Synthesis and Characterization of Gallosilicate Sodalite Containing NO_2^- Ions

Ashok V. Borhade, Sanjay G. Wakchaure

Abstract**—**Pure phase gallosilicate nitrite sodalite has been synthesized in a single step by low temperature (373 ^oK) 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 373^0K 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 Reitveld refinement of X-ray powder diffraction data. The crystal structure of this sodalite has been refined in the space group $P\bar{4}3n$; with a cell parameter 8.98386Å, V= 726.9 Å, (Rwp= 0.077 and Rp=0.0537) and Si-O-Ga angle is found to be 132.92^0. MAS NMR study confirms complete ordering of Si and Ga in the gallosilicate framework. The surface area of single entity with stoichiometry $Na_8[GaSiO_4]_6(NO_2)_2$ was found to be 8.083 $x10^{-15}$ cm^2/g.

Keywords**—**Gallosilicate, hydrothermal, nitrite, Reitveld 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 $Na_8[GaSiO_4]_6X_2$, 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 enclatharated 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 cathodochromic 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 ^oK and autogenous pressure for reaction time of seven days. The stiochiometric 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^oK 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.

Ashok V. Borhade is a Reader with Research Centre and Department of Chemistry, HPT Arts and RYK Science College, Nasik 422005, India, *Corresponding author Tel. 91-9421831839
(e-mail: ashokborhade2007@yahoo.co.in)

Sanjay G. Wakchaure is a Senior Lecturer in Department of Chemistry, S.V.M. Engineering College, Chincholi, Nasik 422101, India.
(e-mail: sanjaywakchaure9@yahoo.co.in)

Author thanks to BCUD, University of Pune, for providing financial support to undertake this work.

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 θ-θ geometry (5-80 ^{o} 2θ, step width 0.017 ^{o}2θ, sample time 1s per step), using CuKα radiation for $5<2\theta<90^o$. Crystallographic data is given in table 2.

TABLE I
EXPERIMENTAL CONDITIONS AND RESULTS

Expt. No.	**NaOH**	**$NaNO_2$ Conc. (mol/L)**	**Product Conc. (mol/L)**	**Yield (gm)**
1	2	2	NO_2-(H_2O)SOD	-
2	2	4	NO_2-SOD	0.2
3	4	4	NO_2-SOD	1.9
4	4	6	NO_2-SOD	0.6

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 ($Rp= \sum | y_o-cy_o | \sum y_o$) and Rwp= 0.077 ($Rwp= [\sum w(y_o-cy_c)^2 / \sum wy_o^2]^{1/2}$), 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 II
CRYSTALLOGRAPHIC DATA FOR THE STRUCTURE REFINEMENT OF NITRITE GALLOSILICATE SODALITE

$Na_8[GaSiO_4]_6(NO_2)_2$ sodalite	
Temperature	20^{o}C
Space group	P$\bar{4}$3n
Formula unit	Z=1
Cell parameter (Å)	8.98386
Molecular weight ($gmol^{-1}$)	1242.74
Cell Volume V (Å)	726.19
Density d (g/cm^{-3})	2.839
Data collection	
2 θ range (^{o})	10-80
Step size (2θ^o)	0.017
Sample time (s/data point)	1s
Number of refined parameters	25
Number of reflections	4410
Agreement factors	Rp = 0.0537 Rwp = 0.077

C. *Spectroscopy*

Infrared spectra in the region 350-4000 cm^{-1} were measured as KBr pellets on a computer interfaced Bruker FTIR spectrophotometer. The Raman spectra were 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 [27].

TABLE III
FRACTIONAL COORDINATES AND EQUIVALENT DISPLACEMENT PARAMETERS OF GALLOSILICATE NITRITE SODALITE.

Atom	**site**	**x**	**y**	**z**	**Uiso**
Ga	6d	0.250	0.00	0.50	0.6159
Si	6c	0.250	0.50	0.00	0.1356
Na	8e	0.1894	0.1894	0.1894	0.2733
O1	24i	0.1475	0.1653	0.4375	0.025
N	24i	0.4940	0.5130	0.5090	0.0999
O21	24i	0.3999	0.4123	0.4858	0.6643
O22	24i	0.5720	0.4480	0.6090	0.6431

Further, structural characterization was also performed by solid state 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 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 3072 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 7 KHz. Upto 65 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 NO_2-SOD 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 Metlor Toledo instrument at a heating rate 10 ^{0}C/min, in the temperature range, room temperature to 1273 ^{0}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 ^{o}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 Figure1. 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 Figure1 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}.

