELXTL.²¹ Final full-matrix refinements were against F^2 and included a correction for secondary extinction and anisotropic displacement parameters. An absorption correction based on orientation matrix, Laue symmetry, and appreciable redundancy in the reflection data was applied using the program SADABS.²² The crystals of NaAlGe-NAT were found to be merohedrally twinned upon inspection of the Flack parameter. A twin law used to describe this twinning revealed two components with equal scattering power. Hydrogen atoms attributed to the sorbed water molecules were not included in the refinement. Crystallographic data collection and refinement parameters are

Table 2 X-Ray crystallographic data collection and refinement parameters for NaAlGe-NAT

Compound	NaAlGe-NAT
Formula	Na ₂ Al ₂ Ge ₃ O ₁₀ ·2H ₂ O
Formula weight	513.67
Crystal system	tetragonal
<i>a</i> /Å	13.314(2)
<i>c</i> /Å	6.818(1)
<i>V</i> /Å ³	1208.7(3)
Temperature/K	298(2)
Space group	<i>I</i> 4̄2 <i>d</i>
<i>Z</i>	4
μ /mm ⁻¹	7.179
Measured/independent reflections/ <i>R</i> _(int)	2272/703/0.0538
<i>R</i> (all data)	0.0496
<i>R</i> _w (all data)	0.1132
$R = \frac{\sum(F_{\text{obs}} - F_{\text{calc}})}{\sum F_{\text{obs}} }$	
$R_w = \sqrt{\frac{\sum w_i(F_{\text{obs}} - F_{\text{calc}})^2}{\sum w_i F_{\text{obs}} ^2}}$	

summarized in Table 2, while atomic coordinates with anisotropic displacement parameters and selected bond distances and angles are listed in Tables 3 and 4, respectively.

Full crystallographic details, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, 2000, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/192. See <http://www.rsc.org/suppdata/jm/a9/a907933e> for crystallographic files in .cif format.

Results and discussion

Structure elucidation

Observation of systematic absences ($h+k+l=2n+1$), coupled with the equivalence of hkl and khl reflections, suggested body-centered tetragonal symmetry. More detailed examination revealed systematic absences consistent with the space groups *I*4̄2*d* and *I*4̄*md*. Both Mikheeva *et al.*¹⁹ and Pechar¹⁷ had previously modeled aluminosilicate tetranatrolite mineral samples in space group *I*4̄2*d* in order to account for disordering of the framework tetrahedra. This choice of space group is consistent with the results obtained here for aluminogermanate natrolite, for which chemically sensible bond angles and interatomic distances were only obtained when using *I*4̄2*d*. In addition, these results are consistent with those involving sodium aluminosilicate (NaAlSi-NAT) and sodium gallosilicate (NaGaSi-NAT) compositions.^{17–19}

Refinement of the individual site occupancies for the tetrahedrally coordinated framework sites, unconstrained except for the assumption of full occupancy of each T-site, resulted in populations of Al_{0.47(1)}Ge_{0.53(1)} on site T1 and Al_{0.46(1)}Ge_{0.54(1)} on site T2. Furthermore, the site occupancy of Na was found to be 0.48(1), close to the maximum of 0.5 allowed for this special position (Table 3). Considering the overall charge balance and electron probe microanalysis (EPMA) data which indicated Na:Al:Ge ratios of 2:2:3, the Ge/Al ratio was constrained to be 1.5 and the site occupancy of Na was fixed at 0.5 for the final refinement (Table 3). This resulted in a stable refinement and the derived formula Na₂Al_{1.9(1)}Ge_{2.8(1)}O₁₀·2H₂O, which is close to the ideal chemical composition, Na₂(T³⁺)₂(T⁴⁺)₃O₁₀·2H₂O, observed for aluminosilicates and gallosilicates with the natrolite topology. Extra-framework sodium cations and water molecules were distinguished based upon their coordination environments with respect to the framework oxygens and previously reported atomic positions in NaAlSi- and NaGaSi-NAT materials.^{18,19}

Table 3 Atomic coordinates^a ($\times 10^4$), occupancies, equivalent isotropic [U_{eq}]^b and anisotropic displacement parameters^c ($\text{\AA}^2 \times 10^3$) for NaAlGe-NAT with standard uncertainties in parenthesis

