Synthesis, Characterization and Crystal Structure of Gallosilicate Perchlorate Sodalite

Ashok V. Borhade (Corresponding Author)
Research Centre and Post Graduate Department of Chemistry
HPT Arts and RYK Science College, Nasik 422005, India
Tel: 91-942-183-1839   E-mail: ashokborhade2007@yahoo.co.in.

Arun G. Dholi
Department of Chemistry, K.G.D.M. Arts,Com and Science College
Niphad 422303, India
E-mail: dholi.arun@rediffmail.com

Sanjay G. Wakchaure
Department of Chemistry, S.V.M. Engineering College, Nasik 422101, India
Tel: 91-901-101-6193   E-mail: sanjaywakchaure9@yahoo.co.in.

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 $^{29}$Si and $^{23}$Na nuclei and by Reitveld refinement of X-ray powder diffraction data. IR and Raman spectroscopy confirms formation of framework and presence of 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 $P\bar{4}$ 3$n$ with $a = 9.15788$ Å, $V = 768.5$ Å, $Z =1$, $R_{wp} = 0.0611$, $R_p = 0.1079$ and Si-O-Ga is 144.036°. The surface area of single entity with stoichiometry Na$_8$[GaSiO$_4$]$_6$(ClO$_4$)$_2$ was found to be 8.385x10$^{-15}$ cm$^2$/g. $^{29}$Si MAS NMR study confirms complete ordering of Si and Ga in the gallosilicate framework. Thermogravimetric 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 Na$_8$[T$_1$T$_2$O$_4$]$_6$X$_2$ is formed by a space filling array of truncated octahedral cages each built up of tetrahedral 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 Na$_8$[AlSiO$_4$]$_6$X$_2$, where X is a monovalent guest anion, X= Cl, Br, ClO$_4$, is formed by 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 enclatharated guest species of different size. Depending on the composition sodalite posses photochromatic, cathodochromatic, 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
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 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 Na$_8$[GaSiO$_4$]$_6$(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 Na$_8$[GaSiO$_4$]$_6$(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 Na$_8$[GaSiO$_4$]$_6$(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 θ-2θ geometry (5-80 ° 2θ, step width 0.017 ° 2θ, sample time 1s per step), using CuKα radiation for 5<2θ<90°. The crystallographic data and experimental conditions are given in Table 1.

2.3 Spectroscopy

An infrared spectrum in the region 350-4000 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 $^{29}$Si and $^{23}$Na MAS NMR. The MAS NMR spectra were recorded on a Bruker solid state MAS NMR Spectrometer DSX 300. The $^{29}$Si MAS NMR spectrum was recorded at 59.62 MHz with 5 μsec 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 $^{23}$Na MAS NMR spectrum was recorded at 79.39 MHz with 40.5 μsec 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 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 Na$_8$[GaSiO$_4$]$_6$(ClO$_4$)$_2$ sodalite was studied by TGA/DTA using Metlor 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 Na$_8$[GaSiO$_4$]$_6$(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, ν$_{as}$ (Ga-O-Si) (asymmetric stretching vibrations) 954.8 cm$^{-1}$,

two absorption bands in the ν$_{s}$ (Ga-O-Si) (symmetric stretching vibrations) 621.1, 534.3 cm$^{-1}$,

two absorption bands due to δ (Ga-O-Si) (bending vibration) 451.3, 343.3 cm$^{-1}$.

In addition, the asymmetric stretching vibration ν$_{as}$ of ClO$_4^-$ at 1116.82 cm$^{-1}$ is clearly visible in the infrared spectrum. This strong absorption peak confirms the encapsulation of 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, \( \nu_{\text{Raman}} \) vibrations can be clearly seen. The Raman spectrum shows bands at 227.56 cm\(^{-1} \) and 442.84 cm\(^{-1} \) (T-O deformation mode), 631.80 cm\(^{-1} \) (symmetric Ga-O-Si vibration) and 931.56 cm\(^{-1} \) can also be classified as framework bands. In addition a deformation band at 1111.56 cm\(^{-1} \) can be assigned to 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 Na\(_8\)[GaSiO\(_4\)]\(_6\)(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 \( E_g = h\nu/\lambda \) which indicates that Na\(_8\)[GaSiO\(_4\)]\(_6\)(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 Na\(_8\)[GaSiO\(_4\)]\(_6\)(ClO\(_4\))\(_2\) is shown in Figure 4 together with the final Reitveld difference plot. The cubic lattice parameter, \( a = 9.15788 \text{ Å} \) 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 2\( 4i \) position of the space group P\( 4 \)\( 3n \). 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 Å (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 Å and Ga-O, 1.85 Å). The ClO\(_4\)-SOD framework consists of the usual face sharing truncated octahedral, built up from an ordered array of alternating SiO\(_4\) and GaO\(_4\) tetrahedral units.

