A Powder Neutron Diffraction Study of Lithium-Substituted Gallosilicate and Aluminogermanate Halide Sodalites

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Received October 26, 1998

Replacement of Na^+ by Li^+ has been achieved for sodalites of composition $Na_8[GaSiO_4]_6X_2$ and $Na_8[AlGeO_4]_6X_2$, where X is a halide, via nitrate melt at 240 °C. The resultant materials have been analyzed by Rietveld analysis of neutron powder diffraction data, and the derived structural parameters are compared with the parent sodium sodalites. The framework collapse associated with lithium exchange is principally accommodated by cooperative rotations about the $\bar{4}$ axis and a decrease in the framework T−O−T bond angle. Complete replacement of sodium by lithium was possible for all of the gallosilicate halide sodalites as well as the aluminogermanate bromide and iodide sodalites. In the case of aluminogermanate chloride sodalite, the required level of structure collapse seems to preclude full replacement of sodium by lithium.

Introduction

Sodalites can be described by the general formula $M_8[ABO_4]_6Y_2$, where M is a cation, such as Na^+, Li^+, and Ag^+,[1−3] A and B are tetrahedral forming species, such as Al and Si, and Y can be a variety of mono- or divalent anions, including Cl, Br, I, $(ClO_4)^-$, $(SO_4)^{2-}$, and $(MoO_4)^{2-}$.[4−8] The structure is based upon a truncated octahedral cage linked in three dimensions,[9] yielding four- and six-membered rings that are directly linked to form the overall structure as shown in Figure 1. A monovalent anion typically resides at every cage center and is coordinated to sodiums, resulting in the formation of M_4X clusters in each β cage.[10]

The sodalite unit is the building block of many important zeolites, such as LTA and FAU,[11] and has the ability to entrap a wide range of anionic species, affording them improved thermal and chemical stability. Since the structure is highly symmetrical, it can also provide an ideal model for the study of host−guest interactions. Normally synthesized with Na^+ as the nonframework cation, sodalites can be modified by ion exchange in which sodium is replaced by a range of other monovalent cations, such as Li^+, K^+, Rb^+, and Ag^+.[1−3] Attempts at direct synthesis, using these other cations, generally results in different frameworks topologies.[11]

The substitution of Ga for Al and Ge for Si in the sodalite framework has been previously reported.[12−23] Fleet described the preparation of aluminogermanate halide sodalites under conditions of high temperature and pressure[20] and their structural properties via single-crystal diffraction studies. In addition, Sieger et al. have prepared a range of germanium-containing sodalites under autogenous pressure by direct reaction of GeO_2, Al_2O_3, NaOH, and the sodium salt to be entrapped.[22] Newsam et al. prepared gallosilicates in a similar manner via a hydrothermal reaction of Ga_2O_3, NaOH, and SiO_2 along with the required sodium salt.[23] Although these authors prepared the parent sodium sodalites, there were no subsequent ion exchange reactions reported.

Halide sodalites have been noted for their photochromic and cathodochromic properties,[24−28] leading to their proposed employment in graphic and digital information storage devices.[29] They also provide an ideal system for the study of sodalite composition: these extremely simple enclathrated anions reside

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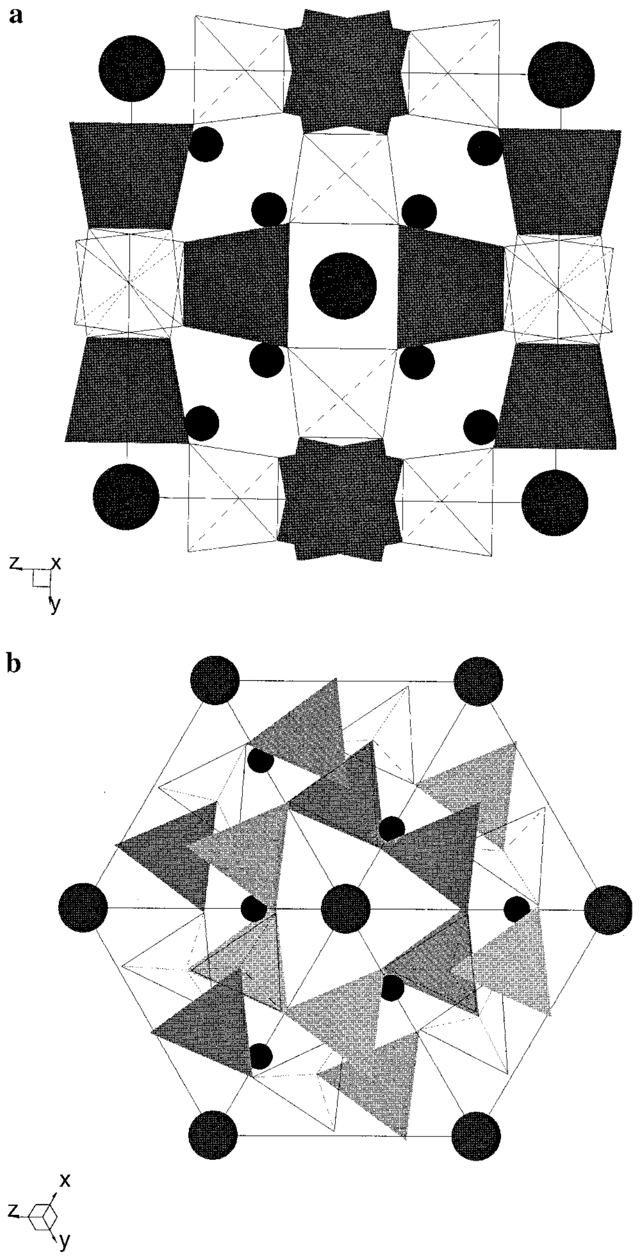

Figure 1. Polyhedral representation of the sodalite structure through the (a) four ring and (b) six ring. Tetrahedra: SiO_4 (filled), AlO_4 (open); Si and Al are located at the vertexes of each tetrahedron.

at the center of the β cage and thus do not complicate the study of how the framework changes with composition. In this paper, we describe the replacement of sodium by lithium for gallosilicate and aluminogermanate sodalites and compare the resultant structural properties with those of the sodium parents. Lithium substitution in gallosilicate and aluminogermanate sodalites has been reported previously by Henderson and Taylor,[2] but their parent sodium sodalites were prepared in borosilicate vessels: the resultant cell parameters indicate that full occupancy of the framework sites by gallium and/or germanium had not been achieved, suggesting that leaching of the vessel components had taken place. In addition, they were not able to achieve full substitution of lithium for sodium, and structural work used only X-ray methods. This paper thus describes the first example of full lithium substitution in gallosilicate and aluminogermanate halide sodalites and their characterization by Rietveld analysis of powder neutron diffraction data.