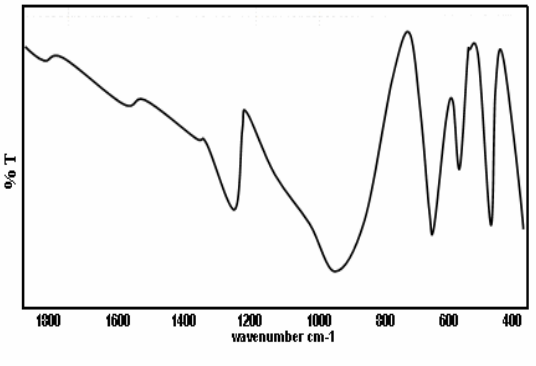


Fig. 1IR spectrum of nitrite gallosilicate sodalite

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

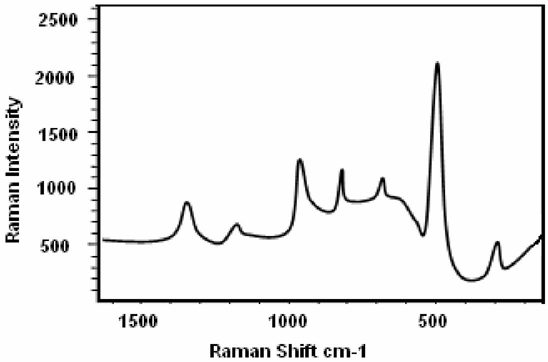


Fig. 2 Raman spectrum of nitrite gallosilicate sodalite

The Raman spectrum shows bands at 264.61cm^{-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 $P\bar{4}3n$. 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.

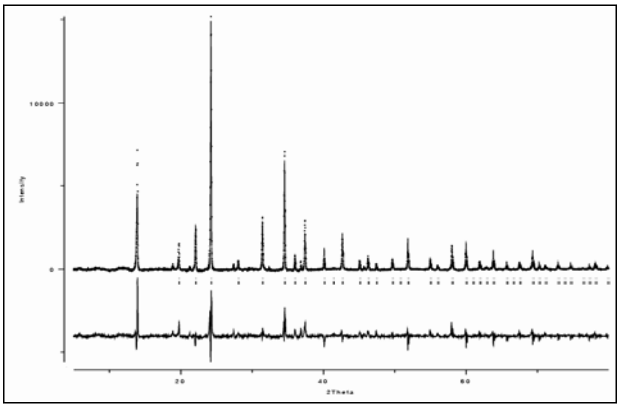


Fig. 3 X-ray powder diffraction pattern for nitrite gallosilicate sodalite. The observed powder pattern shows reflection positions together with the difference between observed and calculated intensities (lower part).

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(Si-O) = 1.62795(1) and d(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 104.58and 119.77 °. Both Si and Ga atoms have site symmetry $\bar{4}$. 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 8.98386 Å and is quite similar to the results reported by Bachman et al

TABLE IV
SELECTED DERIVED BOND DISTANCES AND BOND ANGLES FOR $Na_8[GaSiO_4]_6(NO_2)_2$ SODALITE.

Bond distances	**(Å)**	**Bond angles**	**(°)**
Ga-O1	1.83536(2)	O1-Ga-O1(4x)	104.580(1)
Si-O1	1.62795(1)	O1-Ga-O1(2x)	119.772(1)
Na-O1	2.27034(2)	O1-Si-O1(2x)	102.620(1)
Na-O21	2.19786(2)	O1-Si-O1(4x)	124.267(1)
Na-O22	2.51843(2)	Ga-O-Si	132.928(0)
N-O21	1.25453(1)	O1-Na-O1	103.945(0)
N-O22	1.28029(1)	O21-N-O22	117.370(0)
Na-N	2.89993(2)	O21-N-O22	113.065(0)
O21-O22	1.97621(2)		
Na-Ga	3.31297(3)		
Na-Si	3.31297(3)		

[25].