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	Occ.	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}^b
T1	16e	604(1)	6323(1)	6278(5)	0.6	9(1)	7(1)	18(1)	1(1)	-1(1)	0(1)	11(1)
T2	4a	0	0	0	0.15	9(1)	9(1)	13(1)	0	0	0	10(1)
O1	8d	6177(4)	2500	1250	0.5	12(3)	14(3)	29(6)	1(3)	0	0	17(1)
O2	16e	910(3)	603(4)	1383(7)	1	28(2)	30(3)	25(2)	2(2)	-7(2)	-12(2)	28(1)
O3	16e	607(3)	1383(3)	5287(8)	1	10(2)	23(2)	40(3)	-10(2)	7(2)	0(2)	24(1)
Ow1	8d	8653(5)	2500	1250	0.5	30(3)	37(4)	42(4)	5(4)	0	0	36(2)
Na1	8d	3072(3)	2500	1250	0.5	27(2)	20(2)	35(2)	6(2)	0	0	27(1)

^aPositional parameters without an estimated standard deviation (number in parentheses) were not varied. ^b $U_{\text{eq}}(\text{\AA}^2) = 1/3[U_{11} + U_{22} + U_{33}]$. ^cThe anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^*U_{11} + \dots + 2hka^*b^*U_{12}]$.

Framework structure of NaAlGe-NAT: structural consequences of germanium incorporation

The overall structure of NaAlGe-NAT is similar to aluminosilicate natrolite¹³ (Fig. 1). The average T–O distances ($\langle \text{T1–O} \rangle = 1.736 \text{ \AA}$ and $\langle \text{T2–O} \rangle = 1.732 \text{ \AA}$) compare well with the expected value of 1.74 \AA derived from ionic radii. Both Al^{3+} and Ge^{4+} have an ionic radius of 0.39 \AA when tetrahedrally coordinated,²³ and hence the Al:Ge ratio has little influence on the average T–O bond distance. As expected, an expansion of the unit cell is observed upon introduction of larger germanium atoms for silicon: the unit cell volume for NaAlGe-NAT is 5.2% larger than that of NaAlSi-NAT and is 4.2% larger than NaGaSi-NAT.^{18,19} The percentage expansion of AlGe over AlSi is greater than that of GaSi over AlSi (1.2%). This is expected since the average framework T–O distances for AlSi, GaSi and AlGe materials in natrolite (taking into account the framework $\text{T}^{4+} : \text{T}^{3+}$ ratio of 3:2) are approximately 1.66, 1.69 and 1.74 \AA , respectively. Table 5 shows a comparison of volume changes on Ga and Ge substitution within the frameworks of SOD, ABW and NAT zeolites. This illustrates that the volume changes associated with Ga and Ge incorporation within NAT are significantly different, due, at least in some part, to the different levels of T atom substitution in the framework compared with SOD and ABW. Although expansion resulting from Ge substitution in the natrolite structure is observed (Table 5), it is accompanied by a reduction in the Al–O–Ge framework bond angle compared with that of the aluminosilicate: average T–O–T angles for NaAlSi-, NaGaSi- and NaAlGe-NAT materials are 137.8, 134.2 and 132.5° , respectively. These values indicate that the mean T–O–T angle decreases as the size of the framework tetrahedral component is increased. This in turn produces a greater degree of relative cell contraction for AlGe materials compared with GaSi and AlSi frameworks, an observation that is consistent

Table 4 Selected interatomic distances and angles for NaAlGe-NAT with standard uncertainties in parentheses. Uncertainties on mean quantities are not given

Bond	Distance/ \AA	Plane	Angle/ $^\circ$
T1–O1	1.743(2)	O1–T1–O2	106.1(2)
T1–O2	1.723(5)	O1–T1–O3	111.6(2)
T1–O3	1.735(4)	O1–T1–O3	103.8(2)
T1–O3	1.745(4)	O2–T1–O3	112.7(2)
$\langle \text{T1–O} \rangle$	1.736	O2–T1–O3	111.2(3)
		O3–T1–O3	111.1(2)
T2–O2	$4 \times 1.732(4)$		
$\langle \text{T2–O} \rangle$	1.732	O2–T2–O2	$2 \times 107.2(4)$
Na1–O1	$2 \times 2.567(4)$	O2–T2–O2	$2 \times 114.0(3)$
Na1–O3	$2 \times 2.396(5)$	O2–T2–O2	$2 \times 107.2(4)$
Na1–Ow1	$2 \times 2.417(5)$		
Ow1–O2	$2 \times 2.947(1)$	T–O1–T	$4 \times 128.1(3)$
		T–O2–T	$2 \times 137.7(3)$
		T–O3–T	$4 \times 134.2(3)$
		$\langle \text{T–O–T} \rangle$	132.5

