Synthesis and Characterization of Gallosilicate Sodalite Containing NO$_2^-$ Ions

Ashok V. Borhade, Sanjay G. Wakchaure

Abstract—Pure phase gallosilicate nitrate sodalite has been synthesized in a single step by low temperature (373 K) hydrothermal technique. The product obtained was characterized using a combination of techniques including X-ray powder diffraction, IR, Raman spectroscopy, SEM, MAS NMR spectroscopy as well as thermogravimetry. Sodalite with an ideal composition was obtained after synthesis at 373 K and seven days duration using alkaline medium. The structural features of the Na$_8$[GaSiO$_4$]$_6$(NO$_2$)$_2$ sodalite were investigated by IR, MAS NMR spectroscopy of $^{29}$Si and $^{23}$Na nuclei and by Rietveld refinement of X-ray powder diffraction data. The crystal structure of this sodalite has been refined in the space group P4 3n; with a cell parameter 8.98386 Å, V= 726.9 Å$^3$. The Si-O-Ga angle is found to be 132.92$^\circ$ and Si-O-Ga angle is found to be 8.083 x10$^{-15}$ cm$^2$/g.

Keywords—Gallosilicate, hydrothermal, nitrite, Rietveld refinement.

I. INTRODUCTION

Studies on encapsulation of various anions into the polyhedral cages of sodalite are of great interest for mineral science. They are microporous tecto silicates of the general composition Na$_8$[GaSiO$_4$]$_6$X$_2$, where X is a monovalent guest anion, X = Cl-, Br-, NO$_2^-$. In the mineral sodalite. First sodalite structure was suggested by Pauling [1] and later refined by Lons et al. [2] exhibits a framework of cubic symmetry. It is formed with a strictly alternating connection of corner sharing SiO$_4$ and GaO$_4$ tetrahedra. This linkage gives rise to the space filling array of truncated octahedral cages, called β-cages in zeolite chemistry. The framework of sodalite is highly flexible and can accommodate its degree of expansion due to enclathrated guest species of different size. Sodalites have attracted considerable attention because of their use in cathode ray screens and information storage devices [3-4]. These materials have included their use as a cathodochromatic and photochromic and as high density optical data storage materials [5]. Sodalites with special guest anion can be used for various technical applications like pigments, ultramarine, graphical and digital storage system, heavy metal exchange, luminescence and catalytic activity [6-7].

Early work [8-20] shows that little attention is given to the synthesis of gallosilicate sodalite of the type Na$_8$[GaSiO$_4$]$_6$(X)$_2$. Complete substitution of Al in zeolite framework by element Ga during the crystallization process is one effective way to modulate systematically their physiochemical and catalytic properties for intended applications and has achieved considerable interest in zeolite science. Ga is the most closely similar element to Al, in particular, isomorphous substitution of Al by this element in the zeolite framework has been the subject of a number of previous studies. Up to now much gallosilicate type of zeolites with different framework topologies have been reported in the literature. To our knowledge, systematic studies on the synthesis of a gallosilicate analog are not available. Here, we report our attempts to crystallize the gallosilicate sodalite containing nitrite ions in its pure form. The characterization of the sodalite is performed by IR, Raman Spectroscopy, X-ray powder diffraction, scanning electron microscopy, thermogravimetry and $^{23}$Na and $^{29}$Si MAS NMR.

II. EXPERIMENTAL

A. Synthesis at low temperature

Sodalites may be synthesized using number of methods including low temperature hydrothermal reactions [21-22], high temperature solid state sintering [23] and structure conversion techniques [7]. Early reports show that most of the sodalites are synthesized using precursors of different type [24-26]. In the present investigation hydrothermal synthesis were carried out in a single step without precursors in Teflon autoclaves at a temperature of 373 K 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) were taken in a Teflon autoclave. After the reaction period, the products were washed and dried overnight at 373 K to remove weakly adsorbed surface water. The various synthesis conditions are summarized in Table 1. Subsequently the products obtained were characterized by IR, Raman spectroscopy, MAS NMR, TGA/DTA and SEM.
B. Crystallography

The characterization of Na$_8$[GaSiO$_4$]$_6$(NO$_2$)$_2$ sodalite was performed by X-ray powder diffraction method using Rietveld refinement GSAS programme. The X-ray powder diffraction data were collected, using diffractometer operating in 0-0 geometry (5-80° 2θ, step width 0.017° 2θ, sample time 1s per step), using CuKα radiation for 5<2θ<90°. Crystallographic data is given in table 2.

