



## Synthesis, Characterization and Crystal Structure of Gallosilicate Perchlorate Sodalite

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### Abstract

Perchlorate enclathrated sodalite with gallosilicate host framework has been synthesized under low temperature (100 °C) hydrothermal technique and characterized by X-ray powder diffraction, IR, Raman spectroscopy, UV DRS, SEM, MAS NMR spectroscopy and thermogravimetry. The structural features were investigated by IR, MAS NMR spectroscopy of  $^{29}\text{Si}$  and  $^{23}\text{Na}$  nuclei and by Reitveld refinement of X-ray powder diffraction data. IR and Raman spectroscopy confirms formation of framework and presence of  $\text{ClO}_4^-$  group. The tetrahedral framework T-atoms are completely ordered and the chloride atoms are located at the centre of the sodalite cages. The crystal structure of this new sodalite was refined in the space group  $P4_3n$  with  $a = 9.15788 \text{ \AA}$ ,  $V = 768.5 \text{ \AA}^3$ ,  $Z = 1$ ,  $R_{wp} = 0.0611$ ,  $R_p = 0.1079$  and  $\text{Si-O-Ga}$  is  $144.036^\circ$ . The surface area of single entity with stoichiometry  $\text{Na}_8[\text{GaSiO}_4]_6(\text{ClO}_4)_2$  was found to be  $8.385 \times 10^{-15} \text{ cm}^2/\text{g}$ .  $^{29}\text{Si}$  MAS NMR study confirms complete ordering of Si and Ga in the gallosilicate framework. Thermo gravimetric analysis has provided information on the extent of perchlorate entrapment, stability within the cage and decomposition properties.

**Keywords:** Gallo silicate, Hydrothermal, Reitveld refinement, Perchlorate, Sodalite

### 1. Introduction

The cubic framework structure of sodalites with general composition  $\text{Na}_8[\text{T}_1\text{T}_2\text{O}_4]_6\text{X}_2$  is formed by a space filling array of truncated octahedral cages each built up of tetrahedral  $\text{TO}_4$  units. The framework T-atoms are usually Si and Al but even others like Ga or Ge can be introduced during synthesis (Johnson *et al.*, 2000). According to the host guest interactions the cage filling ions and the type of framework T-atoms are both responsible for the chemical and physical properties of a certain sodalite species. Mean while many sodalites have been synthesized with large number of element combinations with compositions  $\text{Na}_8[\text{AlSiO}_4]_6\text{X}_2$ , where X is a monovalent guest anion,  $\text{X} = \text{Cl}^-, \text{Br}^-, \text{ClO}_4^-$ , is formed by  $\text{TO}_4$  tetrahedra as elementary building unit (Pauling, 1930; Lons *et al.*, 1967). The gallosilicate framework is made of regularly alternating tetrahedrally coordinated Ga and Si atoms, which are connected through oxygen atoms. The framework of sodalite is highly flexible and can accommodate its degree of expansion due to enclathrated guest species of different size. Depending on the composition sodalite posses photochromic, cathodochromic, ion conducting properties and as high density optical data storage materials. Sodalites with special guest anion can be used for various technical applications like pigments, ultramarine, graphical and digital storage system, luminescence and catalytic activity (Hassan *et al.*, 1984; Schipper *et al.*, 1972; Van Doorn *et al.*, 1972; Mclaughan *et al.*, 1970; Bolwijn *et al.*, 1972; Chang, 1974).

Earlier work shows that, little attention is given on synthesis and detailed characterization of gallosilicate sodalite

(Piontkovskaya *et al.*, 1970, Suzuki *et al.*, 1985, McCusker *et al.*, 1986, Newsam *et al.*, 1987, Johnson *et al.*, 1997, Bu, Xianhui *et al.*, 1998, Johnson *et al.*, 1999; Gesing *et al.*, 2000, Buhl *et al.*, 2006, Murshed *et al.*, 2007, Gesing, *et al.*, 2007, Murshed *et al.*, 2008).

Sodalites are expected to be an interesting model system for studying simple principle of perchlorate storage in small cavities of framework structure (Weitkamp *et al.*, 1995), we extend our experimental work here on synthesis, characterization and structure of perchlorate encapsulated sodalite with gallosilicate framework. Substitution of framework by gallium is of special interest to study interactions of encapsulated  $\text{ClO}_4^-$  guest anion with a host framework of certain composition. The aim of the present paper is to establish synthesis and crystal structure of  $\text{Na}_8[\text{GaSiO}_4]_6(\text{ClO}_4)_2$  sodalite as a new model compound for long time in a solid matrix.