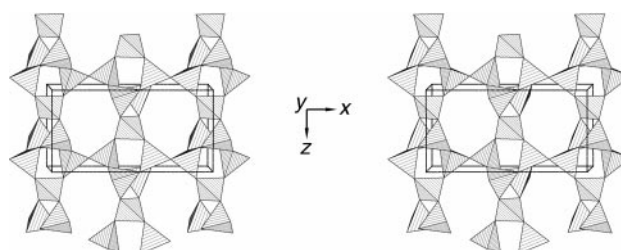


Fig. 1 A stereoview of the NaAlGe-NAT framework viewed down [010] as a polyhedral representation. Elongated chains composed of four disordered tetrahedra (GeO_4 and AlO_4) are connected to a third type of disordered tetrahedral unit every 6.82 \AA to form cross-linked chains of tetrahedra in which the secondary building unit (SBU) is $4 = 1^\dagger [\text{T}_5\text{O}_{10}]$. These chains are connected to one another by sharing the oxygens at the corners of the tetrahedra, forming channels with irregular openings which run perpendicular to the crystallographic *c*-axis. Na cations and water molecules have been omitted for clarity (Fig. 3). Straight lines define the unit cell.

with isomorphous framework substitution in other topologies, such as ABW, RHO and SOD.^{1,2,24}

The second mechanism by which unit cell contraction/expansion is manifested in natrolites is the rotation angle, Ψ . This has been defined as the average angle between the sides of the quadrilateral around the chain and the *a*- and *b*-axes.^{14,25} For NaAlGe-NAT, $\Psi = 20.4^\circ$, compared with 21.7 and 22.9° calculated for NaGaSi- and NaAlSi-NAT, respectively.^{18,19} These values show a small decrease in Ψ upon Ga and Ge substitution in NaAlSi-NAT, indicating that framework substitution is accompanied by a modest variation in Ψ . However, this is not surprising given that changes in Ψ are most apparent upon exchange of non-framework cations in natrolite, which occurs via chain rotation^{25–27} ($\Psi = 17.5$ and 18° for KGaSi-NAT²⁸ and K-natrolite²⁵ respectively). The mechanism of relative cell contraction upon introduction of larger framework T species thus appears to be more strongly governed by a reduction in the T–O–T angle rather than changes in Ψ . Table 6 compares selected structural properties for tetranatrolite materials.

Distribution of extra-framework species

The arrangement of extra-framework atoms in NaAlGe-NAT is similar to that found in NaAlSi- and NaGaSi-NAT (Fig. 2 and 3). Each sodium cation in the extended octagonal channels along [001] between adjacent tubular bands coordinates to six nearest neighbors forming a twisted trigonal prism, in which four vertices are formed by O1 and O3 from T1 tetrahedra, and two by Ow1. The Na polyhedra are joined by a common edge

[†]The term $4 = 1$ is based upon specific combinations of tetrahedra called “secondary building units” (SBUs). In this case it specifies a configuration of 5 tetrahedra (T_5O_{10} linked units) present in the structure.

Table 5 Comparison of volume increase upon Ga and Ge substitution for three topologies. The increase upon Ga substitution in NAT is smaller than for the other two topologies shown

Topology	Composition ^a	Unit cell volume/Å ³	%Volume increase over AlSi ^b topology	Reference
ABW	Li ₄ Al ₄ Si ₄ O ₁₆ ·4H ₂ O	421.7	0	31
	Li ₄ Ga ₄ Si ₄ O ₁₆ ·4H ₂ O	432.0	2.4	32
	Li ₄ Al ₄ Ge ₄ O ₁₆ ·4H ₂ O	448.9	6.4	1
SOD	Na ₈ Al ₆ Si ₆ O ₂₄ Cl ₂	350.1	0	24
	Na ₈ Ga ₆ Si ₆ O ₂₄ Cl ₂	359.7	2.7	24
	Na ₈ Al ₆ Ge ₆ O ₂₄ Cl ₂	368.5	5.2	24
NAT	Na ₈ Al ₈ Si ₁₂ O ₄₀ ·8H ₂ O	1146.2	0	19
	Na ₈ Ga ₈ Si ₁₂ O ₄₀ ·8H ₂ O	1160.3	1.2	18
	Na ₈ Al ₈ Ge ₁₂ O ₄₀ ·8H ₂ O	1208.7	5.5	This work

^aCompositions for a given topology are identical apart from different T atoms. This means that direct volume comparisons can be made, without having to account for others factors such as different levels of hydration. ^bThe percentage increase over AlSi must necessarily equal zero for an aluminosilicate framework.