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= 8.930Å and for present NO_2-GaSi-SOD a_o= 8.9838 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.

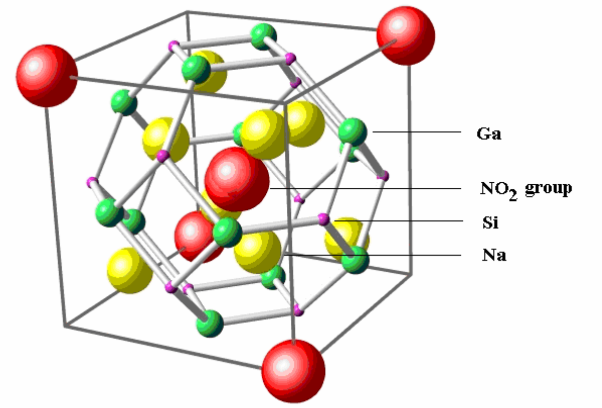


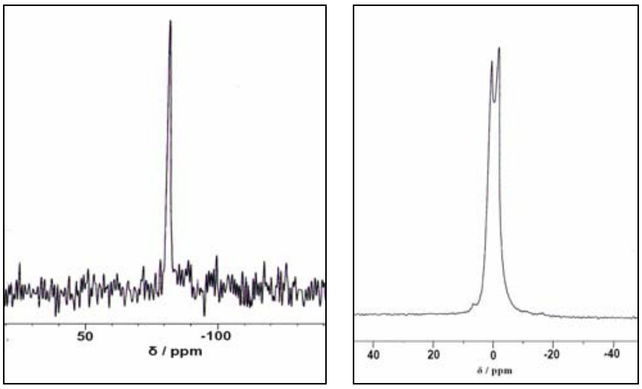
Fig. 4 Proposed crystal structure for nitrite gallosilicate sodalite.

Further, the surface area of single entity of $Na_8[GaSiO_4]_6(NO_2)_2$ was found to be 8.083x10^{-15} cm^2/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}Si and ^{23}Na nucleus. Present paper shows that, the ^{29}Si MAS NMR spectroscopy is a suitable method to study the sodalites quantitatively. The ^{29}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 δiso = -81.30 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}Na MAS NMR spectrum for the NO_2-GaSi-SOD is also shown in Figure 5b. The ^{23}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}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 δiso= -2.392 ppm and δiso = 0.003 ppm.



(a) **(b)**

Fig. 5 MAS NMR spectra of nitrite gallosilicate sodalite (a) ^{29}Si MAS NMR (b) ^{23}Na MAS NMR

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].

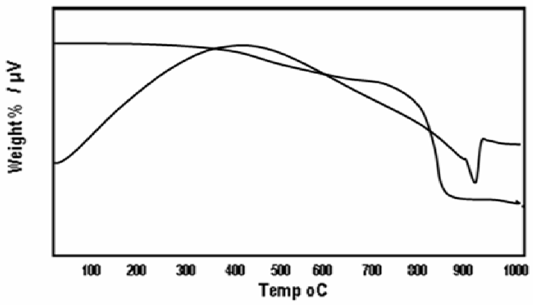


Fig. 6 Weight-temperature behavior of nitrite gallosilicate sodalite.

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.

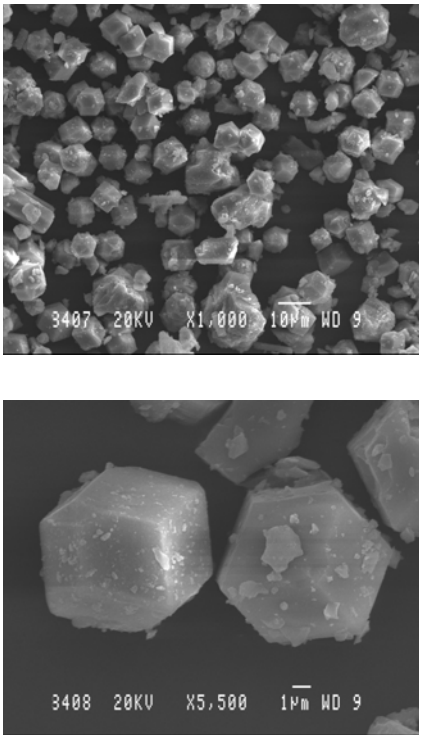


Fig. 7 Scanning electron micrographs of nitrite Gallosilicate sodalite

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 ^{o}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 P$\bar{4}$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 8.083x10^{-15} cm^{2}/g. SEM study supports the cubic structure of gallosilicate nitrite sodalite.