## 2. Experimental

### 2.1 Synthesis at low temperature

Apart from several methods (Barrer *et al.*, 1970; Veit *et al.*, 1991; Buhl *et al.*, 1991; Fleet, 1989) low temperature hydrothermal technique has been employed for the synthesis of  $\text{Na}_8[\text{GaSiO}_4]_6(\text{ClO}_4)_2$  sodalite. The synthesis was carried out in a single step without precursors in Teflon autoclaves at a temperature of 100 °C and autogenous pressure for reaction time of seven days. The stoichiometric amount of gallium oxide (source of gallium), silicic anhydride (source of silicon) along with NaOH (as a mineralizing agent) and sodium salt of perchlorate were taken in a Teflon autoclave. After the reaction period, the product was washed with deionized water and dried overnight at 100 °C to remove weakly adsorbed surface water. The product obtained was characterized by IR, Raman, MAS NMR spectroscopy, UV DRS, TGA/DTA and SEM.

### 2.2 Crystallography

The characterization of  $\text{Na}_8[\text{GaSiO}_4]_6(\text{ClO}_4)_2$  sodalite was performed by X-ray powder diffraction method using Rietveld refinement GSAS program. The X-ray powder diffraction data were collected, using diffractometer operating in  $\theta$ - $\theta$  geometry (5-80 ° 2 $\theta$ , step width 0.017 °2 $\theta$ , sample time 1s per step), using  $\text{CuK}\alpha$  radiation for 5<2 $\theta$ <90°. The crystallographic data and experimental conditions are given in Table 1.

### 2.3 Spectroscopy

An infrared spectrum in the region 350-4000  $\text{cm}^{-1}$  was measured as KBr pellets on a computer interfaced Bruker FTIR spectrophotometer. The Raman spectrum was collected at room temperature using Nicolet Almega XR dispersive Raman Spectrophotometer (Thermo Electron Corporation) with 780 nm Laser. The sample was mixed with KBr and pressed into a disk which was rotated during excitation to minimize heating effect (Kiefer *et al.*, 1971).

Further, structural characterization was also performed by solid state MAS NMR technique. The use of high magnetic field, combined with spatial-averaging sample reorientations NMR technique like magic angle spinning (MAS) is used to obtain detailed structural information on solid lattice. This work concentrates on the application of  $^{29}\text{Si}$  and  $^{23}\text{Na}$  MAS NMR. The MAS NMR spectra were recorded on a Bruker solid state MAS NMR Spectrometer DSX 300. The  $^{29}\text{Si}$  MAS NMR spectrum was recorded at 59.62 MHz with 5  $\mu\text{sec}$  pulse duration, 15 sec pulse delay and a spinning rate of 5 KHz. Upto 3447 scans were accumulated at a rotation frequency in a 5 mm probe (Tetramethylsilane as a internal standard). The  $^{23}\text{Na}$  MAS NMR spectrum was recorded at 79.39 MHz with 40.5  $\mu\text{sec}$  pulse duration, 1 sec pulse delay and a spinning rate of 5 KHz. Upto 429 scans were accumulated at a rotation frequency in a 5 mm probe (sodium chloride is used as a internal standard). The crystal morphology and EDAX of  $\text{ClO}_4^-$  sodalites were carried out using scanning electron microscopy on a JEOL JEM-6360A model equipped with JEOL JEC\_560 auto carbon coater SEM.

### 2.4 Thermogravimetry

The thermal stability of the  $\text{Na}_8[\text{GaSiO}_4]_6(\text{ClO}_4)_2$  sodalite was studied by TGA/DTA using Mettler Toledo instrument at a heating rate 10 °C/min, in the temperature range, room temperature to 900 °C.

## 3. Results and Discussion

### 3.1 IR and Raman spectroscopy

The IR spectrum of  $\text{Na}_8[\text{GaSiO}_4]_6(\text{ClO}_4)_2$  sodalite, obtained in the mid infrared and far- infrared region is shown in Figure 1. In the mid-infrared region the symmetric and asymmetric T-O-T, (where T=Ga or Si) vibrations of the sodalite framework appears. The spectrum can be divided into three sets of framework mode:

One absorption band for, $\nu_{\text{as}}$ (Ga-O-Si) (asymmetric stretching vibrations)	954.8 $\text{cm}^{-1}$ ,
two absorption bands in the $\nu_{\text{s}}$ (Ga-O-Si) (symmetric stretching vibrations)	621.1, 534.3 $\text{cm}^{-1}$ ,
two absorption bands due to $\delta$ (Ga-O-Si) (bending vibration)	451.3, 343.3 $\text{cm}^{-1}$

In addition, the asymmetric stretching vibration  $\nu_3$  of  $\text{ClO}_4^-$  at 1116.82  $\text{cm}^{-1}$  is clearly visible in the infrared spectrum. This strong absorption peak confirms the enclathration of  $\text{ClO}_4^-$  ion in the gallosilicate sodalite cage.