Experimental Section

Synthesis. All of the halide series, $Na_8[ABO_4]X_2$, where A = Al and Ga, B = Si and Ge, and X = Cl, Br, and I, were synthesized hydrothermally under autogenous pressure at 180 °C for 48 h. The aluminogermanates were prepared using the precursor Na_2GeO_3 in conjunction with $NaAlO_2$: 15 g of NaX, where X is the anion to be entrapped, was added to 0.91 g of $NaAlO_2$, 1.85 g of Na_2GeO_3, and 5 mL of H_2O, the components were mixed to form a gel, transferred to a 23 mL Teflon lined autoclave, and heated at 180 °C for 48 h. The gallosilicates were prepared, using a modified version of the method reported by Newsam,[23] with $NaGaO_2$ and Na_2SiO_3 as the preferred sources of framework cations: 1.39 g of $NaGaO_2$, 2.46 g of $Na_2SiO_3 \cdot 5H_2O$, and 15 g of NaX, where X is the desired anion, were mixed with 5 mL of H_2O to form a gel, transferred to a 23 mL Teflon lined autoclave and heated at 180 °C for 48 h. In all cases, the products were isolated by filtration, washed with 200 mL of distilled water, and dried overnight at 110 °C. In both systems, an excess of the sodium salt to be entrapped was used to promote formation of the desired sodalite. Detailed synthetic conditions pertaining to a wide range of framework-modified sodalites are described elsewhere.[30]

Lithium Ion Exchange. Sodium halide sodalites were subjected to lithium exchange by the nitrate melt method. The parent sodium sodalite (0.5 g) was mixed with 2 g of lithium nitrate and heated to 240 °C, just beyond the melting point of the nitrate. After approximately 3 h, the reaction was air-cooled, the product was washed with 200 mL of H_2O to remove the excess nitrate, and the product was dried overnight at 110 °C. After this initial treatment, all materials were heated at 500 °C overnight to improve their crystallinity.

In the case of the aluminogermanate chloride sodalite, structural collapse occurred after treatment with $LiNO_3$ at 240 °C for 3 h. The experiment was, therefore, repeated at the same temperature for 2 h, and the product was collected as outlined above.

The lithium contents of the products were analyzed, following dissolution in 2 M nitric acid, using a Corning 400 flame photometer that indicated full lithium exchange had taken place for all of the gallosilicates and for the aluminogermanate bromide and iodide samples. Full replacement of sodium by lithium was not achieved for the aluminogermanate chloride sodalite, and hence a more detailed elemental analysis was performed (Galbraith Laboratories: Li, Na, Al, Ge, and Cl measured, O assigned from stoichiometry). This revealed a composition of $Li_{7.9}Na_{0.3}[Al_{6.2}Ge_{5.8}O_{24}]Cl_{1.8}$, showing 3.7% residual sodium upon lithium exchange. Such a low level of sodium indicates that lithium exchange is virtually complete and justifies our refinement with Li^+ as the sole cation (see below). Other elements are close to their expected value, with Ge/Al = 0.94; for Rietveld refinement in space group $P\bar{4}3n$, Ge/Al = 1 was assumed.

Powder Diffraction Data Collection. Initial determination of phase composition, sample purity, and cell size was achieved using powder X-ray diffraction data collected on a Siemens D5000 diffractometer. Having determined that lithium exchange had been successful, samples were examined by powder neutron diffraction, which has the ability to locate light atoms, such as lithium and oxygen, more precisely than is possible using X-rays as the radiation type.

All powder neutron diffraction (PND) data were collected on the LAD instrument at ISIS, at d spacings between 0.67 and 3.08 Å, with acquisition times of approximately 4 h. Rietveld analysis[31,32] of the data was undertaken using the GSAS Powder Diffraction Suite of Larson and Von Dreele.[33]

Results

Structural Analysis. For each of the lithium exchanged halide sodalites, all peaks in the PND patterns could be indexed using a primitive lattice indicating the space group $P\bar{4}3n$

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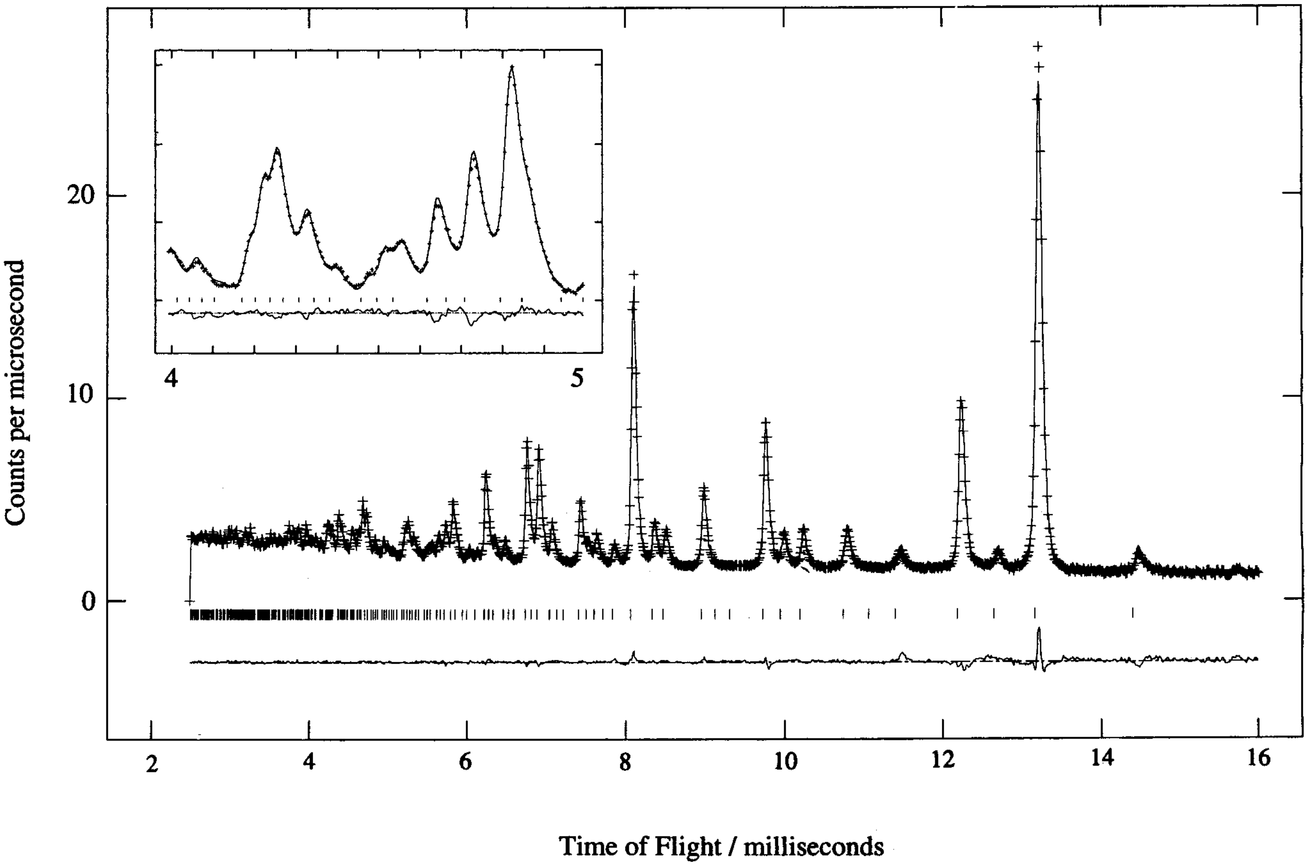