Table 3 shows that, O-T-O tetrahedral angles in SiO\(_4\) and GaO\(_4\) are somewhat distorted from their regular tetrahedral geometry. The O-Si-O values are 105.631 and 117.459°, while for O-Ga-O bond values are 106.012 and 116.637°. The perchlorate anion occupies the centre of the sodalite cage. For a chlorine atom, which has exact tetrahedral coordination in the free ClO\(_4\) ion, in NaClO\(_4\)-SOD is comparable. A bond distance within the anions of sodalite is in good agreement with those in NaClO\(_4\) solid (Cl-O, 1.44Å). Considering different distances and angle the structure proposed for single unit cell of Na\(_8\)[GaSiO\(_4\)]\(_6\)(ClO\(_4\))\(_2\) is shown in Figure 5. Figure shows sodium cations and Ga ordering of the framework in the synthesized sodalite (Engelhardt et al., 1989, Weller et al., 1997, Johnson et al., 2000).

Further, the surface area of single entity of Na\(_8\)[GaSiO\(_4\)]\(_6\)(ClO\(_4\))\(_2\) was found to be 8.385x10\(^{-15} \text{ cm}^2/\text{g} \). 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 Na\(_8\)[GaSiO\(_4\)]\(_6\)(ClO\(_4\))\(_2\) sodalite consists of a sharp single resonance line at \( \delta_{\text{iso}} = -82.93 \text{ ppm} \) for Si(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 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 Na\(_8\)[GaSiO\(_4\)]\(_6\)(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 further Na-O(1) contacts in the same ring.

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 600-700 °C, is due to the decomposition of encapsulated salt molecules. The thermal analysis shows high thermal stability of sodalite.
framework after 700 °C. The Na$_8$[GaSiO$_4$]$_6$(ClO$_4$)$_2$ sodalite onset decomposition temperature ~600°C, where as the solid NaClO$_4$ decomposes nearly at 400 °C. This behavior is similar to aluminosilicate perchlorate sodalite (Weller et al., 1991) which shows onset decomposition temperature ~620 °C. The weight loss indicates full occupancy of anion sites in the sodalite cages by ClO$_4^-$ anions and negligible amount of water. Gallosilicate perchlorate sodalite can be converted to chloride sodalite via heating in air at 700°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 Na$_8$[GaSiO$_4$]$_6$(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 P 4 3 n with a unit cell parameter a = 9.15788 Å. The bond distances and bond angles are considerably modified comparative to other gallusilicate 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 8.385x10$^{-15}$ cm$^2$/g. SEM study supports the cubic structure of gallosilicate perchlorate sodalite.

Acknowledgements

Authors are thankful to Department of physics IIT, Mumbai for providing XRD and NMR research center IISc, Banglore for MAS NMR facilities, Dr. Sudarshan for Rietveld Refinement and BCUD University of Pune, for providing financial support to undertake this work.

References

Barrer, R.M., & Cole, J.F. (1970). Chemistry of soil minerals. Part VI. Salt entrainment by sodalite and cancrinite during their synthesis, J. Chem. Soc., A, 1516-1523.

Bolwijin, P.T., Schipper, D.J, & Van Doorn, C.Z. (1972). Cathodrochromic properties of sodalite. J.Appl. Phys., 43, 132-137.

