

Synthesis and characterization of aluminosilicate and gallosilicate sodalites containing acetate ions

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One pot synthetic aluminosilicate and gallosilicate sodalites containing acetate guest anion have been synthesized successfully under hydrothermal conditions at 100 °C. This paper deals with the comparison of X-ray powder data with single crystal data for $\text{Na}_8[\text{AlSiO}_4]_6(\text{CH}_3\text{COO})_2$ and the characterization of a new $\text{Na}_8[\text{GaSiO}_4]_6(\text{CH}_3\text{COO})_2$ sodalite. The products obtained were characterized by IR, X-ray powder diffraction, MAS NMR, SEM and thermogravimetry technique. Crystal structures were refined in the space group $P\bar{4}3n$ from X-ray powder data using the Rietveld refinement method with the unit cell parameter $a = 9.0679 \text{ \AA}$, for aluminosilicate and $a = 9.2119 \text{ \AA}$, for gallosilicate sodalite. The aluminosilicate and gallosilicate framework shows regular bonding with bond angles of $\text{Al}-\text{O}-\text{Si} = 146.241^\circ$, $\text{Ga}-\text{O}-\text{Si} = 141.294^\circ$. ²⁹Si MAS NMR chemical shift values verify Al/Si and Ga/Si ordering of the framework constituents.

Keywords: *hydrothermal synthesis, gallosilicate, aluminosilicate, acetate, Rietveld refinement*

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1. Introduction

Sodalites have been studied mainly as model compounds for large zeolite systems as they form a convenient matrix for a variety of encapsulated guests. The composition of most of the sodalites is expressed as $\text{M}_8[\text{T}^1\text{T}^2\text{O}_4]_6\text{X}_2$, where M is typically an alkali metal or alkaline earth metal – most frequently Na^+ , T^1 is typically a trivalent cation (eg. Al^{3+} , Ga^{3+}), T^2 is a tetravalent cation (eg. Si^{4+} , Ge^{4+}) and X represents an entrapped guest species (such as Cl^- , OH^- , ClO_3^- , SO_4^{2-} etc.). The sodalite framework can be described as being built up from T^1O_4 and T^2O_4 tetrahedral building blocks alternately linked together to form a truncated octahedron which is known as β -cage. The β -cage contains six–eight atom rings and eight–twelve atom rings, containing four and six T-atoms

respectively. The regular, all space filling framework of sodalites provides a temperature stable homogenous microporous matrix of sodalite cavities. This is suitable for stabilizing small isolated or interacting molecules, atoms and clusters in the form of neutral species, ions, or radicals. The structure of sodalite is known from early work of Pauling [1]. Sodalites have cubic symmetry and crystallize in the space group $P\bar{4}3n$. The sodalite structure is a space-filling arrangement of identical cages which have the form of truncated octahedra with an inner diameter of $\sim 6.5 \text{ \AA}$. The framework T-atoms are usually Si and Al, but others like Ga or Ge can also be introduced. The gallosilicate framework is made of regularly alternating tetrahedrally co-ordinated Ga and Si atoms, which are connected through oxygen atoms. Each sodalite cage is filled by an ion $[\text{Na}_4\text{X}]^{3+}$, where X^- is a monovalent ion. The framework is highly flexible and can accommodate

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its degree of expansion due to enclathrated guest species of different size [2–5].

A variety of sodalites can be used for the purification of gaseous as well as liquid mixtures and solutions by sorption, for storing molecules, for sieving and filtering, for ion exchange purposes and also for catalysis under nonoxidizing or oxidizing environments. These materials have shown their usefulness as cathodochromic, photochromic and high density optical data storage materials [6–8]. Sodalites with a special guest anion can be used for various technical applications like pigments, ultramarine, graphical and digital storage systems, luminescence and catalytic activity [9–11].

Previous reports revealed that most of the works on sodalites have been devoted to sodalites containing inorganic templates but very few reports are available on organic templates [12–14]. Here, an attempt is made to ‘construct’ new materials with a special guest anion and to observe organic–inorganic matter interaction within the sodalite cage. In the present work we have synthesized aluminosilicate sodalite containing acetate anion, $\text{Na}_8[\text{AlSiO}_4]_6(\text{CH}_3\text{COO})_2$ by one pot hydrothermal synthesis method. The polycrystalline product obtained is characterized by different techniques and is compared with the single crystal data reported elsewhere [12]. This paper also reports the details of the preparation and characterization of novel gallosilicate acetate sodalite, $\text{Na}_8[\text{GaSiO}_4]_6(\text{CH}_3\text{COO})_2$.