ACKNOWLEDGMENT

Authors are thankful to Department of physics IIT, Bombay for providing X-ray powder diffraction and NMR research center IISc, Banglore for MAS NMR facilities, Dr. Sudarshan for Rietveld Refinement.

REFERENCES

[1] L. Pauling, The structure of sodalite and helvite, *Z. Kristallogr.,* vol. 74, pp. 213-225, 1930.

[2] L. Lons, and H. Schulz, Strukturverfeinerung von Sodalith, Na$_8$Si$_6$Al$_6$O$_{24}$Cl$_2$, *Act. Crystallogr*., vol. 23, pp.434-436, 1967.

[3] C. Z. Van Doorn, D. J. Schipper and P. T. Bolwijn, Optical Investigation of Cathodochromic Sodalite, *J. Electrochem. Soc*., vol. 119, pp. 85-92, 1972.

[4] S. D. Mclaughan and D. J. Marshall, Paramagnetic resonance of F-type centres in photochromic sodalites, *Phys. Lett*., vol. 32A, pp. 343-344, 1970.

[5] P. T. Bolwijn, D. J. Schipper and C. Z. Van Doorn, Cathodrochromic Properties of Sodalite, *J. Appl. Phys*., vol. 43, pp. 132-137, 1972.

[6] S. Kowalak, M. Pawlowska, M. Monika, et al., Synthesis of ultramarine from synthetic molecular sieves, *Colloids surfaces A, Physico Chem. Eng. Aspects*, vol. 101, pp.179-185, 1951..

[7] I. Chang, Synthesis of Photochromic and Cathodochromic Sodalite *J.Electrochem. Soc.*, vol. 121, pp. 815-820, 1974.

[8] K. Suzuki, Y. Kiyozumi, S. Shin, et al., Synthesis of new gallosilicate zeolite with sodalite structure, *Zeolites*, vol. 5, pp. 11-14, 1985.

[9] L. B. McCusker, W. M. Meier, K. Suzuki, et al., The crystal structure of a sodium gallosilicate sodalite, *Zeolites,* vol. 6, pp. 388-91, 1986.

[10] J. M. Newsam, and J. D. Jorgensen, Gallosilicate sodalite further syntheses and structural details, *Zeolites*, vol. 7, pp. 569-73, 1987.

[11] G. M. Johnson, and M. T. Weller, Synthesis and characterisation of gallium and germanium containing sodalites, *Studies in Surface Science and Catalysis,* vol. 105A, pp. 269-275, 1987.

[12] B. Xianhui, F. Pingyun, G. Thurman., et al., Hydrothermal Synthesis and Structural Characterization of Zeolite-like Structures Based on Gallium and Aluminum Germanates, *Journal of the American Chemical Society,* vol.120, pp. 13389-13397, 1998.

[13] G. M. Johnson, & M. T. Weller, A Powder Neutron Diffraction Study of Lithium Substituted Gallosilicate and Aluminogermanate Halide Sodalites, *Inorganic Chemistry,* vol.38, pp. 2442-2450, 1999.

[14] G. M. Johnson, P. J. Mead and M. T. Weller, Structural trends in the sodalite family, *Phys. Chem. Chem*., vol. 1, pp. 3709-371, 1999.

[15] T. M. Gesing, Structure and properties of tecto-gallosilicates. I. Hydrosodalites and their phase transitions, *Z. Kristallogr*., vol. 215, pp. 510-517, 2000.

[16] T. M. Gesing, Structure and properties of tecto-gallosilicates II. Sodium chloride, bromide and iodide sodalites, *Z. Kristallogr.,* vol. 222, pp. 289-296, 2007.