Bu, Xianhui; Feng, Pingyun; Gier, Thurman E.; Zhao, Dongyuan; Stucky & Galen D. (1998). Hydrothermal synthesis and structural characterization of zeolite-like structures based on gallium and aluminum germinates. Journal of the American Chemical Society, 120, 13389-13397.

Buhl, J. C.; Gesing, T. M.; Hoefs, T; Ruescher C. H. (2006). Synthesis and crystal structure of gallosilicate- and aluminogermanate tetrahydroborate sodalites Na$_8$[GaSiO$_4$]$_6$(BH$_4$)$_2$ and Na$_8$[AlGeO$_4$]$_6$(BH$_4$)$_2$. Journal of Solid State Chemistry, 179, 3877-3882.

Buhl, J.Ch. (1991). Basic nitrite sodalite Na$_8$[AlSiO$_4$]$_6$(OH · H$_2$O)(NO$_2$) A suitable material for the uptake of carbon dioxide J. Solid State Chem., 94, 19-26.

Buhl, J.Ch., Engelhart, E & Felsche, L. (1989). Synthesis, X-ray diffraction, and MAS n.m.r. characteristics of tetrahydroxoborate sodalite, Na$_8$[AlSiO$_4$]$_6$[OH(BOH)$_4$]$_2$. Zeolites 9, 40-44.

Chang, I. (1974). Synthesis of photochromic and cathodochromic sodalite. J.Electrochem. Soc, 121, 815-820.

Engelhardt, G, Luger, S. Buhl, J. Ch. & Felsche, J. (1989). $^{29}$Si MAS n.m.r. of aluminosilicate sodalites: Correlations between chemical shifts and structure parameters, Zeolites, 9, 182-186.

Gesing, T.M. (2007). Structure and properties of tecto-gallosilicates II. Sodium chloride, bromide and iodide sodalites. Z.Kristallogr, 222, 289-296.

Gesing, Th. M. (2000). Structure and properties of tecto-gallosilicates. I. Hydrosodalites and their phase transitions, Zeitschrift fuer Kristallographie. 215, 510-517.

Hassan, I. Grundy, H.D. (1984). The crystal structures of sodalite-group minerals, Acta. Crystallogr. B40, 6-13.

Johnson, G. M. & Weller, M. T. (1999). A powder neutron diffraction study of lithium-substituted gallosilicate and aluminogermanate halide sodalites. Inorganic Chemistry. 38, 2442-2450.
Johnson, G. M. & Weller, M.T. (1997). Synthesis and characterization of gallium and germanium containing sodalites, *Studies in Surface Science and Catalysis* 105A (Progress in Zeolite and Microporous Materials, pt. A), 269-275.

Johnson, G. M., Mead, P. J., Dann, S. E. & Weller, M. T. (2000). Multinuclear MAS NMR studies of sodalitic framework materials. *Journal of Physical Chemistry B*, 104, 1454-1463.

Johnson, G.M. Mead P.J. & Weller, M.T. (1999). Structural trends in the sodalite family. *Phys. Chem. Chem.*, 1, 3709-3713.

Johnson, G.M., Mead, P. J. & Weller, M.T. (2000). Synthesis of a range of anion-containing gallium and germanium sodalites, *Micro. and Meso. Mate* 38, 445-460.

Kiefer, W, & Bernstein, H. (1971). Resonance Raman spectroscopic study on iodine in various organic solvents: Spectroscopic constants and halfband widths of the I2 vibration. *J. Appl. Spectro.* 25, 500-509.

Lons, L., & Schulz, H. (1967). *Strukturverfeinerung von Sodalith, Na8Si6Al6O24Cl2*. *Act. Crystallogr.* 23, 434-436.

McCusker, L. B., Meier, W. M., Suzuki, K. & Shin, S. (1986). The crystal structure of a sodium gallosilicate sodalite, *Zeolites*, 6, 388-91.

Mclaughan, S.D & Marshall, D.J. (1970). Paramagnetic resonance of F-type centres in photochromic sodalites. *Phys. Lett.* 32A, 334-344.