2. Experimental

Earlier reports show that most of the sodalites have been synthesized by hydrothermal method [15], high temperature method [16] and solid state synthesis [17]. In the present study we have developed one pot hydrothermal synthesis method for sodalite synthesis. Aluminosilicate sodalite with a composition of $\text{Na}_8[\text{AlSiO}_4]_6(\text{CH}_3\text{COO})_2$ was prepared from 2 g of Zeolite-A, 1.6 g NaOH and an excess of sodium acetate. The ingredients were mixed in a Teflon coated steel autoclave of 50 mL interior volume at an elevated temperature (373 K) and at autogenous pressure. Gallosilicate acetate sodalite, $\text{Na}_8[\text{GaSiO}_4]_6(\text{CH}_3\text{COO})_2$,

was prepared with 0.468 g Ga_2O_3 (Fluka), 0.3 g SiO_2 (Fluka), NaOH (Merck), an excess of sodium acetate (Merck) and 5 mL of decarbonated water which were mixed in a 25 mL Teflon coated steel autoclave and kept in an oven at 373 K for one week at autogenous pressure. The products obtained were washed with 300 mL distilled water and dried for 24 hours at 373 K.

Fourier transform infrared (FTIR) spectra were measured on a Shimadzu 8400 FTIR spectrophotometer in the range of 350 cm^{-1} to 4000 cm^{-1} using the KBr method. For structure refinement, high resolution X-ray powder diffraction data were collected on a Phillips PW-1710 diffractometer. The measurements were carried out with an angular integral of 0.017° and a sample time of 1 s per step, in the 2θ range of $5\text{--}80^\circ$ using $\text{CuK}\alpha$ radiation. XRD powder data Rietveld refinements were carried out using GSAS powder diffraction suite by Larson and Von Dreele 1990. During the refinement, parameters such as scale factor, background parameters, profile parameters, cell parameters, atomic positional parameters and displacement parameters were refined. Magic angle spinning nuclear magnetic resonance (MAS NMR) spectra were recorded on a Bruker solid state MAS NMR Spectrometer DSX 300. ^{29}Si MAS NMR measurements were recorded using standard 5 mm MAS probes. Similarly, the magic angle spinning nuclear magnetic resonance for ^{23}Na and ^{13}C measurements were recorded.

The thermal stability of the dopant and framework was determined by thermogravimetry (TGA) with Mettler Toledo instrument at a heating rate of 10 K/min, in the temperature range of 300 K to 1473 K. Scanning electron micrographs were obtained on a JEOL JEM-6360A model equipped with JEOL JEC_560 auto carbon coater SEM.

3. Results and Discussion

3.1. IR spectroscopy

The IR spectra of both the newly synthesized sodalites are shown in Fig. 1 (a and b). In the mid IR region the symmetric and asymmetric T–O–T (where T = Ga/Al/Si) vibrations of

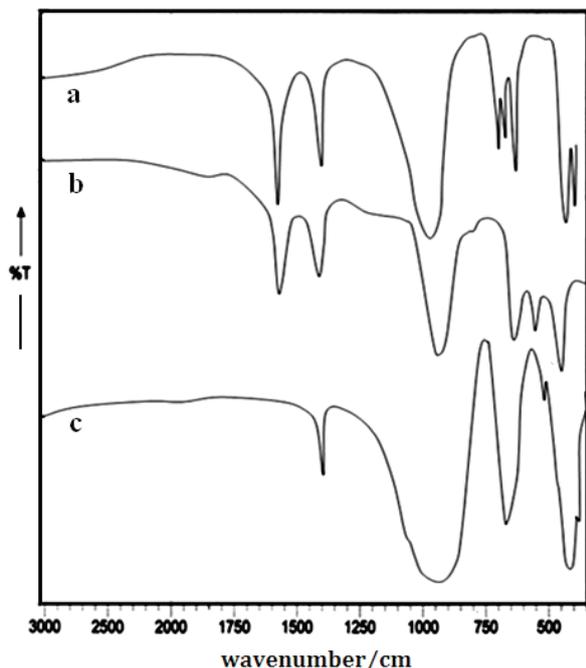


Fig. 1. IR spectra of
 a) $\text{Na}_8[\text{AlSiO}_4]_6(\text{CH}_3\text{COO})_2$,
 b) $\text{Na}_8[\text{GaSiO}_4]_6(\text{CH}_3\text{COO})_2$ sodalite and
 c) $\text{Na}_8[\text{AlSiO}_4]_6\text{CO}_3$ sodalite.