Figure 2. Results of Rietveld refinement of the structure of lithium gallosilicate chloride sodalite, using powder neutron diffraction data at room temperature. The tick marks indicate the positions of reflections, and the difference curve is shown at the bottom on the same scale.

consistent with their aluminosilicate sodalite analogues. The starting model for each of the lithium halide sodalites was the sodium halide analogue.[34] Aluminum or gallium and silicon or germanium were placed on the 6(c) ($^1/_4$, $^1/_2$, 0) and 6(d) ($^1/_4$, 0, $^1/_2$) sites, respectively, the halide on the 2(a) (0, 0, 0), lithium on the 8(e) (x, x, x) site with $x \approx 0.18$, and the framework oxygen O(1) on the 24(i) (x, y, z) site with $x \approx 0.14$, $y \approx 0.15$, and $z \approx 0.45$. This produces a fully ordered framework with alternating tri- and tetravalent cations.

Scale factor and background parameters were then introduced followed by lattice parameters, zero point correction, and sample displacement, thus pinpointing reflection positions. Atomic positions were next incorporated to generate peak intensities, initially of the framework species followed by nonframework ions; variation of isotropic thermal parameters accounts for atomic vibrations and peak shape parameters for sample broadening.

Refinement proceeded well for all materials, except the exchanged aluminogermanate chloride derivative, and convergence was achieved quickly for each structural model. For $Li_n[AlGeO_4]_6Cl_2$, a large temperature factor was obtained for the noncationic-framework site, and this together with inspection of the lattice parameter (Table 3) indicates that incomplete cation exchange had taken place. This is in agreement with the chemical analysis, which revealed that ~3.7% residual sodium was present on the 8(e) extraframework cationic site. For a material with two nonframework cations, it is difficult to model two separate sites as they lie close together and are strongly correlated; this is particularly true if one of these has a very low level of occupancy. Therefore, the refinement was continued using a single cation site but with reduced occupancy (95%) to reflect partial occupation of the site by sodium and a permitted high-temperature factor to reflect the distribution of scattering density. In all other refinements, lithium was the sole occupant of the 8(e) extraframework cation site, and the results obtained vindicate the absence of sodium. Figures 2−7 illustrate how well the observed and calculated profile fits match. Final refinement parameters, atomic coordinates, and thermal parameters are presented in Tables 1 and 3 for gallosilicates and aluminogermanates, respectively, with selected bond distances and angles given in Tables 2 and 4. Table 5 summarizes the structural properties for sodium and lithium gallosilicate and aluminogermanate sodalites, with sodium gallogermanates also included for comparison.

TOF (Time of Flight) PND Study of Lithium Gallosilicate Halide Sodalites. Table 1 summarizes the final atomic coordinates and refinement parameters, and Table 2 shows selected bond distances and angles for the lithium exchanged gallosilicate halide sodalites. A dramatic reduction in cell parameter is observed following the introduction of lithium on the sodium sites, as would be expected upon full replacement of Na^+ by Li^+: for example, unit cell edges of approximately 8.96 and 8.54 Å were observed for the sodium and lithium gallosilicate chloride sodalites, respectively. Cell contraction is accompanied by a decrease in framework Ga−O−Si angle amounting to approximately 12° compared with the parent sodium materials for each of the halide samples studied. Although in theory T−O−T angles of 109.5 ° are possible, these are never experimentally observed, and the values obtained herein are some of the lowest ever reported for sodalites. Previous neutron

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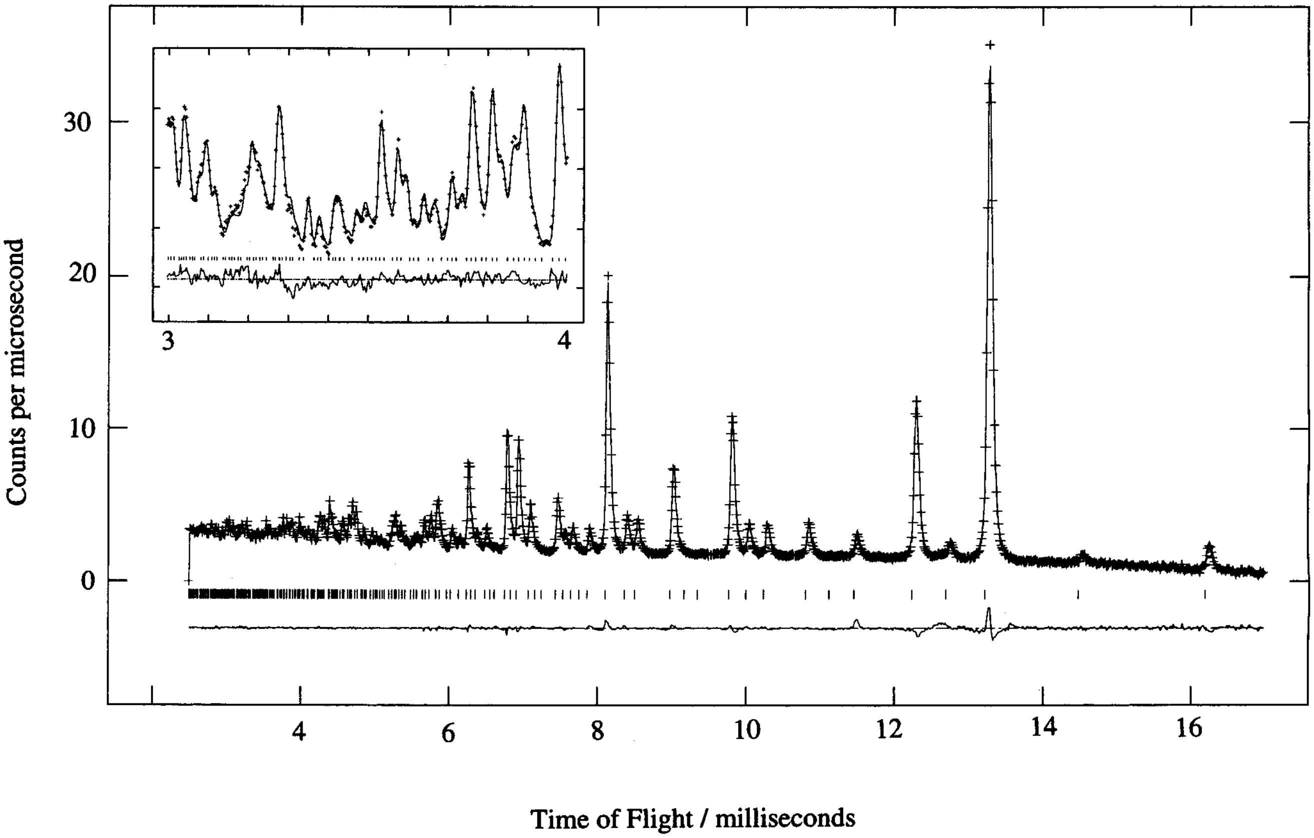