<table>
<thead>
<tr>
<th>Expt. No.</th>
<th>NaOH Conc. (mol/L)</th>
<th>NaNO$_2$ Conc. (mol/L)</th>
<th>Product Yield (gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>2</td>
<td>NO$_2$-(H$_2$O)SOD</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>4</td>
<td>NO$_2$-SOD</td>
</tr>
<tr>
<td>3</td>
<td>4</td>
<td>4</td>
<td>NO$_2$-SOD</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>6</td>
<td>NO$_2$-SOD</td>
</tr>
</tbody>
</table>

The final atomic parameters are summarized in Table 3. The refinement for 25 variables and 4410 observations resulted in final agreement factors of Rp = 0.0537 (Rp = $\sum |y_o-y_c|^2/\sum y_o^2$, Rwp = $\sum (w(y_o-cy_c)^2/\sum w y_o^2)^{1/2}$), c is a scale factor. Different synthesis at the end of the refinement revealed no significant regions of extra atomic electron density. No correction for extinction and absorption were applied. Careful inspection of X-ray pattern suggest that no existence of amorphous material and hence no phase transfer in the product obtained.

<table>
<thead>
<tr>
<th>Atom</th>
<th>site</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Uiso</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
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<td>0.1894</td>
<td>0.1894</td>
<td>0.1894</td>
<td>0.2733</td>
</tr>
<tr>
<td>Si</td>
<td>6c</td>
<td>0.250</td>
<td>0.500</td>
<td>0.00</td>
<td>0.1356</td>
</tr>
<tr>
<td>Na</td>
<td>8e</td>
<td>0.1894</td>
<td>0.1894</td>
<td>0.1894</td>
<td>0.2733</td>
</tr>
<tr>
<td>O1</td>
<td>2a</td>
<td>0.1475</td>
<td>0.1653</td>
<td>0.4375</td>
<td>0.025</td>
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<tr>
<td>N</td>
<td>2e</td>
<td>0.4940</td>
<td>0.5130</td>
<td>0.5090</td>
<td>0.0999</td>
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<tr>
<td>O2</td>
<td>2a</td>
<td>0.3999</td>
<td>0.4123</td>
<td>0.4858</td>
<td>0.6643</td>
</tr>
<tr>
<td>O2</td>
<td>2a</td>
<td>0.5720</td>
<td>0.4480</td>
<td>0.6090</td>
<td>0.6431</td>
</tr>
</tbody>
</table>

The characterization of Na$_8$[GaSiO$_4$]$_6$(NO$_2$)$_2$ sodalite was carried out using Scanning Electron microscopy on a JEOL JEM-6360A model equipped with JEOL JEC_560 auto carbon coater SEM.

D. Thermogravimetry

The thermal stability of the Na$_8$[GaSiO$_4$]$_6$(NO$_2$)$_2$ sodalite was performed by using Mettler Toledo instrument at a heating rate 10 °C/min, in the temperature range, room temperature to 1273 °K. The thermal stability of encapsulated NaNO$_2$ and framework is studied by TGA/ DTA.

III. RESULTS AND DISCUSSION

Present work reports the single step reaction scheme without precursors, for the synthesis of Na$_8$[GaSiO$_4$]$_6$(NO$_2$)$_2$ sodalite. All the experiments were carried out at 373 °K for the period of seven days. The concentration of NaOH is varied (see Table 1). A careful inspection of Table 1 shows that, NaOH has an important role during synthesis of nitrite gallosilicate sodalite. The optimum conditions required for the crystallization of Na$_8$[GaSiO$_4$]$_6$(NO$_2$)$_2$ are shown by experiment 3 in Table 1.

