

# Synthesis and crystal structure of chlorate-enclathrated in aluminogermanate sodalite $\text{Na}_8[\text{AlGeO}_4]_6(\text{ClO}_3)_2$

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Encapsulation of chlorate in sodalite with aluminogermanate host framework has been obtained by one pot hydrothermal synthesis at 393 K. The crystal structure of  $\text{Na}_8[\text{AlGeO}_4]_6(\text{ClO}_3)_2$  sodalite was refined from X-ray powder data in the space group  $P43n$ :  $a = 9.169 \text{ \AA}$ , where Al-O-Ge angle is  $137.6^\circ$ . The  $^{27}\text{Al}$  MAS NMR study confirmed alternate Ge and Al ordering of the sodalite framework, while  $^{23}\text{Na}$  gave insight into the structure and dynamics of the cage fillings. Infrared spectrum confirmed the encapsulation of chlorate as well as the framework formation of aluminogermanate sodalite. SEM study showed the retention of cubical morphology of the aluminogermanate sodalite. Thermogravimetric analysis provided information on the extent of chlorate entrapment, stability within the sodalite cages and decomposition properties.

Keywords: *aluminogermanate sodalite; IR shift; Rietveld refinement; MAS NMR; thermogravimetry*

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## 1. Introduction

Sodalites are well known class of anions containing a framework consisting of  $\beta$ -cages, formed from (Be, Al, Si, Ga, Ge, Zn or P) tetrahedra, directly linked through six membered rings, with centrally placed anion co-ordinated tetrahedrally to four cations. The composition of sodalite is very diversified, for example, the anion incorporated into  $\text{M}_8[\text{ABO}_4]_6\text{X}_2$  (where, M is a cation, such as  $\text{Na}^+$ ,  $\text{Li}^+$ , and  $\text{Ag}^+$  [1, 2], A and B are tetrahedral forming species, such as Al and Si, and X can be monovalent or divalent anions such as  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{MnO}_4^-$ ,  $\text{ClO}_4^-$ , . . . . etc). Sodalites are characterized by a lattice structure consisting of a cage of twelve  $\text{AlO}_4$  tetrahedrons or similar unit and twelve tetrahedral  $\text{GeO}_4$  or  $\text{SiO}_4$  units and similar five units, linked together by oxygen bridges in an alternating pattern to form a truncated octahedron with eight single 6-ring openings and six single 4-rings. Typically, the cage has a diameter of  $6.6 \text{ \AA}$ . The hexagonal six-membered ring opening is between  $2.2 - 2.6 \text{ \AA}$  and the four-membered ring opening is between  $1.5 - 1.6 \text{ \AA}$ .

Investigation on the salt enclathration inside the sodalite aluminosilicate matrix and its effect on the thermochemical properties of sodalite have recently become an area of special interest. The simplicity of sodalites makes them an ideal system to study the phenomenon such as host-guest interaction and variation in structural parameters as a function of composition. By encapsulating such materials inside a sodalite host matrix, one can create clusters of the guest components. Sodalites have been studied mainly as a convenient matrix for a variety of encapsulated guests [3–11]. The aluminogermanate framework of the sodalite structure formed by the space-filling array of  $[4^6 6^8]$  polyhedral cages, the so called  $\beta$ -cages, can be regarded as a non porous matrix with well defined opening for the enclathration of guest molecules. The regular space filling framework of sodalite provides a temperature stable homogenous microporous matrix of sodalite cavities.

Sodalites can be synthesized using a variety of routes, including low temperature condensation reactions in basic solution [1, 2], solid state reactions at high temperature [12] and structure conversion [13]. The synthesis method of sodalite is often

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determined by the stability of the cavity anion towards temperature and base.