Table 6 Selected crystal data for various tetranatrolites in space group $I\bar{4}2d$

Compound	Unit cell composition	<i>a</i> /Å	<i>c</i> /Å	<i>V</i> /Å ³	$\langle T-O-T \rangle / ^\circ$	$\Psi / ^\circ$	Reference
NaAlSi-NAT	Na _{8.20} K _{0.88} Ca _{0.08} Al ₉ Si ₁₁ O ₄₀ ·8H ₂ O	13.141(8)	6.638(2)	1146.2	137.8	22.9	19
NaGaSi-NAT	Na ₈ Ga ₈ Si ₁₂ O ₄₀ ·8H ₂ O	13.196(5)	6.663(2)	1160.3	134.2	21.7	18
NaAlGe-NAT	Na ₈ Al ₈ Ge ₁₂ O ₄₀ ·8H ₂ O	13.314(2)	6.818(2)	1208.7	132.5	20.4	This work
KGaSi-NAT	K ₈ Ga ₈ Si ₁₂ O ₄₀ ·6H ₂ O	13.369(2)	6.545(1)	1217.6	131.3	17.5	28

into columns parallel to the *z*-axis (Fig. 3). The mean Na–O distance of 2.46 Å is consistent with those in NaAlSi-NAT (2.49 Å) and KGaSi-NAT (2.43 Å).^{18,19} The water molecule lies between two Na cations at a distance of 2.42 Å and two framework oxygen atoms at a distance of 2.95 Å. The interatomic separation between the oxygens of the water molecules and those of the framework suggests that that water is linked to framework oxygens *via* hydrogen bonds. Since water effectively has two bonding interactions, the largest $U_{(eq)}$ is observed for the oxygen atom of the water molecule (Table 3). The largest components of the anisotropic displacement parameters for Na and the oxygens in the water molecules are in the direction of the *c*-axis (Table 3, Fig. 2). This is the most open part of the structure with an octahedral cage between the tubular bands. Thus the overall arrangement of Na

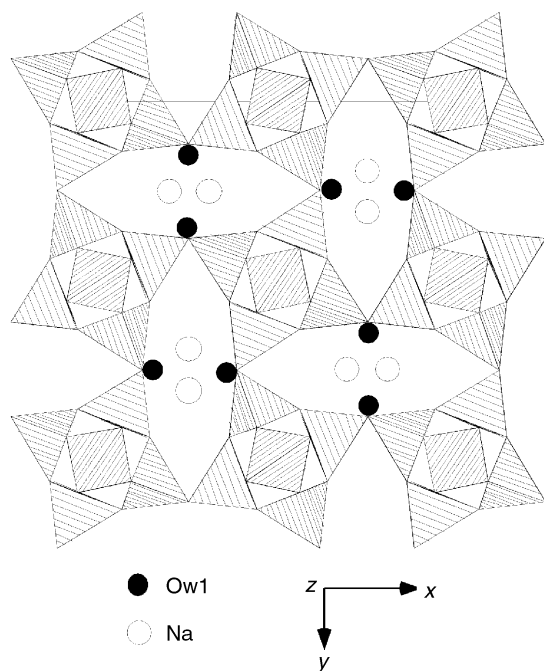


Fig. 2 A slice of the NaAlGe-NAT framework viewed down [001]. Four disordered tetrahedral chains are linked together to form intra-framework octagonal channels that contain Na and H₂O (Ow1). Straight lines define the unit cell.

atoms and water molecules gives rise to zigzag –Na–Ow1–Na–Ow1– chains along the channels, as shown in Fig. 3. This configuration of Na cations and sorbed water molecules is similar to that found in the GaSi- and AlSi-NAT materials.