A. IR and Raman spectroscopy

A product of the composition Na$_8$[GaSiO$_4$]$_6$(NO$_2$)$_2$ (experiment no.3), has been selected for all the structural...
investigations. The IR spectrum of this pure product 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. A careful examination of Figure 1 shows very strong absorption band, due to asymmetric Ga-O-Si stretching, at 946.98 cm\(^{-1}\), two symmetric Ga-O-Si stretching vibrations occur at 630.08 and 551.60 cm\(^{-1}\) and bending mode of vibrations O-T-O (where T=Ga or Si) at 455.17 and 356.81 cm\(^{-1}\). The enclathrated guest (NO\(_2\)) can be detected according to presence of intensive absorption band at 1271.0 cm\(^{-1}\). Small water content is seen in the weak band of low intensity at 3458.13 cm\(^{-1}\)as well as little bending mode at 1627 cm\(^{-1}\).

The Raman spectrum of nitrite gallosilicate sodalite is shown in Fig 2.

The Raman spectrum shows bands at 264.61 cm\(^{-1}\), 337 cm\(^{-1}\) and 468.19 cm\(^{-1}\) (T-O deformation mode), 635 cm\(^{-1}\) (symmetric Ga-O-Si vibration), 867 cm\(^{-1}\) (asymmetric Ga-O-Si vibrations) and 955.40 cm\(^{-1}\) can also be classified as framework bands. In addition a deformation band at 1335 cm\(^{-1}\) for NO\(_2\) anion is clearly visible.

B. Structure refinement

The crystallographic data and conditions for the structure refinement of nitrite gallosilicate sodalite are given in Table 2. The refinement was performed on arranging nitrogen at the centre and the two oxygen at 24i position of the space group \(P\overline{4}3n\). The quantity of the final cycle of the Reitveld refinement for Na\(_8\)[GaSiO\(_4\)]\(_6\)(NO\(_2\))\(_2\) with difference between observed and calculated intensities is shown in Figure 3.

The final residuals for the pattern and structure factors are \(Rwp= 0.077\) and \(Rp=0.0537\) (see Table 2). Atomic positions and thermal parameters are listed in Table 3 and selected geometrical data are given in Table 4.

The NO\(_2\)-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. This is indicated by the bond distance results listed in Table 4; \(d(\text{Si-O}) = 1.62795(1)\) and \(d(\text{Ga-O}) = 1.83536(2)\) Å are in good agreement with the expected distance from ionic radii sum [28].

In SiO\(_4\) and GaO\(_4\), O-T-O tetrahedral angles are somewhat distorted from their regular tetrahedral geometry, O-Si-O values are 102.62 and 124.26°, while for O-Ga-O bond values are 104.58 and 119.77°. Both Si and Ga atoms have site symmetry \(4\). A notable feature of the framework geometry in the large Si-O-Ga angle 132.92° is observed. The lattice constant of the Na\(_8\)[GaSiO\(_4\)]\(_6\)(NO\(_2\))\(_2\)-SOD material is 8.9838 Å and is quite similar to the results reported by Bachman et al

<table>
<thead>
<tr>
<th>Bond distances (Å)</th>
<th>Bond angles (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ga-O1</td>
<td>1.83536(2)</td>
</tr>
<tr>
<td>Si-O1</td>
<td>1.62795(1)</td>
</tr>
<tr>
<td>Na-O1</td>
<td>2.27634(2)</td>
</tr>
<tr>
<td>Na-O2</td>
<td>2.19786(2)</td>
</tr>
<tr>
<td>Na-O22</td>
<td>2.51843(2)</td>
</tr>
<tr>
<td>Na-N</td>
<td>2.08939(2)</td>
</tr>
<tr>
<td>O21-O22</td>
<td>1.97621(2)</td>
</tr>
<tr>
<td>Na-Ga</td>
<td>3.31297(3)</td>
</tr>
</tbody>
</table>
On comparison of present sodalite with aluminosilicate sodalite, the substitution of framework Al by Ga leads to an expansion of framework. The lattice constant for NO$_2$-AlSi-SOD [29] is $a_o = 8.930\, \text{Å}$ and for present NO$_2$-GaSi-SOD $a_o = 8.9838\, \text{Å}$. This shows that the angles and distances in Na$_8$(GaSiO$_4$)$_6$(NO$_2$)$_2$SOD are modified considerably (Table-4). Considering, present crystal data the proposed crystal structure for nitrite gallosilicate sodalite is shown in Figure 4.