Isomorphous substitution of Ge for Si has been reported to compose a framework of aluminogermanate sodalite [14–16]. Synthesis of aluminogermanate sodalites has been reported in [12, 17–30]. Although these authors prepared the parent sodalite, they used a precursor of germanium at very high temperature and pressure to synthesize the aluminogermanate sodalites. The methods described by G.M. Johnson [31] are extremely suitable for entrapping the anions of limited thermal stability. More convenient low-temperature methods were thus sought. The synthesis led to crystalline material of very high quality with homogeneous distribution of guest molecules within the sodalite.

Sodalites have been shown to be useful for a wide variety of applications. In pigment industry, ultramarine is a very important thermally stable pigment [32]. Sodalite also shows photochromic and cathodochromic properties. Sodalites are also used as cluster components in insulators, semiconductor materials, nano composites in non linear optics or for host matrix of semiconductor quantum superlattices. Sodalites show electrochemical properties and can be used as potential ion selective membranes. They can be used for waste gas immobilization, and seem to be a versatile tool for material science [12, 13, 33–35].

In the present study we report the synthesis of aluminogermanate sodalite of  $\text{Na}_8[\text{AlGeO}_4]_6(\text{ClO}_3)_2$  and its characterization by means of a Rietveld structure refinement based on powder X-ray diffraction, as well  $^{27}\text{Al}$ ,  $^{23}\text{Na}$  MAS NMR, FT-IR, and by thermal analysis.

## 2. Experimental methods and results

Hydrothermal reactions have been shown to be particularly suited for the preparation of the framework modified sodalites. Low temperature solution reactions have been far more successful with aluminogermanate sodalite containing halide [24] and perchlorate [36] anions. In the present work,

hydrothermal synthesis of 1:1 aluminogermanate chlorate sodalite was carried out in aqueous solutions of sodium hydroxide containing germanium oxide as a source of germanium and  $\text{NaAlO}_2$ . These sources of aluminium and germanium were taken into Teflon autoclave of 30 mL capacity, NaOH was used as mineralizing agent and 15 g sodium chlorate was added. The composition of  $\text{GeO}_2:\text{NaAlO}_2:\text{NaOH}:\text{NaClO}_3$  in the ratio of 1M:1M:4M:6M was used for gel formation. This reaction mixture was shaken vigorously and kept at 120 °C for 120 hours in the oven (Biotech India, BTI, 230V – 15 A). The white, microcrystalline product was filtered in gooch crucible ( $G_4$ ). After washing with deionised water, the product was dried overnight at 100 °C. Subsequently, the obtained product was characterized by IR spectroscopy, thermogravimetry, X-ray powder diffraction, MAS NMR and SEM.

IR absorption analysis (KBr pellets) was performed on a Shimadzu, 8400-S FT spectrometer in the range of 4000 to 400  $\text{cm}^{-1}$ . X-ray powder diffraction pattern for the synthesized sodalite was collected using a Philips PW-1710 operating at 25 kV and 25 mA, using  $\text{Cu-K}\alpha$  radiation with a wavelength  $\lambda = 1.54 \text{ \AA}$ . The sample was evaluated using a step size of 0.017°. The powder diffraction pattern of this material was recorded in an angle range of 0 – 90° at 25°.  $^{27}\text{Al}$  MAS NMR spectrum was recorded at 130.0 MHz on a Bruker Advance 500 MHz widebore spectrometer with 6.15  $\mu\text{s}$  pulse duration, 3 s pulse delay and a spinning rate of 5 KHz with a 2.5 mm probe (alumina as a internal standard). The  $^{23}\text{Na}$  MAS NMR spectrum was recorded at 79.39 MHz with 40.5  $\mu\text{s}$  pulse duration, 1 s pulse delay and a spinning rate of 7 kHz with a 2.5 mm probe, using sodium chloride as an internal standard.

Scanning electron microscopy (SEM) was carried out to provide information about the particle morphology and crystal growth mechanism. The SEM was recorded on JEOL JEM-6360A model equipped with JEOL JEC 560 auto carbon coater. Simultaneous thermal analysis, TGA was carried out in argon with a Mettler Thermoanalyzer 146 at a heating rate of 20 °C/min in the range of 25 –

1000 °C. The filling of sodalite cages with the guest species was checked by thermogravimetry.