The Raman spectrum is shown in Figure 2. The framework vibrations are weak in the Raman and hence,  $\nu_1, \nu_2$  and  $\nu_4$  vibrations can be clearly seen. The Raman spectrum shows bands at  $227.56 \text{ cm}^{-1}$ , and  $442.84 \text{ cm}^{-1}$  (T-O deformation mode),  $631.80 \text{ cm}^{-1}$  (symmetric Ga-O-Si vibration) and  $931.56 \text{ cm}^{-1}$  can also be classified as framework bands. In addition a deformation band at  $1111.56 \text{ cm}^{-1}$  can be assigned to  $\text{ClO}_4^-$  anion.

### 3.2 Photo physical properties

The photo-absorption of the photocatalyst depends on the mobility of electron-hole pairs, which determines the probability of electrons and holes to reach reaction sites on the surface of the photocatalyst. Figure 3 shows the diffuse reflection spectrum of the  $\text{Na}_8[\text{GaSiO}_4]_6(\text{ClO}_4)_2$  sodalite. This shows absorption in the UV region at 248 nm (The band gap of  $E_g = 5 \text{ eV}$ , by the formula  $E_g = hc/\lambda$ ) which indicates that  $\text{Na}_8[\text{GaSiO}_4]_6(\text{ClO}_4)_2$  have the ability to respond to the wavelength of ultra violet region.

### 3.3 Structure refinement

The crystallographic data and experimental conditions for the structure refinement of gallosilicate perchlorate sodalite are given in Table 1. The refined positional, displacement and occupancy parameters are given in Table 2. The X-ray powder pattern of sodalite synthesized with an ideal composition  $\text{Na}_8[\text{GaSiO}_4]_6(\text{ClO}_4)_2$  is shown in Figure 4 together with the final Reitveld difference plot. The cubic lattice parameter,  $a = 9.15788 \text{ \AA}$  was refined for the gallosilicate sodium perchlorate sodalite. The final residuals for the pattern and the structure factor are  $R_{wp} = 0.0611$ ,  $R_p = 0.1079$ . The refinement was performed on arranging chloride at the centre and the four oxygen at 24i position of the space group  $P4_3n$ . Selected geometrical data are given in Table 3. The gallosilicate framework consists of a long-range disordered arrangement of the gallium and silicon atoms. The average bond length between the tetrahedrally coordinated atoms and oxygen atoms of  $1.70202 \text{ \AA}$  (Table 3) is close to that expected from the weighted average of typical Si-O and Ga-O distances in tetrahedral environments (Si-O,  $1.62 \text{ \AA}$  and Ga-O,  $1.85 \text{ \AA}$ ). The  $\text{ClO}_4^-$ -SOD framework consists of the usual face sharing truncated octahedral, built up from an ordered array of alternating  $\text{SiO}_4$  and  $\text{GaO}_4$  tetrahedral units.

Table 3 shows that, O-T-O tetrahedral angles in  $\text{SiO}_4$  and  $\text{GaO}_4$  are somewhat distorted from their regular tetrahedral geometry. The O-Si-O values are  $105.631$  and  $117.459^\circ$ , while for O-Ga-O bond values are  $106.012$  and  $116.637^\circ$ . Both Si and Ga have site symmetry  $4$ . A considerable feature of the framework geometry is the large Si-O-Ga angle of  $144.036^\circ$ . The perchlorate anion occupies the centre of the sodalite cage. For a chlorine atom, which has exact tetrahedral coordination in the free  $\text{ClO}_4^-$  ion, in  $\text{NaClO}_4$ -SOD is comparable. A bond distance within the anions of sodalite is in good agreement with those in  $\text{NaClO}_4$  solid (Cl-O,  $1.44 \text{ \AA}$ ). Considering different distances and angle the structure proposed for single unit cell of  $\text{Na}_8[\text{GaSiO}_4]_6(\text{ClO}_4)_2$  is shown in Figure 5. Figure shows sodium cations approximately occupy the twelve atom rings and are closely coordinated by three framework oxygen atoms with three further Na-O(1) contacts in the same ring.

Further, the surface area of single entity of  $\text{Na}_8[\text{GaSiO}_4]_6(\text{ClO}_4)_2$  was found to be  $8.385 \times 10^{-15} \text{ cm}^2/\text{g}$ . The surface area of single entity is successfully calculated by using equation (Overman, 1965),  $b = (M/dL)^{2/3}$ , where,  $b$  - surface area,  $M$  - formula weight,  $d$  - density and  $L$  - Avogadro's number.