Further, the surface area of single entity of Na$_8$(GaSiO$_4$)$_6$(NO$_2$)$_2$ was found to be $8.083 \times 10^{-15}\, \text{cm}^2/\text{g}$. The surface area of single entity is successfully calculated by using equation $b = (M/dL)^{2/3}$, where, $b$ - surface area, $M$ - formula weight, $d$ - density and $L$ - Avogadro’s number.

C. MAS NMR Spectroscopy

Apart from X-ray diffraction results, additional structural data could be estimated using MAS NMR of $^{29}\text{Si}$ and $^{23}\text{Na}$ nucleus. Present paper shows that, the $^{29}\text{Si}$ MAS NMR spectroscopy is a suitable method to study the sodalites quantitatively. The $^{29}\text{Si}$ MAS NMR spectrum of the reaction product Na$_8$(GaSiO$_4$)$_6$(NO$_2$)$_2$ sodalite consists of a sharp single resonance line at $\delta_{iso} = -81.30\, \text{ppm}$ for Si(OGa)$_4$ units (Figure 5a). This indicates Si/Ga ratio of 1.0 and confirms the alternate Si, Ga ordering of the framework in the synthesized sodalite [30].

The $^{23}\text{Na}$ MAS NMR spectrum for the NO$_2$-GaSi-SOD is also shown in Figure 5b. The $^{23}\text{Na}$ MAS NMR spectrum shows a quadrupole pattern depending more or less upon the nitrite cage contents of the Na$_8$(GaSiO$_4$)$_6$(NO$_2$)$_2$ sodalite. 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 [31]. An inspection of Figure 5b also shows quadrupole pattern with two well resolved peaks with $\delta_{iso} = -2.392\, \text{ppm}$ and $\delta_{iso} = 0.003\, \text{ppm}$.

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 of nitrite gallosilicate sodalite within the nitrogen atom at the centre of the sodalite cage shows a spherical polyhedron arrangement of the sodium within a nitrite gallosilicate sodalite.

D. Thermal analysis

The weight temperature behavior of the nitrite gallosilicate sodalite is shown in Figure 6. An endothermic behavior in the temperature range of 973- 1173 °K, is due to the decomposition of encapsulated salt molecules. The thermal analysis shows about 7% loss in weight up to 973°K and high thermal stability of sodalite framework. The NaNO$_2$ salt decomposes at ~593 °K, where as the observed decomposition onset temperature for Na$_8$(GaSiO$_4$)$_6$(NO$_2$)$_2$ sodalite is 973 °K and this is similar to the thermal behavior found by G.M. Johnson et al [24].

The weight loss indicates full occupancy of anion sites in the sodalite cages by NO$_2$- anions and negligible amount of water. In an analogous fashion to aluminosilicate nitrite sodalite [32] gallosilicate nitrite sodalite can be converted to nitrate sodalite via heating in air at 823 °K for 4 hrs. This provides an indirect route to the nitrate sodalite as direct synthesis using NaNO$_3$ as the cavity salt yields cancrinite for all three framework composition [25,33].

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E. 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 7 shows the scanning electron microscopic pictures of the synthesized sodalite loaded with sodium nitrite.

Figure 7  Scanning electron micrographs of nitrite Gallosilicate sodalite

Careful inspection of sodium nitrite Ga-Si-SOD SEM (Figure 7) 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.

IV. Conclusion

Nitrate anions have been successfully encapsulated within gallosilicate sodalite at 373 °K with reaction period of seven days. Investigations show that, the concentration of NaOH has important role in the synthesis of the nitrite sodalite. The nitrite sodalite crystallizes in a space group $P4_3 3n$ with a unit cell parameter $a = 8.9882$ Å. The bond distances and bond angles are considerably modified comparative to other gallosilicate sodalites. The surface area of single entity of the sodalite is $8.083 \times 10^{-15}$ cm$^2$g. SEM study supports the cubic structure of gallosilicate nitrite sodalite.

Acknowledgment

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References