### 3. Results and discussion

#### 3.1. Hydrothermal synthesis of aluminogermanate sodalite

In order to obtain pure aluminogermanate sodalite, Fleet [24] used beryllonite phase  $\text{NaAlGeO}_4$ . G. M. Johnson et al [31] described the synthesis in detail by using sodium meta germanate phase. Hydrothermal synthesis of aluminosilicate sodalite analogues is easy to compare with its aluminogermanate sodalites as the germanium source plays an important role. If higher concentration is used for dissolving of germanium source, sodalite nucleation is faster, anion entrapment in templates is slower whereas solubility of the formed sodalites is high. These observations are very similar to the results presented by S. Bachmann et al, Johnson et al, and Buhl et al, [28, 31, 37] respectively. Aluminosilicate sodalite can be obtained by hydrothermal synthesis at 100 °C, while aluminogermanate sodalite requires higher temperature except for halide, perchlorate, and chlorate entrapment. In this study, one pot synthesis was carried out in 4 M NaOH with educts (germanium oxide and sodium aluminate) and kept in Teflon autoclave at 120 °C for five days.

#### 3.2. Infrared spectroscopy

Fig. 1 shows IR spectrum for aluminogermanate sodalite containing chlorate ions. Sodalite framework shows three kinds of vibrations [14, 38–40], symmetric stretch, asymmetric stretch and bending mode of vibration. The IR spectrum of chlorate sodalite shows framework peaks at 868, 629, 598 and  $386\text{ cm}^{-1}$ . In addition, the intense asymmetric stretching vibration ( $\nu_3$ ) and symmetric stretching vibration ( $\nu_1$ ) of  $\text{ClO}_3^-$  [41] are clearly visible in the infrared spectrum at  $992$  and  $486\text{ cm}^{-1}$  respectively, confirming enclathration of chlorate anion in aluminogermanate sodalite.

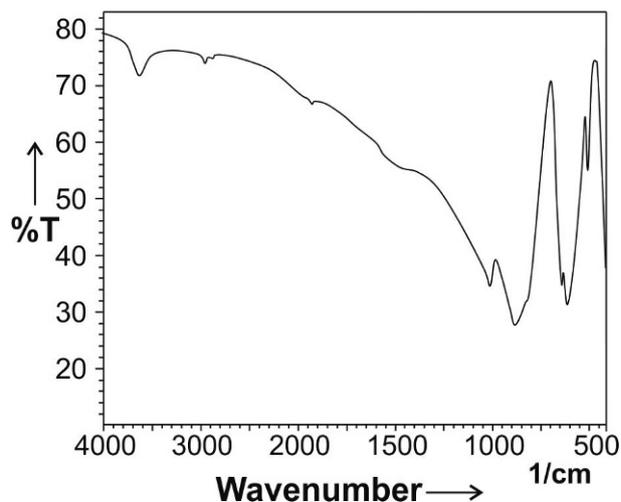


Fig. 1. IR spectrum of aluminogermanate  $\text{Na}_8[\text{AlGeO}_4]_6(\text{ClO}_3)_2$  sodalite.

#### 3.3. Structure refinement

The X-ray crystallographic data and experimental conditions for aluminogermanate chlorate sodalite are listed in Table 1. Atomic positions and thermal parameters are given in Table 2. The X-ray powder profile is shown in Fig. 2. Chlorate sodalite was refined in the space group  $\text{P}\bar{4}3\text{n}$ , using GSAS X-ray powder diffraction suite. For refinement of the sodalites, the aluminum and germanium were placed in the  $6c$  ( $1/4, 0, 1/2$ ) and ( $1/4, 1/2, 0$ ) sites respectively. The chlorine atom was refined at the centre of the cage, sodium was treated as a single atom and cage oxygen was placed in the  $24i$  ( $x, y, z$ ) site  $x \sim 0.14, y \sim 0.15, z \sim 0.45$ . This produced a fully ordered framework with alternating tri- and tetravalent cations [42]. In GSAS refinement, a first lattice parameter, scale factor and background parameter were added. Further, atomic positions and histogram were introduced. Convergence occurred in the early stage of the refinement for aluminogermanate sodalite.