Figure 3. Results of Rietveld refinement of the structure of lithium gallosilicate bromide sodalite, using powder neutron diffraction data at room temperature. The tick marks indicate the positions of reflections, and the difference curve is shown at the bottom on the same scale.

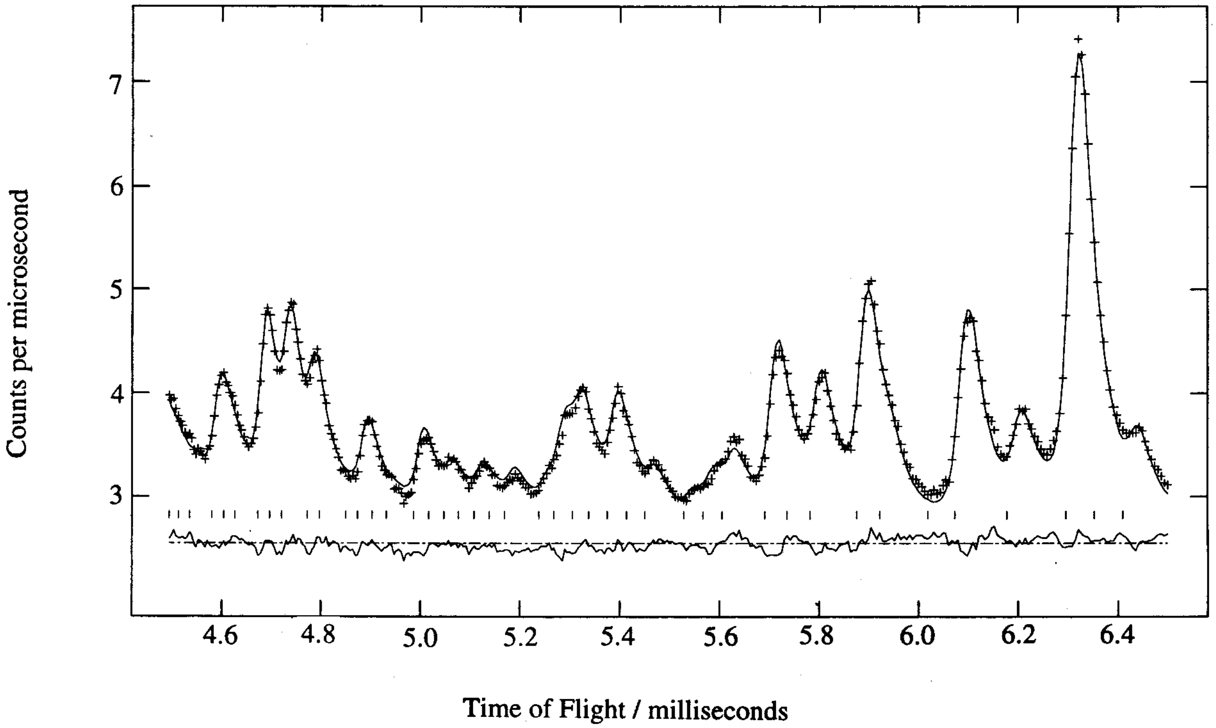

Figure 4. Expanded section of the results of Rietveld refinement of the structure of lithium gallosilicate iodide sodalite, using powder neutron diffraction data at room temperature. The tick marks indicate the positions of reflections, and the difference curve is shown at the bottom on the same scale.

diffraction studies were performed on $Li_8[AlSiO_4]_6Cl_2$ and $Li_8[AlSiO_4]_6Br_2$ by Wong[8], revealing cell parameters of 8.444 and 8.508 Å and framework bond angles of 124.5° and 126.4°, respectively.

Table 2 summarizes the gallium and silicon to oxygen bond distances, which are close to those expected, although in the iodide sample the Ga−O bond is a little shorter and the Si−O bond a little longer than those predicted from the respective