### 3.4 MAS NMR Spectroscopy

In order to confirm the framework structure and Na interaction with other atoms,  $^{29}\text{Si}$  and  $^{23}\text{Na}$  MAS NMR is studied. The  $^{29}\text{Si}$  MAS NMR spectrum of the reaction product  $\text{Na}_8[\text{GaSiO}_4]_6(\text{ClO}_4)_2$  sodalite consists of a sharp single resonance line at  $\delta_{\text{iso}} = -82.93 \text{ ppm}$  for  $\text{Si}(\text{OGa})_4$  units (Figure 6a). This indicates Si/Ga ratio of 1.0 and confirms the alternate Si, Ga ordering of the framework in the synthesized sodalite (Engelhardt *et al.*, 1989, Weller *et al.*, 1997, Johnson *et al.*, 2000).

The  $^{23}\text{Na}$  MAS NMR spectrum for the  $\text{ClO}_4^-$ -GaSi-SOD is also shown in Figure 6b. The  $^{23}\text{Na}$  MAS NMR spectrum shows a quadrupole pattern depending more or less upon the perchlorate cage contents of the  $\text{Na}_8[\text{GaSiO}_4]_6(\text{ClO}_4)_2$  sodalite.  $^{23}\text{Na}$  MAS NMR shows quadrupole pattern with two well resolved peaks with  $\delta_{\text{iso}} = -6.135 \text{ ppm}$  and  $\delta_{\text{iso}} = -33.608 \text{ ppm}$ . Due to the  $3/2$  spin, the  $^{23}\text{Na}$  nucleus exerts a quadrupole moment, interacting with local electric field gradient. This causes line broadening as well as specific line shapes of the spectrum. The line width and the isotropic chemical shift position are proportional to the square of the quadrupole interaction constant.

The above results confirm that, the sodium cations are located above the centre of the six-ring windows of the cages and are co-ordinated with three oxygen atoms and anions in the sodalite cage. Calculated Na-O1 and Na-O2 distances show that chloride atom at the centre of the sodalite cage.

### 3.5 Thermal analysis

The weight temperature behavior of the perchlorate gallosilicate sodalite is studied in detail. Figure 7 shows the TGA/DTA of perchlorate gallosilicate sodalite. An endothermic behavior in the temperature range of  $600\text{-}700^\circ\text{C}$ , is due to the decomposition of encapsulated salt molecules. The thermal analysis shows high thermal stability of sodalite

framework after 700 °C. The  $\text{Na}_8[\text{GaSiO}_4]_6(\text{ClO}_4)_2$  sodalite onset decomposition temperature  $\sim 600^\circ\text{C}$ , where as the solid  $\text{NaClO}_4$  decomposes nearly at 400 °C. This behavior is similar to aluminosilicate perchlorate sodalite (Weller *et al.*, 1991) which shows onset decomposition temperature  $\sim 620^\circ\text{C}$ . The weight loss indicates full occupancy of anion sites in the sodalite cages by  $\text{ClO}_4^-$  anions and negligible amount of water. Gallosilicate perchlorate sodalite can be converted to chloride sodalite via heating in air at  $700^\circ\text{C}$  for 4 hrs. This provides an indirect route to the chloride sodalite.

### 3.6 Crystal morphology

SEM study were carried out to provide information about the particle morphology and the macroscopic crystal growth mechanism, as well as to determine the distribution of different cages (with or without anion) through out the lattice. Figure 8 shows the scanning electron microscopic pictures of the synthesized sodalite loaded with sodium perchlorate.

SEM (Figure 8) shows balanced crystal size with cubic morphology. The surfaces of these crystals are smoother than those of the silica sodalite crystals. Atomic proportions in the same product were determined using energy dispersive X-ray Spectroscopy (EDX). EDX analysis has detected that Ga, Si and Na are present in the crystal with respective compositions.

## 4. Conclusions

Perchlorate anions have been successfully encapsulated within gallosilicate sodalite. The  $\text{Na}_8[\text{GaSiO}_4]_6(\text{ClO}_4)_2$  sodalite can be synthesized directly without any precursors at 100 °C with reaction period of seven days. The perchlorate sodalite crystallizes in a space group  $P4_3n$  with a unit cell parameter  $a = 9.15788 \text{ \AA}$ . The bond distances and bond angles are considerably modified comparative to other gallosilicate sodalites. Present study shows that perchlorate ion decomposes between 620 – 700 °C in gallosilicate sodalite and the sodalite is stable there after. The perchlorate sodalite can respond to wavelength of ultra violet region and the surface area of single entity of the sodalite is  $8.385 \times 10^{-15} \text{ cm}^2/\text{g}$ . SEM study supports the cubic structure of gallosilicate perchlorate sodalite.