Table 3 shows selected bond lengths and bond angles for chlorate sodalite. The lattice constant is found to be  $9.169\text{ \AA}$ . The T-O band distances are  $d(\text{Ge-O}) = 1.739\text{ \AA}$  and  $d(\text{Al-O}) = 1.734\text{ \AA}$ . In  $\text{GeO}_4^-$  and  $\text{AlO}_4^-$ , O-T-O tetrahedral angles are somewhat distorted from their regular tetrahedral geometry as both Ge and Al atoms have site symmetry 4. A remarkable feature of the framework

Table 1. Crystallographic data and experimental conditions for the structure refinement of chlorate aluminogermanate sodalite.

Compound	$\text{Na}_8[\text{AlGeO}_4]_6(\text{ClO}_3)_2$
Temperature	20 °C
Space group	$\text{P}\bar{4}3\text{n}$
Formula unit	$Z = 1$
Cell parameter a (Å)	9.169
Density (gm/cm <sup>3</sup> )	3.577
Data collection	
2 $\theta$ range (°)	10 – 90
Step size (2 $\theta$ °)	0.017
Sample time (s/data point)	1 s
Number of refined parameters	13
Number of reflections	140
Agreement factors	
R <sub>p</sub>	0.1609
R <sub>wp</sub>	0.2230

Table 2. Fractional coordinates of aluminogermanate chlorate sodalite.

Atom	x	y	z
$\text{Na}_8[\text{AlGeO}_4]_6(\text{ClO}_3)_2$			
Ge	0.2500	0.5000	0.0000
Al	0.2500	0.0000	0.5000
O1	0.1513	0.1517	0.4432
Na	0.1981	0.1981	0.1981
Cl	0.0000	0.0000	0.0000
O2	0.1495	0.0688	0.0706

geometry is the large Ge-O-Al angle of 137.892°. The chlorine anion occupies the central position in the sodalite cage. Sodium cations approximately occupy the twelve-atom rings and are closely coordinated by three framework oxygen atoms with three further Na-O neighbors in the same ring. The interatomic distances show deviations compared to the geometry of pure  $\text{NaClO}_3$  solid; in enclathrated  $\text{ClO}_3^-$  anion,  $d(\text{Cl-O})$  is 1.546 Å, while this distance in pure  $\text{NaClO}_3$  solid is 1.481 Å [41, 43].

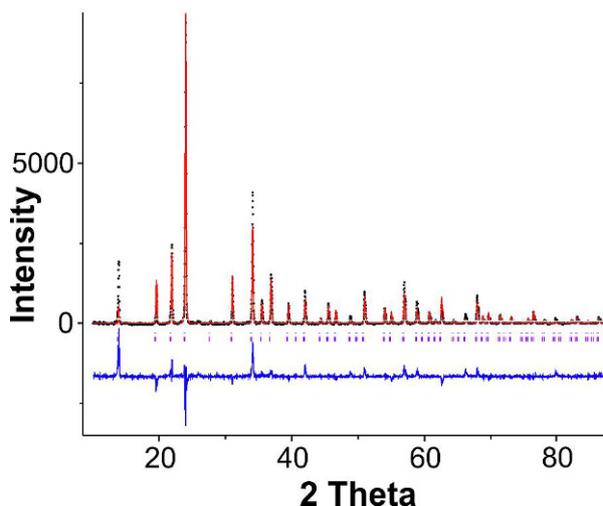


Fig. 2. X-ray powder diffraction pattern for  $\text{Na}_8[\text{AlGeO}_4]_6(\text{ClO}_3)_2$  sodalite. The observed powder pattern together with the difference between observed and calculated intensities (lower part) and the reflected peak positions.