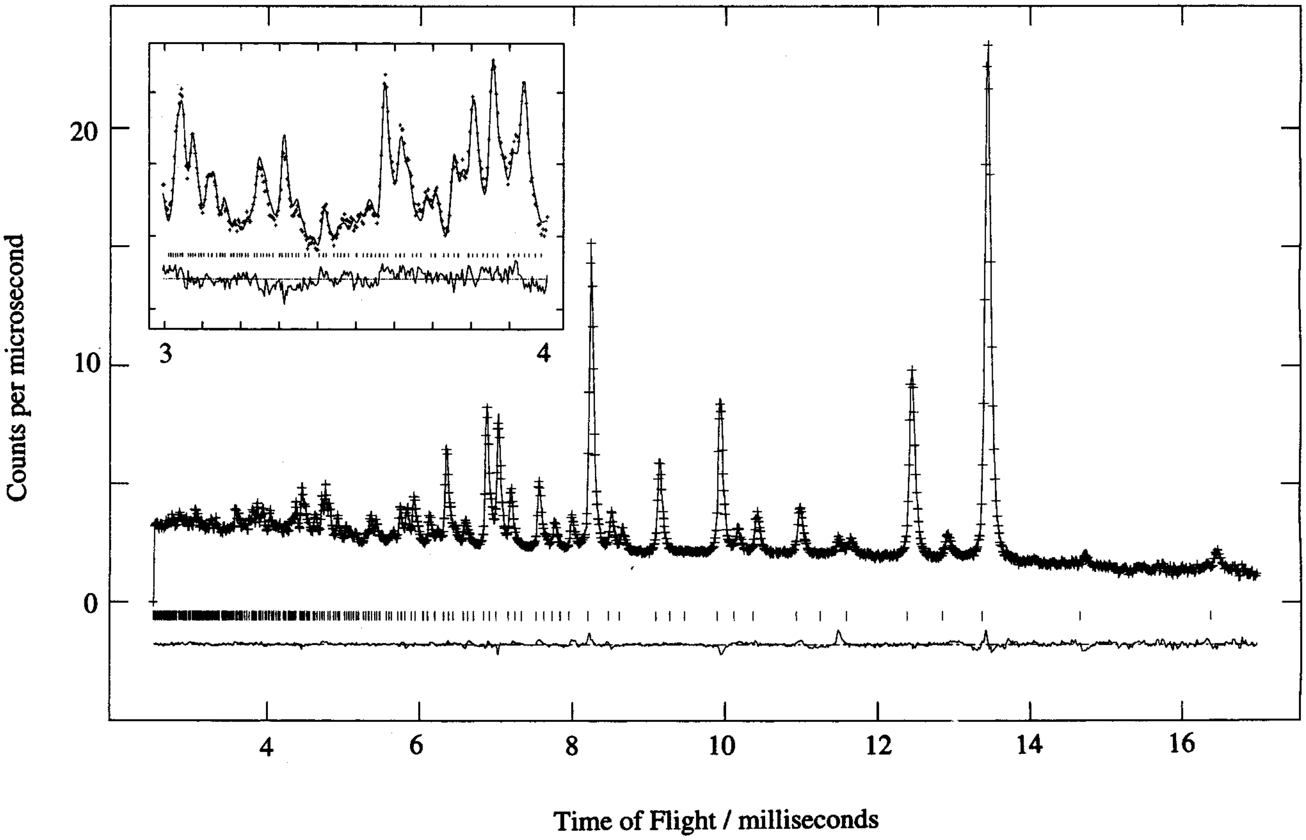

Figure 5. Results of Rietveld refinement of the structure of lithium aluminogermanate chloride sodalite, using powder neutron diffraction data at room temperature. The tick marks indicate the positions of reflections, and the difference curve is shown at the bottom on the same scale.

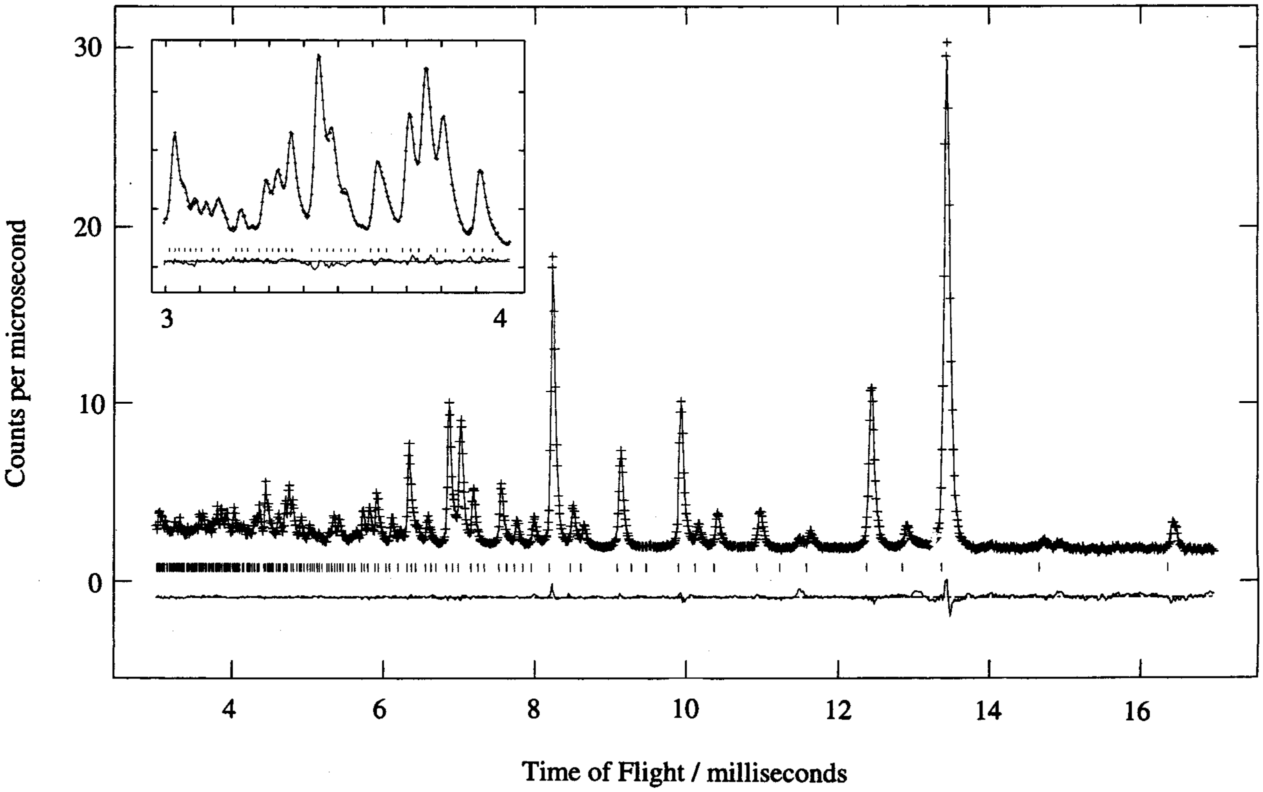

Figure 6. Results of Rietveld refinement of the structure of lithium aluminogermanate bromide sodalite, using powder neutron diffraction data at room temperature. The tick marks indicate the positions of reflections, and the difference curve is shown at the bottom on the same scale.

ionic radii.[35] In a manner similar to the parent sodium sodalites, a smooth variation of intra-tetrahedral bond angles is evident with the greatest deviation from tetrahedral symmetry seen for the iodide derivative. It is also clear that the O−Si−O angles are those that display the greatest deviation from the ideal tetrahedral value of 109.48°. Refinement results are displayed