Murshed, M. M. & Gesing, T. M. (2008). Gallium substitution in the aluminosilicate framework: synthesis and structural studies of hydro sodalites. *Zeitschrift fuer Kristallographie*, 223, 178-185

Murshed, M. M. & Gesing, T. M. (2007). Isomorphous gallium substitution in the aluminum silicate sodalite framework: synthesis and structural studies of chloride and bromide containing phases. *Zeitschrift fuer Kristallographie*, 222, 341-349.

Murshed, M. M; Baer, A. J. & Gesing, T. M. (2008). Isomorphous framework cation substitution in the aluminosilicate sodalites: synthesis, structural and spectroscopic studies of nitrite containing phases. *Zeitschrift fuer Kristallographie*. 223, 575-583.

Newsam, J. M. & Jorgensen, J. D. (1987). Gallosilicate sodalite-further syntheses and structural details, *Zeolites* 7, 569-73.

Overman, R.T. (1965). *Basic concepts of nuclear chemistry*, London, Chapman and Hall.

Pauling, L. (1930). The structure of sodalite and helvite. *Z. Kristallogr.* 74, 213-225.

Piontkovskaya, M. A., Shameko, G. S. & Neimark, I. E. (1970). Synthesis and study of the properties of crystalline sodium galloaluminosilicates. *Neorganicheskie Materialy*. 6, 794-9.

Schipper, D.J. Van Doorn, & C.Z. Bolwijn, P.T. (1972). Preparation of cathodochromic sodalites *J.A.Ceramic. Soc*, 55, 256-559.

Suzuki, Kunio, Kiyozumi, Yoshimichi, Shin, Shigemitsu & Satoru, Ueda. (1985). Synthesis of new gallosilicate zeolite with sodalite structure. *Zeolites*, 5, 11-14.

Van Doorn, C.Z., Schipper, D.J. & Bolwijn, P.T. (1972). Optical investigation of cathodochromic sodalite. *J.Electrochem.Soc.*119, 85-92.

Veit, T, Buhl, J.Ch. & Haffmann, W. (1991). Hydrothermal synthesis, characterization and structure refinement of chlorate- and perchlorate-sodalite. *Cat.Today*, 8, 405-413.

Weitkamp, J., Fritz M.& Ernst S. (1995). Zeolites as media for hydrogen storage. *International Journal of Hydrogen Energy*, 20 (12), Pages 967-970.

Weller, M. T.; Dann, S. E.; Johnson, G. M. & Mead, P. J. (1997). MAS NMR chemical shifts and structure in frameworks. *Studies in Surface Science and Catalysis*, 105A, 455-462.

Weller, M.T. & Haworth, Karen E. (1991). Synthesis and thermal decomposition of sodalites Na8[SiAlO4]6.(XO4)2, X = Cl, Mn. *Journal of the Chemical Society, Chemical Communications*, 10, 734-5.
Table 1. Crystallographic data and experimental conditions for the structure refinement of perchlorate gallosilicate sodalite

| Compound | Na₈[GaSiO₄]₆(ClO₄)₂ |
|----------|---------------------|
| Temperature | 20°C |
| Space group | P₄ 3n |
| Formula unit | Z=1 |
| Cell parameter a (Å) | 9.15788 |
| Cell Volume V (Å³) | 768.52 |
| Data collection |  |
| 2θ range (°) | 10-80 |
| Step size (2θ°) | 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 Na₈[GaSiO₄]₆(ClO₄)₂ sodalite

Figure 2. Raman spectrum of Na₈[GaSiO₄]₆(ClO₄)₂ sodalite
Figure 3. Diffuse reflection spectrum of Na₈[GaSiO₄]₆(ClO₄)₂ sodalite

Figure 4. X-ray powder diffraction pattern for Na₈[GaSiO₄]₆(ClO₄)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 Na₈[GaSiO₄]₆(ClO₄)₂ sodalite

Fig. 6(a)
Figure 6. MAS NMR spectra of Na₈[GaSiO₄]₆(ClO₄)₂ sodalite (a) ²⁹Si MAS NMR (b) ²³Na MAS NMR

Figure 7. Weight-temperature behavior (TGA/DTA) of Na₈[GaSiO₄]₆(ClO₄)₂ sodalite
Figure 8. Scanning electron micrographs of perchlorate gallosilicate sodalites