Compositional variations in the NAT topology

The natrolite topology is typically associated with the chemical formula Na₂(T³⁺)₂(T⁴⁺)₃O₁₀·*w*H₂O, with Al and Si usually occupying the T-sites.²⁷ The hydration level, *w*, can vary somewhat, but experimental observations have shown it to adopt well defined values: *w* = 3 for parnatrolite, *w* = 2 for natrolite and tetranatrolite, and *w* = 0 for metanatrolite.¹⁹ Full disorder of framework species is observed for our alumino-

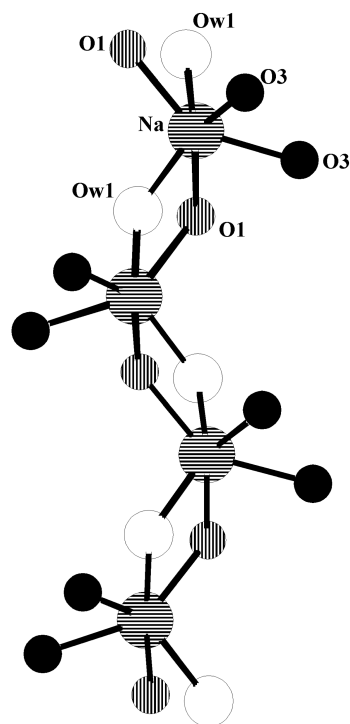


Fig. 3 The zigzagging –Na–Ow1–Na–Ow1– chain along the [001] channels. Each Na coordinates to six nearest neighbors forming a twisted trigonal prism, in which four vertices are formed by O1 and O3 from T1 tetrahedra and two by water molecules (Ow1).

germanate material, in a similar manner to the KGaSi-NAT material of Lee *et al.*²⁸ In contrast, NaGaSi-NAT displays only partial disorder amongst the framework components. Whilst a significant number of aluminosilicate natrolites appear to be ordered, initial results suggest that synthetic gallosilicate and aluminogermanate analogues favor disorder. The reason for this is unclear, but could be influenced by factors such as the crystallization conditions. Further work to prepare and characterize a wider variety of framework-substituted natrolites may shed some light on this phenomenon.

The use of a SDA appears to be important in the formation of synthetic sodium natrolites. The gallosilicate of Xie *et al.* was prepared in the presence of TMA cations.²⁹ Occelli *et al.* employed benzyl trimethylammonium (BTMA) hydroxide in their route to KNaGaSi-NAT.³⁰ Similarly, the aluminogermanate reported here can be made in presence of a variety of different SDAs (Table 1). In light of this, it is interesting to note that the recently synthesised KGaSi-NAT, which was prepared in the absence of any organic additive²⁸ and formed simply within the $K_2O-Ga_2O_3-SiO_2-H_2O$ system, had potassium ions statistically distributed in the intersecting channels perpendicular to the *c*-axis instead of the usual arrangement of extra-framework cations along channels parallel to the *c*-axis. One possible explanation for this observation is that sodium (unlike potassium) is not sufficiently large to promote the formation of natrolite and requires a more voluminous moiety to prevent the nucleation and crystallization of competing phases, such as sodalite and gismondine. In some cases, the SDA is occluded within the zeolitic voids, as noted for BTMA by Occelli and co-workers. Indeed, elemental analysis (Galbraith Laboratories) of a crystalline powder of NaAlGe-NAT revealed a small amount of nitrogen in the material,¹² suggesting that some of the tetramethylammonium hydroxide used to promote the NAT structure had been retained in the final product. However, the synthetic conditions were significantly different to those required for the preparation of single crystals of NaAlGe-NAT; EPMA and the single crystal X-ray diffraction study of this latter material indicated that the SDA was not present, since all of the observed scattering density for extra-framework atoms was accounted for by sodium and water. This difference in stoichiometry is not entirely surprising, given that the products of zeolite syntheses have been shown to be particularly sensitive to small variations in synthetic parameters such as reagent composition, reaction time and temperature. Ion exchange, *in situ* dehydration and *in situ* synthesis studies are underway to resolve such questions as the nature and relationship between structural properties and unit cell composition, and the influence of the SDA on the nature of the product. The latter point is poorly understood at present. As suggested above, it could be involved in governing the size and shape of the zeolitic cages formed during synthesis, but may also be important in producing a pH conducive to natrolite formation.

Conclusions

Single crystals of an aluminogermanate material with the natrolite topology have been grown for the first time and their structural properties examined. A completely disordered distribution of framework Ge and Al tetrahedra is observed for NaAlGe-NAT tetranatrolite with $I\bar{4}2d$ symmetry, for which the Ge/Al ratio is approximately 1.5. The replacement of silicon by germanium results in unit cell expansion, which is limited to some extent by contraction in the framework T–O–T angle. This is the main mechanism by which the NAT topology accommodates germanium in the framework, since there is no significant difference in chain rotation (Ψ) compared with aluminosilicate or gallosilicate natrolite analogues.

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