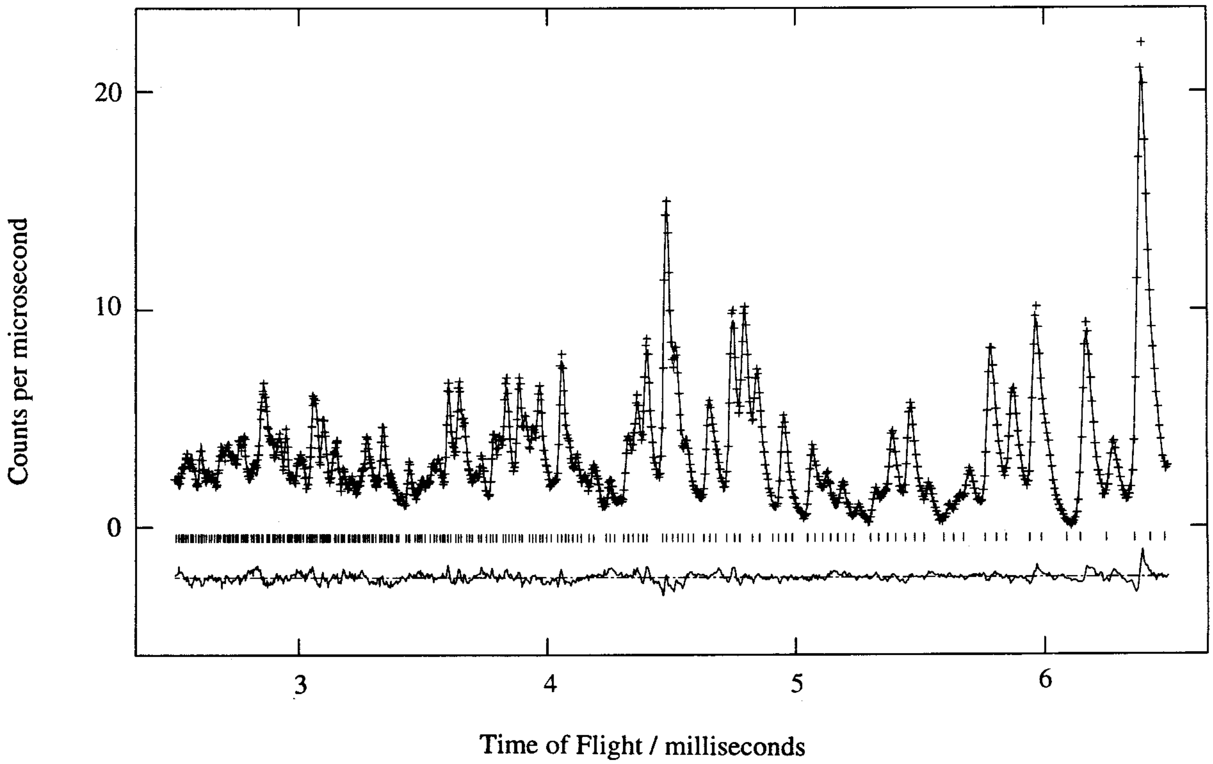

Figure 7. Expanded section of the results of Rietveld refinement of the structure of lithium aluminogermanate iodide sodalite, using powder neutron diffraction data at room temperature. The tick marks indicate the positions of reflections, and the difference curve is shown at the bottom on the same scale.

Table 1. Final Refinement Parameters, Atomic Positions, and Thermal Parameters (Å^2) with Estimated Errors in Parentheses from Powder Neutron Diffraction Data for Lithium Gallosilicate Halide Sodalites

		$Li_8[GaSiO_4]_6X_2$		
		Cl	Br	I
a (Å)		8.5362(6)	8.5776(5)	8.6489(5)
R_{wp}/R_{exp}		2.62/1.60	2.72/1.93	2.67/2.52
Ga	B	0.55(4)	0.51(4)	0.99(1)
Si	B	0.19(2)	0.27(4)	0.08(2)
X	B	2.50(4)	2.10(4)	2.49(9)
O	*x*	0.1269(1)	0.1282(1)	0.1319(2)
	y	0.1456(1)	0.1466(1)	0.1472(2)
	z	0.4027(1)	0.4051(1)	0.4102(1)
	B	0.78(3)	0.81(4)	1.04(5)
Li	*x*	0.1744(4)	0.1818(1)	0.1897(1)
	B	2.94(8)	1.88(3)	2.59(2)

Table 2. Selected Derived Framework Bond Distances (Å) and Angles (deg) from Powder Neutron Diffraction Data for Lithium Gallosilicate Halide Sodalites at 298 K with Estimated Errors in Parentheses

	multiplicity	Cl	Br	I
Ga−O	4	1.827(1)	1.826(2)	1.808(1)
Si−O	4	1.630(1)	1.631(1)	1.641(1)
Li−O	3	2.006(2)	1.996(2)	2.006(3)
Li−A	1	2.578(6)	2.692(5)	2.841(6)
O−Ga−O	4	109.32(3)	109.10(3)	108.63(5)
O−Ga−O	2	109.78(7)	110.22(7)	111.17(1)
O−Si−O	4	107.39(4)	107.21(4)	107.06(5)
O−Si−O	2	113.72(8)	114.09(7)	114.41(9)
Ga tilt		33.8(1)	32.9(1)	31.2(1)
Si tilt		37.5(2)	36.5(1)	34.3(1)
Ga−O−Si		121.48(5)	122.56(5)	124.81(8)
O−Li−O	3	106.9(2)	109.2(1)	111.4(2)
O−Li−A	3	111.9(2)	114.3(2)	112.0(2)

graphically in Figures 2−4, with Figure 4 showing an expanded portion of the plot for lithium gallosilicate iodide sodalite to indicate that the data and model are in good agreement at lower *d* spacings.

TOF PND Study of Lithium Aluminogermanate Halide Sodalites. Calculated and observed profiles are shown for the chloride and bromide in Figures 5 and 6 and matched extremely closely, reflecting the reliability of these results. An expanded section of the profile fit is displayed in Figure 7 for lithium aluminogermanate iodide sodalite. Table 3 summarizes the final atomic coordinates and refinement parameters, and Table 4 shows selected bond distances and angles for the lithium exchanged aluminogermanate halide sodalites. The level of cell contraction is again high, and framework Al−O−Ge angles are only marginally bigger than those for the gallosilicate exchanged sodalites. Examination of cell parameters as given in Table 3 shows how the bromide sample (a = 8.6786(5) Å) is in fact slightly smaller than the chloride (a = 8.6848(9) Å), contrary to expectations. It seems likely that the decreased contraction of the chloride analogue is linked to the shortened reaction time that was necessary to prevent complete collapse of the aluminogermanate framework. Refinement of the cation site occupancy did not suggest a large level of residual sodium in the structure; however, the large thermal parameter for the cation in the chloride material, in conjunction with a long cation to chloride distance (Table 4) supports this proposition of a small amount of residual sodium in the aluminogermanate material. The size difference in the lithium exchanged chloride and bromide sodalites is small, and the chloride version still shows a marginally smaller Al−O−Ge angle than the bromide. This is explained by the fact that lithium exchange is virtually complete (96.5% by elemental analysis) for the aluminogermanate chloride material.