the sodalite framework appear. In both spectra, the enclathrated acetate anions can be clearly detected due to characteristic $\nu(\text{C}-\text{O})$ vibrations at 1419.51 cm^{-1} , 1593.09 cm^{-1} for aluminosilicate sodalite and 1419.50 cm^{-1} , 1579.60 cm^{-1} for gallosilicate sodalite. The absorption bands for the vibration modes of gallosilicate sodalite differ from the aluminosilicate sodalite as the expansion of the sodalite framework affects the position of the band in the IR spectra. The substitution of framework aluminum by gallium leads to an expansion of the framework ($\text{GaSi-acetate-SOD } a = 9.2682\text{ \AA}$ and $\text{AlSi-acetate-SOD } a = 9.0376\text{ \AA}$), and different bonding conditions. This expansion in the framework causes a shift of the vibration modes to lower wave numbers.

3.2. Structure refinement

The structure of single crystal aluminosilicate sodalite has already been solved by Sieger et al. [12]. In the present study an attempt is made to compare the X-ray powder pattern of

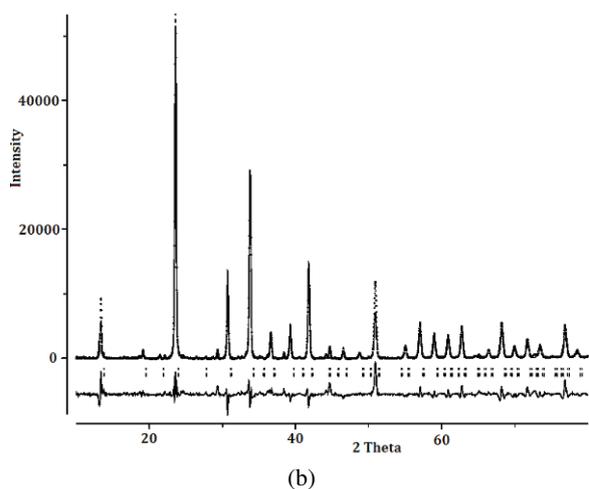
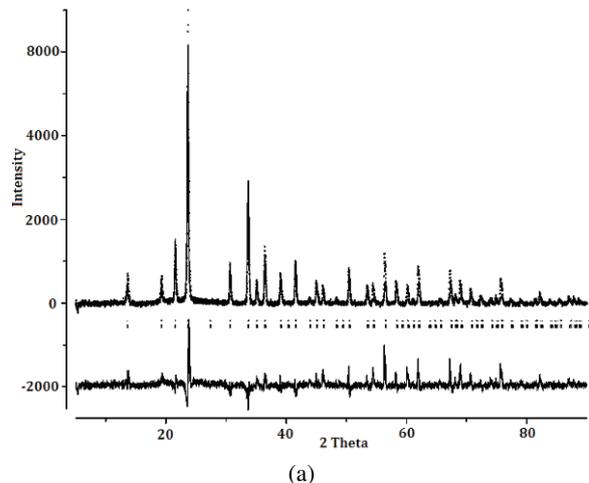


Fig. 2. X-ray powder profiles of
 (a) $\text{Na}_8[\text{AlSiO}_4]_6(\text{CH}_3\text{COO})_2$,
 (b) $\text{Na}_8[\text{GaSiO}_4]_6(\text{CH}_3\text{COO})_2$ sodalites.
 The observed (cross) and calculated (continuous line) pattern and difference curve (bottom line) of refinement in the space group $\text{P}\bar{4}3\text{n}$.