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Table 1. Crystallographic data and experimental conditions for the structure refinement of perchlorate gallosilicate sodalite

Compound	$\text{Na}_8[\text{GaSiO}_4]_6(\text{ClO}_4)_2$
Temperature	20°C
Space group	$\bar{P}4\ 3n$
Formula unit	Z=1
Cell parameter a (Å)	9.15788
Cell Volume V (Å <sup>3</sup> )	768.52
Data collection	
2 $\theta$ range (°)	10-80
Step size (2 $\theta$ °)	0.017
Sample time (s/data point)	1s
Number of refined parameters	38
Number of reflections	108
Agreement factors	Rp = 0.1079 Rwp = 0.0611

Table 2. Fractional coordinates and equivalent displacement parameters of perchlorate sodalite

Atom	Occupancy	x	y	z	Uiso
Ga	0.8400	0.2500	0.0	0.500	0.0354
Si	0.784	0.2500	0.5	0.0	0.0598
Na	1.196	0.2173	0.2173	0.2173	0.1283
O1	0.914	0.1548	0.1510	0.4584	0.0854
Cl	0.960	0.0	0.0	0.0	0.0485
O2	1.036	0.1200	0.0974	-0.0347	0.1155

Table 3. Selected derived bond distances and bond angles for perchlorate gallosilicate sodalite

Bond distances	(Å)	Bond angles	(°)
Ga-O1	1.72558(5)	O1-Ga-O1	106.012(2)
Ga-O1	1.72558(7)	O1-Ga-O1	116.637(3)
Si-O1	1.67847(5)	O1-Si-O1	105.631(1)
Si-O1	1.67847(6)	O1-Si-O1	117.459(0)
Na-O1	2.36004(8)	Ga-O-Si	144.036(1)
Na-O1	2.90597(9)	O2-Cl-O2	154.680(1)
Na-O2	2.70778(8)	O2-Cl-O2	119.808(0)
Na-Ga	3.27886(10)	O2-Cl-O2	115.750(0)
Na-Si	3.27886(10)	Ga-O1-Na	105.697(1)
Cl-O2	1.45135(4)	Si-O1-Na	107.360(1)

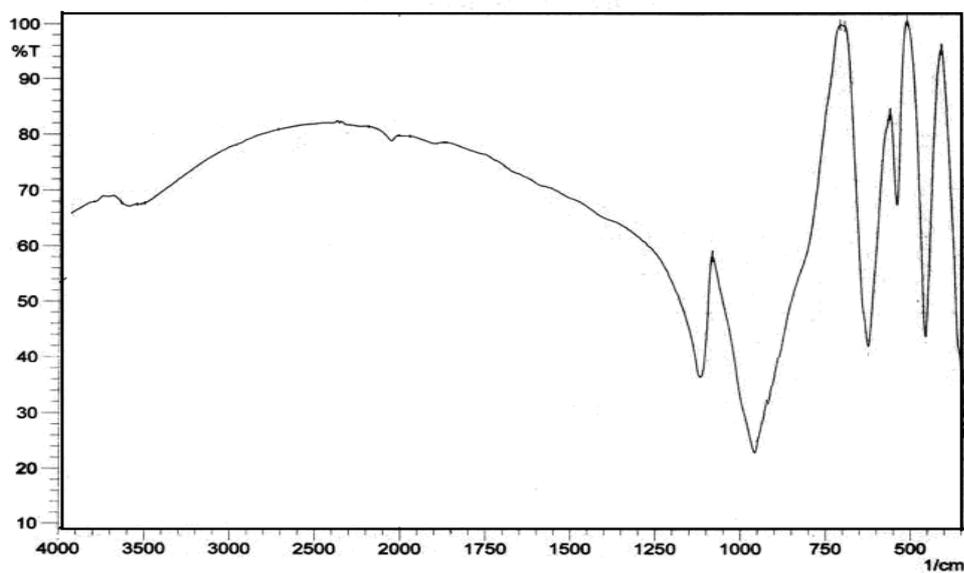


Figure 1. IR spectrum of  $\text{Na}_8[\text{GaSiO}_4]_6(\text{ClO}_4)_2$  sodalite