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Table 3. Final Refinement Parameters, Atomic Positions and Thermal Parameters (Å^2) with Estimated Errors in Parentheses from Powder Neutron Diffraction Data for Lithium Aluminogermanate Halide Sodalites

		$Li_8[AlGeO_4]_6X_2$		
		Cl	Br	I
a (Å)		8.6848(9)	8.6786(5)	8.7505(5)
R_{wp}/R_{exp}		2.62/1.60	2.72/1.93	2.67/2.52
Al	B	0.47(15)	0.44(11)	0.31(12)
Ge	B	0.43(7)	0.44(4)	0.53(7)
X	B	6.43(9)	2.59(5)	2.44(5)
O	x	0.1396(2)	0.1377(2)	0.1399(1)
	y	0.1374(2)	0.1399(2)	0.1416(2)
	z	0.4052(1)	0.4054(1)	0.4094(1)
	B	0.86(8)	0.75(9)	0.78(7)
Li/Na	x	0.1830(4)	0.1828(3)	0.1928(2)
	B	3.30(12)	2.21(8)	1.99(8)

Table 4. Selected Derived Framework Bond Distances (Å) and Angles (deg) from Powder X-ray Diffraction Data for Lithium Aluminogermanate Halide Sodalites at 298 K with Estimated Errors in Parentheses

	multiplicity	Cl	Br	I
Al−O	4	1.762(2)	1.760(2)	1.759(2)
Ge−O	4	1.738(2)	1.736(2)	1.740(2)
Li−O	3	2.006(2)	2.006(2)	2.002(1)
Li/Na−A	1	2.753(6)	2.748(4)	2.922(4)
O−Al−O	4	107.95(4)	107.86(3)	107.48(3)
O−Al−O	2	112.56(9)	112.74(6)	113.53(6)
O−Ge−O	4	107.72(3)	107.64(3)	107.30(3)
O−Ge−O	2	113.04(9)	113.21(7)	113.90(6)
Al tilt		34.6	34.1	32.6
Ge tilt		34.2	34.5	32.9
Al−O−Ge		122.64(6)	122.69(4)	124.36(4)
O−Li−O	3	109.5(2)	109.3(1)	112.3(1)
O−Li−A	3	109.5(2)	114.3(1)	112.0(1)

Table 5. Selected Structural Data from PND Data for Framework Modified Sodalites

sodalite	a/Å	θ/deg^a	$\phi_{Al/Ga}$/deg^b	$\phi_{Si/Ge}$/deg
Li[GaSi]Cl	8.54	121.5	33.8	37.5
Li[GaSi]Br	8.58	122.6	32.9	36.5
Li[GaSi]I	8.65	124.8	31.2	34.3
Na[GaSi]Cl	8.96	133.7	25.4	28.1
Na[GaSi]Br	9.00	135.9	24.1	26.9
Na[GaSi]I	9.09	138.8	21.3	24.2
Li[AlGe]Cl	8.68	122.6	34.6	34.2
Li[AlGe]Br	8.68	122.7	34.1	34.5
Li[AlGe]I	8.75	124.4	32.6	32.9
Na[AlGe]Cl	9.04	133.1	26.6	26.9
Na[AlGe]Br	9.13	134.9	25.1	25.3
Na[AlGe]I	9.18	137.5	22.7	23.0
Na[GaGe]Cl	9.12	129.0	29.0	29.7
Na[GaGe]Br	9.17	130.5	27.8	28.5
Na[GaGe]I	9.27	133.2	25.9	25.9

[a] θ = framework T−O−T bond angle. [b] ϕ = tetrahedral tilt angle.

Discussion

Lithium Ion Exchange of Gallosilicate and Aluminogermanate Halide Sodalites. The halide sodalites have been shown to be an excellent system for the study of structural variation as a function of composition due to their simplicity. Rietveld refinement of powder neutron data for all parent sodium sodalites provides structural parameters indicating that framework collapse is directly linked to a decrease in framework T−O−T bond angle.

Full lithium exchange has been achieved for all gallosilicate halide sodalites and for aluminogermanate bromide and iodide sodalites, using the nitrate melt method after 3 h of reaction time. Full exchange was not achieved using this method for the aluminogermanate chloride sodalite. This melt method has thus proved particularly effective for lithium exchange of framework substituted sodalites for which low-temperature solution exchange has proven inefficient.[36] It is likely that the short reaction time is a consequence of the size of the lithium cation that can diffuse quickly through the sodalite framework. Furthermore, the high temperatures involved in exchange, using alkali metal halides, are avoided, hence widening the range of materials which can be treated to include sodalites of limited thermal stability. PND data allows the extent of cell contraction to be monitored and shows how Ga−O−Si and Al−O−Ge bond angles approaching 120° have been obtained highlighting the degree of collapse accompanying lithium introduction.

The gallosilicate halides were successfully exchanged by nitrate melt for 3 h, with refinement confirming full occupancy of lithium on the extraframework cation sites. The aluminogermanate bromide and iodide samples also displayed complete exchange after 3 h at 240 °C, using $LiNO_3$, but the chloride was destroyed. The reason for this was unclear: it is possible that since the chloride is the smallest of the series, prolonged treatment resulting in a high level of lithium exchange produces a structure with bond angles too strained to be sustained by the sodalite structure. Extrapolation of the T−O−T angles as a function of halide would predict an angle close to 121°, which seems to be the experimental limit for sodalite materials. This would reduce the stability of the structure relative to lithium chloride and a condensed tetrahedral structure, for example, $LiAlGeO_4$. At short reaction times, such as the 2 h successfully used herein, with only partial replacement (96.5%) of sodium by lithium, the composition is able to sustain the sodalite structure.

Attempted Lithium Exchange of Gallogermanate Halide Sodalites. In contrast to the gallosilicates and aluminogermanates, gallogermanates show no ability to undergo exchange with lithium, confirming the narrow band of structural parameters accessible, using the synthetic techniques employed in this work.[30] All of the materials subject to lithium nitrate melt treatment were destroyed, even for short reactions. The gallogermanate framework will form for only a very limited range of cell parameters and framework bond angles. This manifests itself by the successful incorporation of only three anions (chloride, bromide, and iodide) and only one type of nonframework cation for this framework composition. It is clear therefore that the thermodynamic stability of gallogermanate sodalites with respect to more condensed structures and alkali metal salts is much more limited. The gallogermanate framework is thus inherently more reactive and decomposes through reaction with the lithium salt.

Mechanism of Framework Collapse. Trends relating bond angles and cell parameter are clearly evident within the halide series. As the cell parameter is increased for a particular framework composition, there are definite trends observed: the O−T−O (×4), O−Na−A, and tetrahedral tilt angles decrease, whereas the O−T−O (×2), the T−O−T, and the O−Na−O angles increase. This general statement holds true whatever the framework composition and once more shows the integrity of the sodalite structure.

The two main mechanisms by which cell collapse occurs are tetrahedral tilting and variation of the framework T−O−T angle. These in turn fix the position of the framework oxygen. For aluminate sodalites where there is only one tetrahedral framework component, framework collapse from the fully expanded

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(36) Mead, P. J. Unpublished data.

space group $Im\bar{3}m$ to $I\bar{4}3m$ occurs via tetrahedral tilting about the $\bar{4}$ axis.[37−41] Sodalites with an ordered array of tetrahedral framework atoms adopt the space group $P\bar{4}3n$, and the tetrahedral tilt angles for each tetrahedral species become slightly different since the symmetry of the framework oxygen site is lowered. In such cases in order to accurately describe the mechanism of framework collapse, it is necessary to distinguish between the two tetrahedral tilt angles. This is achieved using the framework oxygen positions, shown in eqs 1 and 2 for silicon and aluminum, respectively.

$$\tan \phi_{\mathrm{Si}} = (1/2 - z)/x \qquad (1)$$

$$\tan \phi_{\mathrm{Al}} = (1/2 - z)/y \qquad (2)$$

where ϕ_{Si} and ϕ_{Al} are the tetrahedral tilt angles and x, y, and z are the atomic coordinates of the framework oxygen.