[17] J. C. Buhl, T. M. Gesing, T. Hoefs, et. al., 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*, vol.179, pp. 3877-3882, 2006.

[18] M. M. Murshed, and T. M. Gesing, Isomorphous gallium substitution in the alumosilicate sodalite framework: synthesis and structural studies of chloride and bromide containing phases, Z. *Kristallogr.*, 2007, vol. 222, pp. 341-349, 2007.

[19] M. M. Murshed, and T. M. Gesing, Gallium substitution in the alumosilicate framework: synthesis and structural studies of hydro sodalites, *Z. Kristallogr.*, vol. 223, pp. 178-185, 2008.

[20] M.M. Murshed, A. J. Baer, and T. M. Gesing, Isomorphous framework cation substitution in the alumosilicatesodalites: synthesis, structural and spectroscopic studies of nitritecontaining phases, *Z. Kristallogr.,* vol. 223, pp. 575-583, 2008.

[21] R. M. Barrer, J. F. Cole, and H. Sticher, Chemistry of soil minerals. Part V. Low temperature hydrothermal transformations of kaolinite *J. Chem. Soc,* pp. 2475-2485, 1968.

[22] F. Hund, Nitrite, Cyanide und Rhodanid-Sodalite, *Z. Anorg. Allg. Chem*, vol. 511, pp. 225-230, 1984.

[23] D. J. Schipper, C.Z. Van Doorn, and P. T. Bolwijn, Preparation of Cathodochromic Sodalites, J. *A. Ceramic. Soc.*, vol. 55, pp. 256-559, 1972.

[24] G. M. Johnson, P. J. Mead, and M. T. Weller, Synthesis of a range of anion-containing gallium and germanium sodalites, *Micro. and Meso. Mate*, vol. 38, pp. 445-460, 2000.

[25] S. Bachmann and J. C. Buhl, Crystallization, characterization and structure of nitrite aluminogermanate sodalite $Na_8[AlGeO_4]_6(NO_2)_2$, *Micro. and Meso. Mate.*, vol. 28, pp. 35-47, 1999.

[26] M. E. Fleet, Structures of sodium alumino-germanate sodalites $[Na_8(Al_6Ge_6O_{24})A_2$, A = Cl, Br, I], *Acta. Cryst*, vol. C45, pp. 843-847, 1989.

[27] W. Kiefer, and H. Bernstein, Resonance Raman spectroscopic study on iodine in various organic solvents: Spectroscopic constants and half band widths of the I_2 vibration *J. Appl. Spectro.,* vol.25, pp. 500-509, 1971.

[28] R. D. Shannon, Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides, *Acta. Crystallgr.*, vol.A32, pp. 751-767, 1976.

[29] P. B. Kempa, G. Engelhardt, J. C. Buhl, et al., X-ray powder diffraction crystal structure analysis and ^{29}Si, ^{23}Na *MAS* n.m.r. studies of nitrite sodalite, $Na_8[AlSiO_4]_6\ (NO_2)_2$, at 295 K, *Zeolites*, vol. 11, pp. 558-562, 1991.

[30] G. Engelhardt, S. Luger, J. C. Buhl, et al., ^{29}Si *MAS* n.m.r. of aluminosilicate sodalites: Correlations between chemical shifts and structure parameters, *Zeolites,* vol. 9, pp. 182-186, 1989.

[31] E. Kundla, A. Samson and E. Lippma, High-resolution NMR of quadrupolar nuclei in rotating solids, *Chem. Phy. Letters*, vol.83, pp. 229-232, 1981.

[32] J. C. Buhl, Hydrothermal synthesis and characterization of nitrite sodalite single crystals, *J. Crystal Growth*, vol. 108, pp. 143-149, 1991.

[33] J. C. Buhl, F. Stief, M. Fechtelkord, et al., Synthesis, X-ray diffraction and MAS NMR characteristics of nitrate cancrinite $Na_{7.6}[AlSiO_4]_6(NO_3)_{1.6}(H_2O)_2$, *J. Alloys and Comp.*, vol.305, pp. 93-102, 2000.