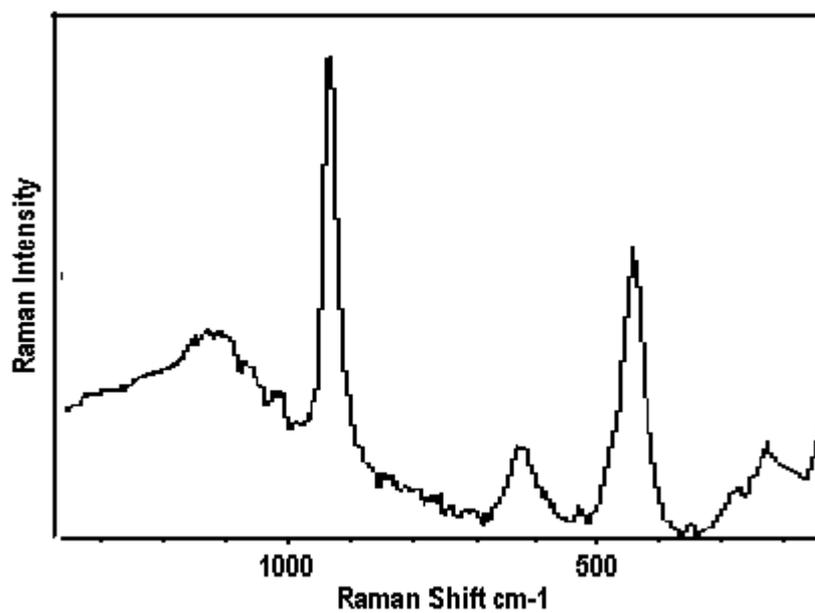


Figure 2. Raman spectrum of  $\text{Na}_8[\text{GaSiO}_4]_6(\text{ClO}_4)_2$  sodalite

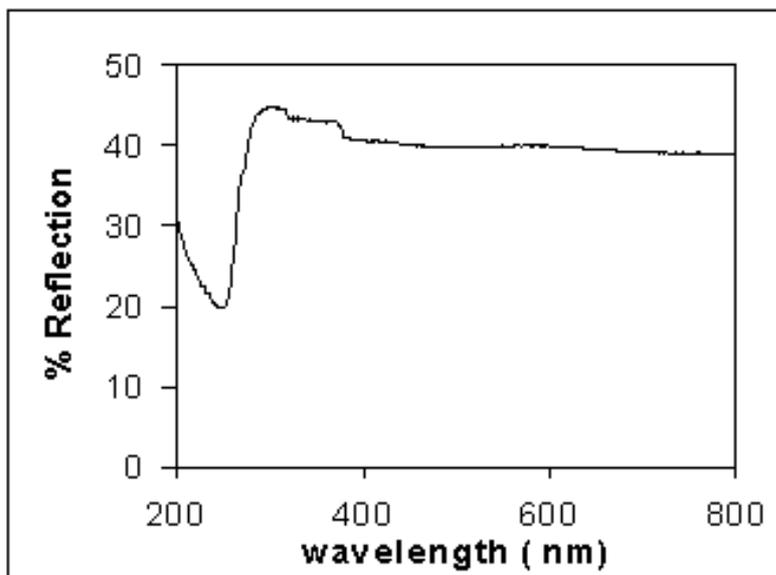


Figure 3. Diffuse reflection spectrum of  $\text{Na}_8[\text{GaSiO}_4]_6(\text{ClO}_4)_2$  sodalite

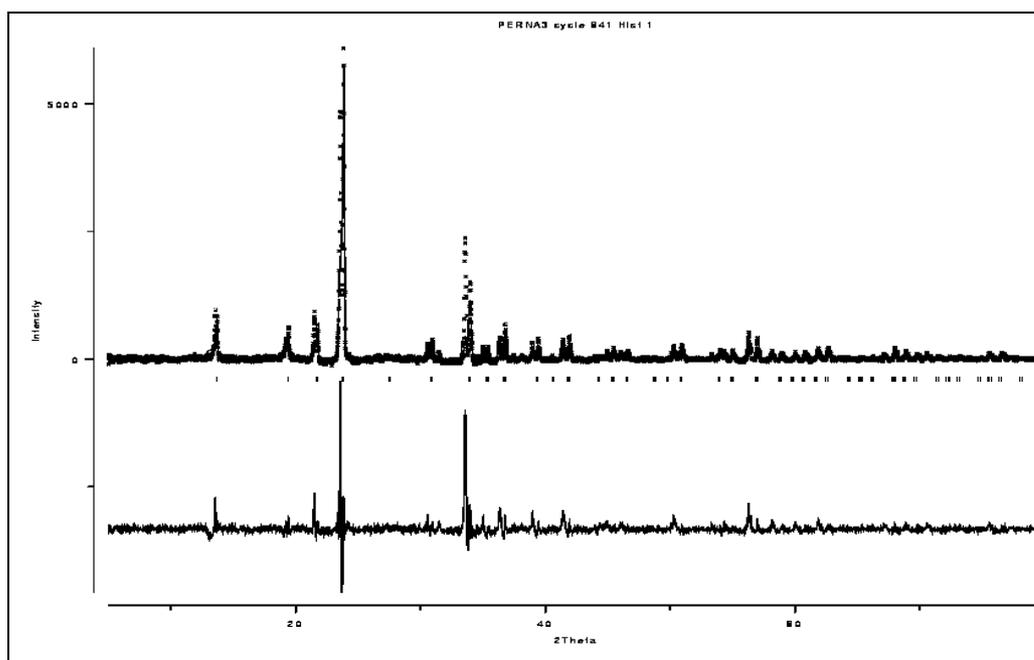


Figure 4. X-ray powder diffraction pattern for  $\text{Na}_8[\text{GaSiO}_4]_6(\text{ClO}_4)_2$  sodalite. The observed powder pattern shows reflection positions together with the difference between observed and calculated intensities (lower part)