$\text{Na}_8[\text{AlSiO}_4]_6(\text{CH}_3\text{COO})_2$ with a single crystal study. Furthermore, we have successfully carried out the X-ray Reitveld refinement of a new $\text{Na}_8[\text{GaSiO}_4]_6(\text{CH}_3\text{COO})_2$ sodalite. The X-ray crystallographic data and experimental conditions for both sodalites are listed in Table 1. The fractional co-ordinates are given in Table 2. The X-ray powder profiles together with the difference plot, for aluminosilicate and gallosilicate acetate sodalites are shown in Fig. 2 (a and b). Both the sodalites were refined in the space group $\text{P}\bar{4}3\text{n}$, using GSAS X-ray powder diffraction suite. For the

Table 1. Crystallographic data and experimental conditions for the structure refinement of acetate sodalites.

| Compound | Na ₈ [AlSiO ₄] ₆ (CH ₃ COO) ₂ | Na ₈ [GaSiO ₄] ₆ (CH ₃ COO) ₂ |
|--|---|---|
| Temperature | 20 °C | 20 °C |
| Space group | P $\bar{4}$ 3n | P $\bar{4}$ 3n |
| Wavelength (Å) | 1.5405 | 1.5405 |
| Molecular weight (gmol ⁻¹) | 1016 | 1276 |
| Formula unit | Z = 1 | Z = 1 |
| Cell parameter a (Å) | 9.0679 | 9.2119 |
| Cell Volume V (Å ³) | 745.62 | 781.71 |
| Density (g/cm ⁻³) | 2.208 | 2.423 |
| Data collection | | |
| 2θ range (°) | 10–80 | 10–80 |
| Step size (2θ°) | 0.017 | 0.017 |
| Sample time (s/data point) | 1s | 1s |
| Number of reflections | 334 | 352 |
| Number of variables | 19 | 28 |
| Agreement factors | | |
| Rwp | 0.1236 | 0.0725 |
| Rp | 0.0860 | 0.0470 |

refinement of aluminosilicate sodalite, aluminum and silicon, and for gallosilicate sodalite, gallium and silicon were placed on the 6c (1/4, 0, 1/2) and (1/4, 1/2, 0) sites respectively. Cage oxygen was placed on the 24i (x,y,z) site with $x \sim 0.14$, $y \sim 0.16$, $z \sim 0.55$. Sodium atoms are refined at two different positions Na₁ and Na₂, with an occupancy factor of 0.5 and a carbon atom of the acetate group at the centre of the cage. The remaining atoms of the carboxylate group were treated as single atoms (X) in the general position. The final residuals are Rwp = 0.1359, Rp = 0.0969 for AlSi–acetate–SOD and Rwp = 0.0725, Rp = 0.0470 for GaSi–acetate–SOD.

Table 3 shows the observed, selected bond lengths and bond angles for aluminosilicate and gallosilicate sodalites. On comparison of aluminosilicate sodalite with gallosilicate sodalites the substitution of Ga in the framework in place of Al, shows an expansion in the framework structure from 9.0679 Å to 9.2119 Å. Though sodalites with an organic anion are difficult to refine satisfactorily, our refinement factors are quite reasonable. For aluminosilicate sodalite the results obtained are comparable with the values obtained for a single crystal aluminosilicate sodalite [12] with acetate

Table 2. Fractional atomic coordinates for acetate sodalites.

| Atom | x | y | z | Occupancy factors |
|---|--------|---------|--------|-------------------|
| Na₈[AlSiO₄]₆(CH₃COO)₂ | | | | |
| Al | 0.2500 | 0.0000 | 0.5000 | 1 |
| Si | 0.2500 | 0.5000 | 0.0000 | 1 |
| O | 0.1442 | 0.1503 | 0.4566 | 1 |
| Na1 | 0.1968 | 0.1968 | 0.1968 | 0.5 |
| Na2 | 0.2300 | 0.2300 | 0.2300 | 0.5 |
| C | 0.0000 | 0.0000 | 0.0000 | 1 |
| X | 0.0326 | -0.1066 | 0.1012 | 0.25 |
| Na₈[GaSiO₄]₆(CH₃COO)₂ | | | | |
| Ga | 0.2500 | 0.0000 | 0.5000 | 1 |
| Si | 0.2500 | 0.5000 | 0.0000 | 1 |
| O | 0.1466 | 0.1599 | 0.4527 | 1 |
| Na1 | 0.2073 | 0.2073 | 0.2073 | 0.5 |
| Na2 | 0.2265 | 0.2265 | 0.2265 | 0.5 |
| C | 0.0000 | 0.0000 | 0.0000 | 1 |
| X | 0.0340 | -0.1040 | 0.1030 | 0.25 |

ion. The Na atoms are refined at two different positions with an occupancy factor of 0.5, because sodium cations experience two different (attractive/repulsive) interactions due to the disordered nature of acetate ions. The Na atoms which experience repulsive interactions with methyl groups

Table 3. Selected inter atomic distances and bond angles for acetate sodalites.