Table 3. Selected derived bond distances and bond angles for aluminogermanate chlorate sodalite.

Bond distances (Å)	Bond angles (°)	
$\text{Na}_8[\text{AlGeO}_4]_6(\text{ClO}_3)_2$		
Ge-O1	1.7392(2)	O1-Ge-O1 105.668(1)
Al-O1	1.7344(2)	O1-Al-O1 105.709(1)
Na-O1	2.3267(2)	Al-O1-Ge 137.892(2)
Na-O2	1.7179(1)	
Na-Ge	3.3482(2)	
Na-Al	3.3445(4)	
Cl-O2	1.5464(2)	

### 3.4. MAS NMR Study

Fig. 3a, b show  $^{27}\text{Al}$  and  $^{23}\text{Na}$  MAS NMR for aluminogermanate chlorate sodalite respectively. Aluminogermanate framework consists of alternately ordered Ge and Al with Ge/Al ratio 1.0.  $^{27}\text{Al}$  chemical shift,  $\delta$ , is influenced by T-O-T bond angle and the nature of cations and anions in the framework.  $^{27}\text{Al}$  is an ideal nucleus for the study of aluminogermanate sodalite as it exhibits single sharp resonance line in the spectrum at 69.697 (Fig. 3a). Single resonance line in the spectrum

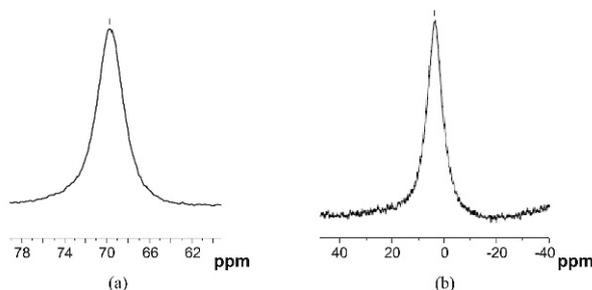


Fig. 3. MAS NMR spectra of (a)  $^{23}\text{Na}$ , and (b)  $^{27}\text{Al}$ .

confirms strictly the alternating ordering of Ge, and Al in the framework [44, 45].

The  $^{23}\text{Na}$  MAS NMR spectrum (Fig. 3b) of the chlorate sodalite shows a single sharp resonance line in the spectrum at 3.364. Aluminogermanate chlorate sodalite does not show quadrupole effect which may be present in other sodalites [36, 44]. The sodium cation experiences the spherical symmetric charge distribution inside the sodalite cage. The sodium cations are located above the centre of the six-ring windows of the cages and are coordinated with three oxygen atoms and anions in the sodalite cage.

### 3.5. Thermogravimetric analysis

The weight-temperature behavior of chlorate sodalite is shown in Fig. 4. TGA shows very slight initial weight loss due to little adsorbed/enclathrated water. Pure sodium chlorate decomposes at  $\sim 300^\circ\text{C}$ , while decomposition of encapsulated chlorate in sodalite cage takes place between  $600^\circ\text{C}$  to  $700^\circ\text{C}$  and thereafter stability of sodalite framework is attained (Fig. 4). The intra-cage reaction takes place without destruction of sodalite framework [46], according to the following reaction:



On decomposition, chlorate sodalite is converted into chloro sodalite with 5.30 % weight loss, which indicates the presence of almost 95 % cage filling in the sodalite. Formation of chloro sodalite is confirmed by infrared spectrum, in which characteristic absorption band of chlorate is absent.