In addition to being linked to tilt angle, the cell parameter is also related to the framework T−O−T bond angle as described by eq 3:

$$\mathrm{T{-}O{-}T/deg} = 2 \sin^{-1}[(a/t)/(32)^{1/2}] \qquad (3)$$

where a is the cell parameter. The minimum cell parameters and T−O−T angles are described by the closest approach possible between framework oxygens in neighboring tetrahedra. This theoretically occurs when the tilt angle is 45° and the T−O−T angle is 109.5°.

Table 5 summarizes the derived structural parameters for the lithium-substituted gallosilicate and aluminogermanate halide sodalites, with the parent sodium materials included for comparison. Sodium gallogermanate halide sodalites have also been shown for completeness. These sodium halide sodalites relate to materials synthesized previously by us[30,34] and hence correspond to the parent sodalites that were used for lithium exchange.

In terms of tetrahedral tilt angles, the lithium halide sodalites have values ∼10° larger than the sodium parents, reflecting greater structural collapse that reaches a maximum for the lithium gallosilicate chloride sodalite—this is as expected, since the framework must contract most for the smallest cavity anion in order to maintain chemically reasonable separation distances. For the gallosilicates, $\phi_{\mathrm{Si/Ge}}$ is noticably larger than $\phi_{\mathrm{Al/Ga}}$, whereas for the aluminogermanates, these are virtually equal. Tilt angles provide further evidence that full lithium exchange has not quite been achieved for the aluminogermanate chloride, since the value of $\phi_{\mathrm{Al/Ga}}$ for the bromide is slightly larger than for the chloride; however, once more, the magnitude of the difference is small implying only a low occupancy of sodium on the 8(e) site. It is evident for the sodium gallogermanates that the tilt angles are larger than those for the gallosilicates and aluminogermanates, illustrating greater structural collapse even in the parent sodium sodalites. In this case, the introducton of lithium simply promotes too great a structural distortion to be synthetically viable for a sodalite containing both gallium and germanium in the framework. In such cases, in-situ ion exchange would be extremely useful, since it would show at what point along the reaction path structural integrity is lost and the corresponding level of lithium exchange attained.

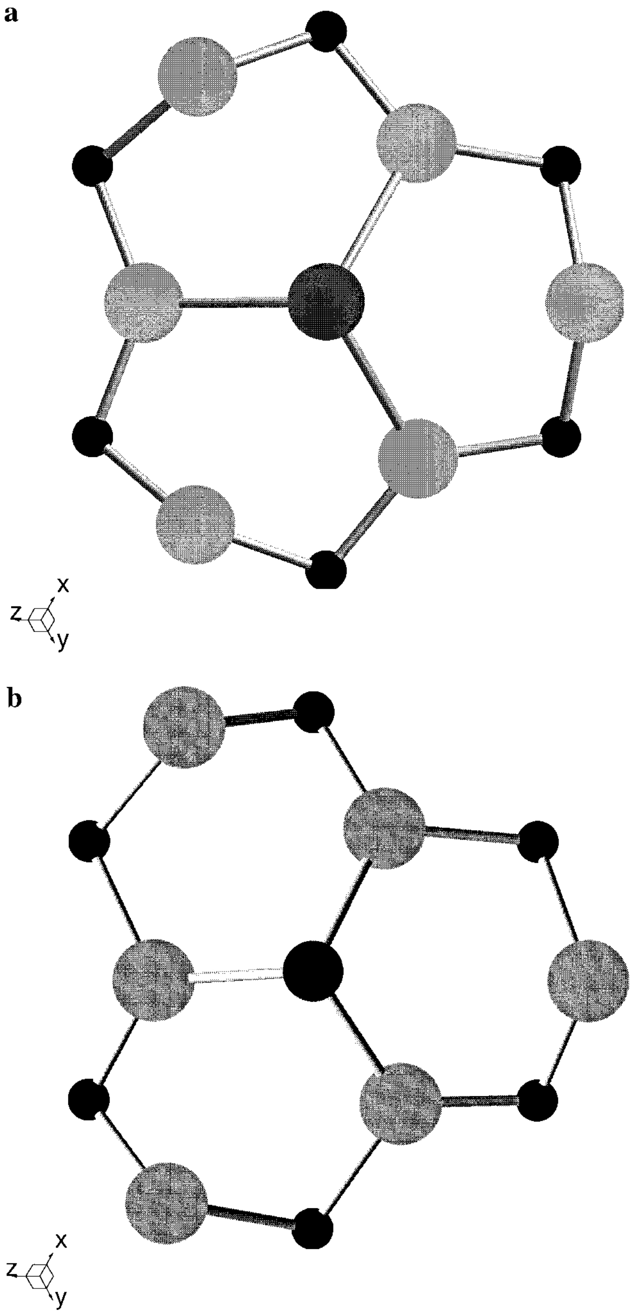

Figure 8. View down the six ring of (a) sodium aluminogermanate iodide and (b) lithium gallosilicate chloride sodalites, showing coordination of the extraframework cations to the framework oxygens. Tetrahedral species are the small black spheres, large spheres are the framework oxygens, and the central sphere represents the halide. The smaller framework T−O−T bond angle for lithium gallosilicate chloride is clearly evident, illustrating how this accounts for framework collapse.

Table 5 also shows how cell contraction is accompanied by significant reduction in framework T−O−T bond angle, with the lithium materials adopting values in the order of 12−14° lower than the sodium equivalents. The lowest of these bond angles is observed for lithium gallosilicate chloride, the value of 121.5° one of the lowest ever encountered for the sodalite structure. Figure 8 shows a view down the six ring for sodium aluminogermanate iodide and lithium gallosilicate chloride sodalites, for which coordination of the extraframework cations to framework oxygens can be seen.

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Conclusions

The nitrate melt method has been shown to be extremely effective for the replacement of sodium by lithium cations in the sodalite structure. The resultant parameters derived from Rietveld analysis indicate that contraction of the unit cell is principally accommodated by a decrease in the T−O−T framework bond angle and an increase in the tetrahedral tilt angles. Aluminogermanate chloride sodalite appears more susceptible to destruction upon lithium exchange, as evidenced by the need to shorten the sodalite/nitrate contact time. Structural investigation allied with elemental analysis suggests that this results in a small residual amount of sodium on the extraframework sites.

IC9812510