| Bond distances | (Å) | Bond angles | (°) |
|---|------------|-------------|------------|
| Na₈[AlSiO₄]₆(CH₃COO)₂ | | | |
| Al–O | 1.71233(3) | Al–O–Si | 146.241(1) |
| Si–O | 1.63792(2) | Al–O–Na1 | 104.464(0) |
| Na1–O | 2.44052(4) | Al–O–Na2 | 105.334(0) |
| Na1–O | 2.95619(4) | Si–O–Na1 | 106.996(0) |
| Na2–O | 2.31292(3) | Si–O–Na2 | 108.020(0) |
| Na2–O | 2.93608(4) | O–Al–O | 108.265(0) |
| C–X | 1.36249(2) | O–Al–O | 111.911(0) |
| | | O–Si–O | 107.721(1) |
| | | O–Si–O | 113.032(1) |
| Na₈[GaSiO₄]₆(CH₃COO)₂ | | | |
| Ga–O | 1.80767(4) | Ga–O–Si | 141.294(1) |
| Si–O | 1.64380(3) | Ga–O–Na1 | 104.816(0) |
| O–Na1 | 2.36917(5) | Ga–O–Na2 | 105.535(0) |
| O–Na1 | 2.96758(5) | Si–O–Na1 | 110.721(0) |
| O–Na2 | 2.29327(4) | Si–O–Na2 | 111.688(0) |
| O–Na2 | 2.97015(5) | O–Si–O | 104.755(1) |
| C–X | 1.38427(2) | O–Si–O | 119.381(1) |
| | | O–Ga–O | 106.115(0) |
| | | O–Ga–O | 116.414(0) |

are named as Na₂ while the Na atoms which experience attractive interactions with the negatively charged acetate ion are named as Na₁ (Table 3). In aluminosilicate sodalite the Al–O bond distance is found to be 1.7123 Å, Si–O bond distance is 1.6379 Å and the average of Al/Si–O bond distance is 1.6751 Å, which is comparable with the average Al/Si–O bond distance, 1.6760 Å for a single crystal acetate sodalite. The T–O–T bond angle is found to be 146.241°.

In gallosilicate sodalite, refinement shows a Ga–O bond distance of 1.8076 Å, and a Si–O bond distance of 1.6438 Å while the average Ga/Si–O bond distance is 1.7257 Å. The Ga–O bonds are longer (about 1.8076 Å) in comparison to Al–O bonds (about 1.7123 Å), but the Ga–O–Si angles are smaller (141.294°) when compared to Al–O–Si angles (146.241°) which leads to smaller cage volumes and pore openings in gallosilicate host framework in comparison to aluminosilicate framework, but at the same time O–T–O bond angles are higher in comparison to aluminosilicate sodalite. The observed fact may

be satisfactorily explained by considering the different behavior of gallosilicate and aluminosilicate hydrosodalites. Gallosilicate has a higher solubility when compared to aluminosilicate in alkaline medium. During hydrothermal synthesis crystalline gallosilicate acetate can only be obtained with a reaction mixture of lower alkalinity.

3.3. MAS NMR spectroscopy

To study the framework ordering and framework composition magic angle spinning nuclear magnetic resonance is used. MAS NMR spectroscopy has proved to be very useful for framework species and it also gives information about non-framework species such as coordination, geometry and mobility of cations and guest molecules or anions [18]. MAS NMR spectra distinguish the structures on the basis of chemical shift, which is directly related to a number of local structural features. Chemical shifts reflect the local magnetic environments of a nucleus and provide information about neighboring tetrahedral cation and T–O–T bond angles. The MAS NMR spectra of ²³Na, ²⁹Si and ¹³C for both the sodalites are shown in Fig. 3 (a–c, aluminosilicate acetate sodalite and d–f, gallosilicate acetate sodalite).