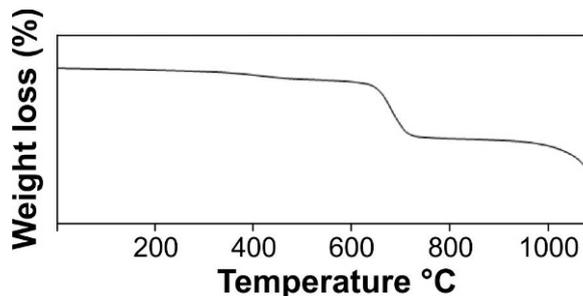


Fig. 4. Thermogram of aluminogermanate chlorate sodalite.

Table 4. EDAX analysis for aluminogermanate chlorate sodalite.

Element	$\text{Na}_8[\text{AlGeO}_4]_6(\text{ClO}_3)_2$
Al	10.64
Ge	10.84
O	57.33
Cl	4.63
Na	14.94

### 3.6. Scanning electron microscopy

Fig. 5a,b depict SEM pictures of chlorate enclathrated aluminogermanate sodalite. The crystals formed are regular and well shaped cubes. The average crystal size ranges between 10 to 15  $\mu\text{m}$ . Combination of thermogravimetric results and EDAX analysis (Table 4) confirms the 4.63 % presence of Cl, which indicates that more than 95 %  $\text{ClO}_3^-$  are enclathrated in aluminogermanate sodalite cages.

## 4. Conclusions

One pot hydrothermal synthesis method was successfully used for the synthesis of chlorate aluminogermanate sodalite. Synthesis conditions of the aluminogermanate sodalite were greatly affected by the solubility of germanium source and temperature. Infrared spectroscopy confirmed the formation of framework as well as encapsulated chlorate anions. Rietveld analysis was carried out with GSAS suite to determine the bond distances and bond angles. Thermogravimetry and EDAX

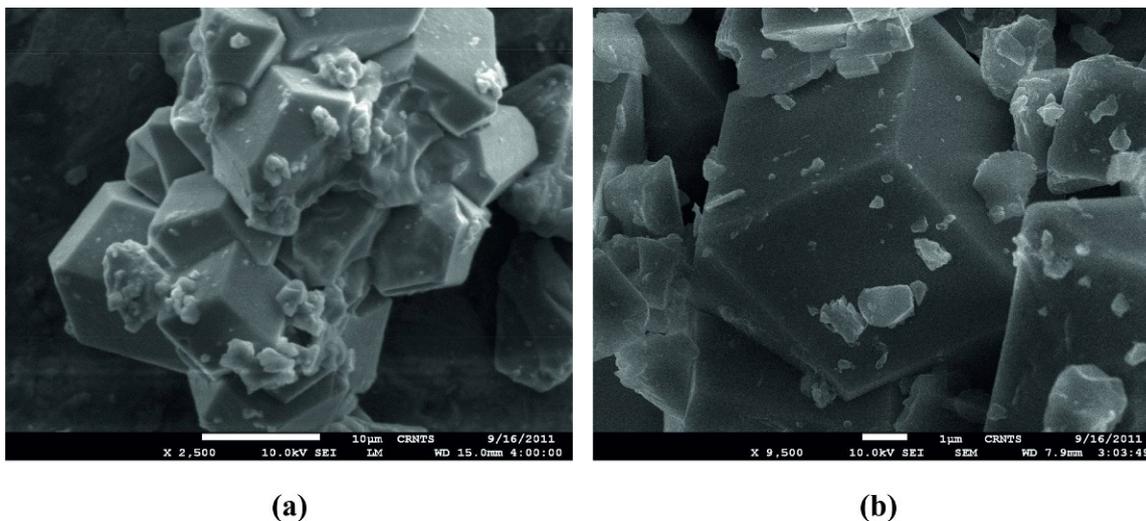


Fig. 5. Scanning electron microscopy showing cubical morphology of aluminogermanate sodalite (a) magnification 2,500 and (b) 9,500.

studies determined the extent of encapsulation of chlorate anion in sodalite.

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