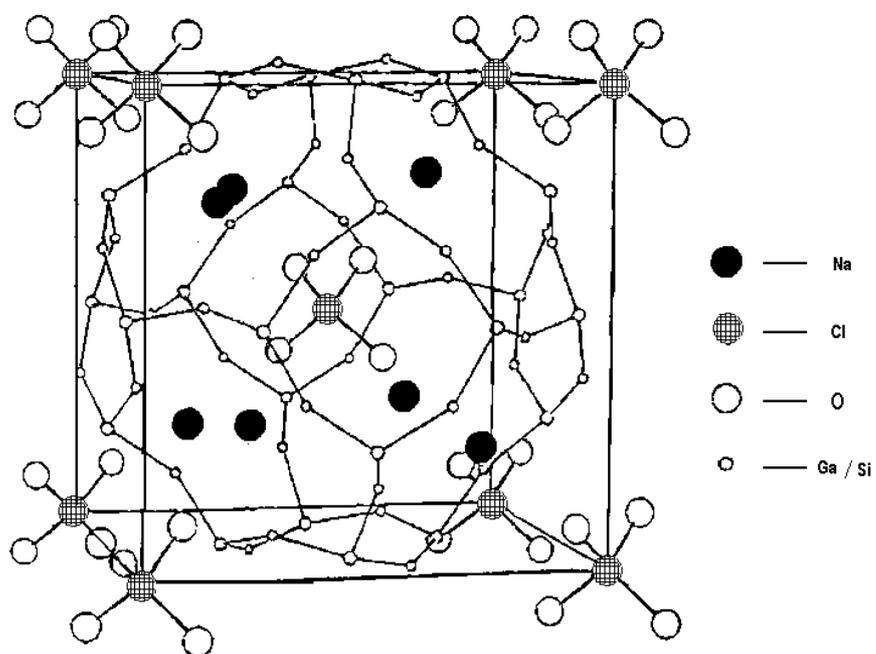


Figure 5. Unit cell of  $\text{Na}_8[\text{GaSiO}_4]_6(\text{ClO}_4)_2$  sodalite

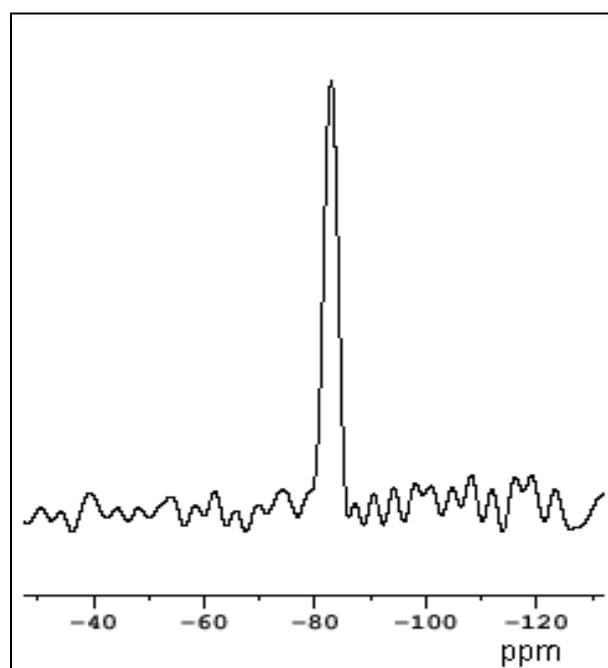


Fig. 6(a)

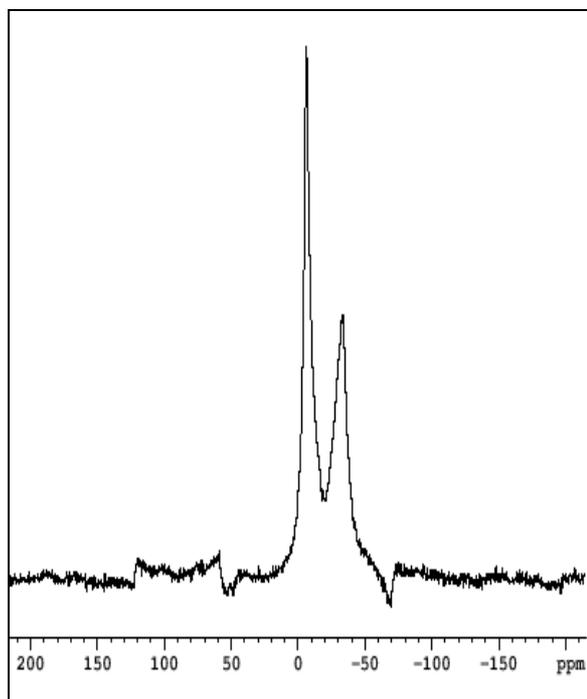


Fig. 6(b)