²⁹Si is an ideal nucleus for the study of aluminosilicate and gallosilicate sodalites since chemical shifts are sensitive to changes in the local framework geometry [19–22]. ²⁹Si spectrum of a sodalite should give a single band due to the perfect ordering of Si, Al and Ga in the framework. ²⁹Si chemical shift (δ) is influenced by the T–O–T bond angle and the nature of cations and anions in the framework. ²⁹Si MAS NMR spectra of both the sodalites exhibit a single sharp resonance line in the spectrum at –89.529 ppm and –81.238 ppm for Na₈[AlSiO₄]₆(CH₃COO)₂ and Na₈[GaSiO₄]₆(CH₃COO)₂ sodalites respectively. The single resonance line in the spectrum confirms strictly the alternating ordering of Si, Al and Si, Ga in the framework. On comparison, ²⁹Si MAS NMR of aluminosilicate and gallosilicate sodalites, the neighboring oxygen environment affects the chemical shift. It is interesting to note that substituting Al with Ga in the framework, results in shifting δ

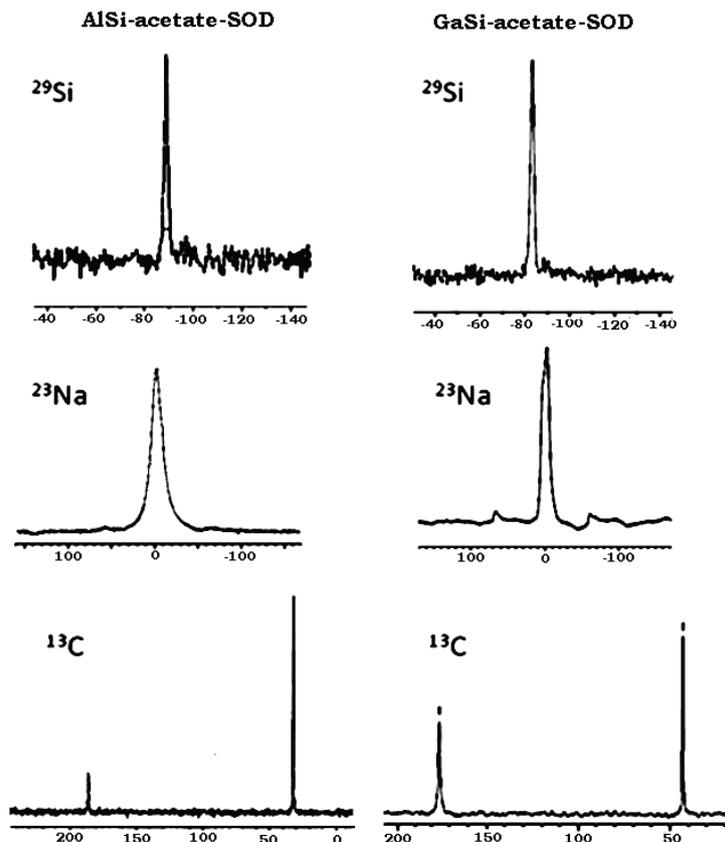


Fig. 3. MAS NMR spectra of $\text{Na}_8[\text{AlSiO}_4]_6(\text{CH}_3\text{COO})_2$ and $\text{Na}_8[\text{GaSiO}_4]_6(\text{CH}_3\text{COO})_2$ sodalites.

value upfield by ~ 8 ppm. This NMR shift is most likely due to the increase in electron withdrawal from the bridging oxygen on replacing Al by Ga in the framework.

Na atoms are expected to locate above the centre of the six-ring windows of the cages and coordinate with three oxygen atoms and anions in the sodalite cage, but the highly disordered nature of the acetate ion is responsible for its low symmetry. ^{23}Na MAS NMR spectra of both the sodalites give a slightly broadened single line in the spectrum at -4.852 ppm and 0.0550 ppm for aluminosilicate and gallosilicate sodalites, respectively. These observed MAS NMR signals support the structure refinement, as the Na atoms are refined at two different positions due to the disordered nature of the attractive and repulsive interactions of the acetate ion.

^{13}C MAS NMR spectroscopy has been used to determine the connectivity of carbons and the

number of protons attached to each carbon atom in the acetate ion and the details of C–H couplings. ^{13}C MAS NMR spectra of both the sodalites show two well resolved peaks in the spectrum, which indicates the presence of the acetate ion. Two well resolved peaks can be assigned to the presence of methyl carbon and carbonyl carbon of the acetate group. The aluminosilicate sodalite shows resonance lines at 32.416 ppm and 186.190 ppm, while the gallosilicate sodalite shows lines at 43.154 and 176.033 ppm. The substitution of aluminum by more electronegative gallium in the framework shields the carbonyl carbon.

3.4. Thermogravimetry

The stability of the acetate anion for both the sodalites was studied by thermal analysis. The weight temperature behaviors of the aluminosilicate and gallosilicate acetate sodalites are shown in Fig. 4.

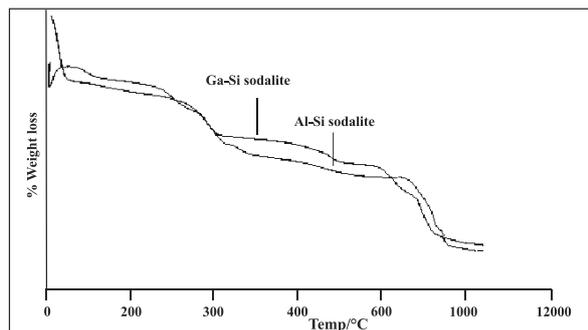
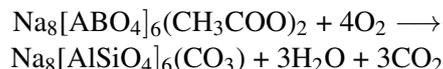


Fig. 4. Thermogravimetric analysis of $\text{Na}_8[\text{AlSiO}_4]_6(\text{CH}_3\text{COO})_2$ and $\text{Na}_8[\text{GaSiO}_4]_6(\text{CH}_3\text{COO})_2$ sodalites.

Fig. 4 shows the gradual weight loss up to 400 °C due to the occluded and entrapped water in the sodalite framework. The acetate anions are oxidized to carbonate anions approximately at 820 °C in gallosilicate sodalite and at about 860 °C in case of aluminosilicate sodalite. The intra-cage reaction takes place without destruction of sodalite framework according to the following reaction:

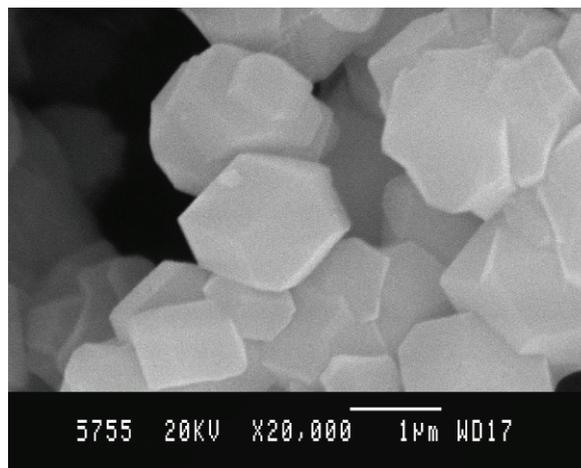


where A = Al or Ga and B = Si.

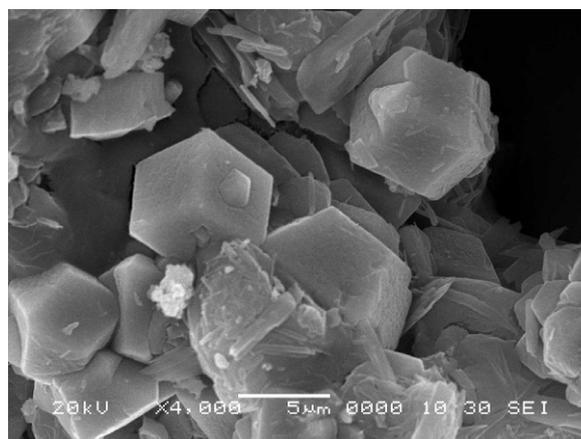
On decomposition, both the sodalites produce water and carbon dioxide and are converted into carbonate sodalites. This was also confirmed by heating aluminosilicate sodalite at 875 °C for 2 hours which resulted in the formation of carbonate sodalite Fig. 1(c).

3.5. Crystal morphology

For the determination of the morphology of the solids, SEM was used (Figs. 5 a and b). This provides information about the macroscopic crystal growth mechanism and distribution of different cages. No amorphous material is visible in the SEM pictures. The sodalite particles are crystallites grown with regular habits and most of the crystals are quite well shaped cubes with sizes of 10–20 μm. Energy dispersive X-ray Spectroscopy (EDX) reveals that Ga, Si, C and Na are present in the crystal with their respective compositions.



(a)



(b)

Fig. 5. SEM micrographs of crystals of (a) $\text{Na}_8[\text{AlSiO}_4]_6(\text{CH}_3\text{COO})_2$ and (b) $\text{Na}_8[\text{GaSiO}_4]_6(\text{CH}_3\text{COO})_2$ sodalites.

Acknowledgements

Authors are thankful to UGC New Delhi (Major research project), for financial support, Department of physics IIT, Bombay for providing X-ray powder diffraction and NMR research center IISc, Bangalore for MAS NMR facilities.

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Received 24.04.2010

Accepted 09.05.2011