Figure 6. MAS NMR spectra of  $\text{Na}_8[\text{GaSiO}_4]_6(\text{ClO}_4)_2$  sodalite (a)  $^{29}\text{Si}$  MAS NMR (b)  $^{23}\text{Na}$  MAS NMR

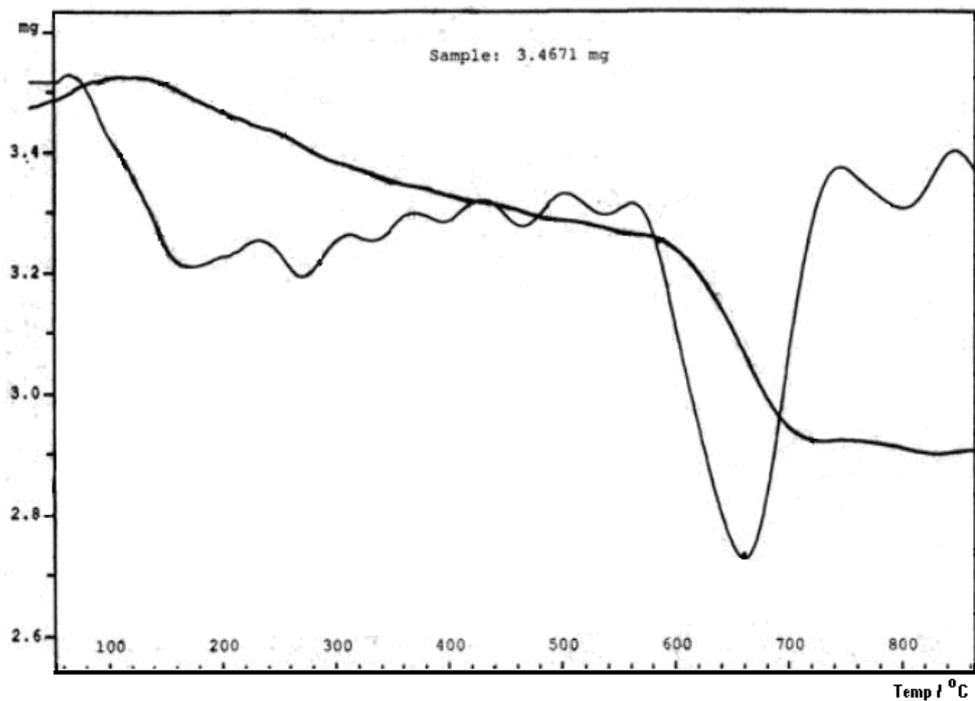


Figure 7. Weight-temperature behavior (TGA/DTA) of  $\text{Na}_8[\text{GaSiO}_4]_6(\text{ClO}_4)_2$  sodalite

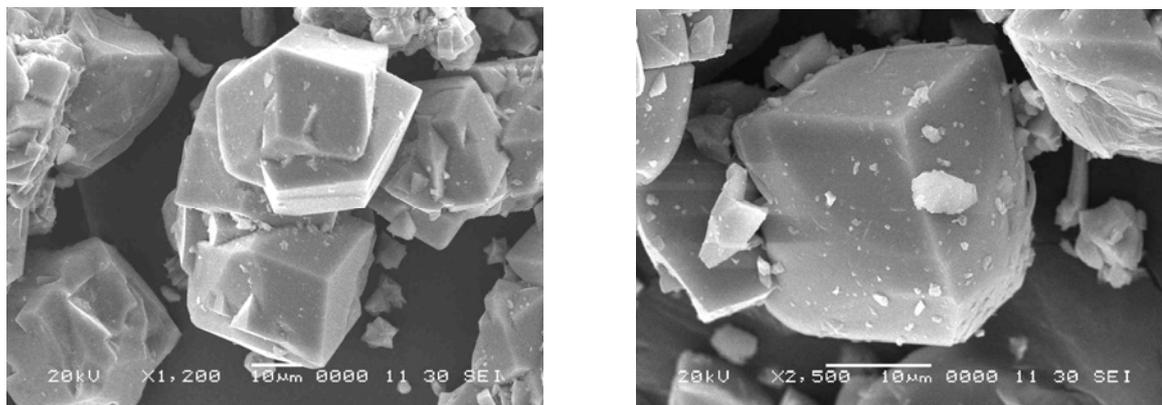


Figure 8. Scanning electron micrographs of perchlorate gallosilicate sodalites