ABSTRACT

The thesis entitled “Synthesis and characterization of enclathrated Alumino-silicate and Alumino-germanate sodalite” deals with encapsulation of anions in the sodalite cages. Throughout the work more emphasis is given on evaluation of crystal structure using Rietveld refinement for various sodalites. The work is undertaken to develop short route synthesis method for sodalite. First time we have applied sodalite for adsorption of heavy metals and further verified Langmuir and Freundlich adsorption isotherm. This thesis also covers cost-effective and eco-friendly synthesis of intense blue ultramarine.

The thesis is divided into four chapters. First chapter gives the brief introduction to sodalites along with literature survey. Second chapter presents the results obtained and discussion on mixed halide sodalites of the type $\text{Na}_8[\text{AlSiO}_4]_6\text{Br}_{2-x}\text{I}_x$ and $\text{Na}_{8-x}\text{Ag}_x[\text{AlSiO}_4]_6\text{Cl}_{2-x}\text{Br}_x$. Synthesis of silver derivatives of $\text{ClO}_4^-$ and $\text{MnO}_4^-$ sodalite and their characterization is given in second chapter. Third chapter covers discussion on results obtained for alumino-germanate sodalite of the type $\text{Na}_8[\text{AlGeO}_4]_6\text{X}_2$, (where $\text{X}= \text{ClO}_4^-, \text{ClO}_3^-, \text{and SCN}$). This chapter also includes discussion on alumino-germanate halide sodalites obtained using organic solvent. Fourth chapter gives discussion on synthesis of sodalite from coal fly ash and its use for adsorption of heavy metals. The solid state synthesis of ultramarine blue using raw fly ash is also discussed in the same chapter.

The first chapter covers the introduction with respect to origin of microporous material with emphasis on zeolite and sodalite. Zeolite microporous material along with zeolite cage and molecular sieves are also discussed. This
chapter also gives the discovery and history of different type zeolites. Secondary building units of zeolite are discussed briefly. Information regarding natural sodalites are also given briefly. Sodalite cage or β-cage as a tertiary building unit of many zeolites is explained in detailed.

This chapter also gives low temperature hydrothermal synthesis for sodalite, which is used for the preparation of alumino-silicate, alumino-germanate sodalite and intense blue ultramarine. Mechanism of sodalite synthesis is also covered in this chapter. Different physical techniques like IR, Raman, XRD, MAS NMR, TGA and SEM are explained with their principle. At the end of this chapter work done and results obtained for alumino-silicate and alumino-germanate sodalites by earlier workers is briefly reviewed, which is followed by the scope of the present work.

The second chapter is dealing with synthesis, infrared and powder X-ray diffraction study of mixed sodalites of the type Na₈[AlSiO₄]₆Cl₂₋ₓBrₓ, Na₈[AlSiO₄]₆Br₂₋ₓIₓ. Further, IR study of silver derivatives of perchlorate and permanganate containing alumino-silicate sodalites of the type Na₈₋ₓAgₓ[AlSiO₄]₆(ClO₄)₂, and Na₈₋ₓAgₓ[AlSiO₄]₆(MnO₄)₂ are discussed in detail. The observed Infrared frequencies in different regions for the mixed sodalites with reaction mixture stoichiometry and analyzed stoichiometry are studied. This study enabled us to find different co-relations among cell constant, T-O-T angle and νₐ (asymmetric mode of vibration).

The third chapter reports the synthesis and characterization of alumino-germanate sodalites of the type Na₈[AlGeO₄]₆(X)₂, where X= Cl⁻, Br⁻, I⁻, OH⁻,
ClO$_4^-$, ClO$_3^-$, SCN$^-$ etc.). This chapter is further divided into three sections. Section- A includes synthesis and characterization of ClO$_4^-$ sodalite and its potassium and silver derivatives. IR spectra for all the synthesized sodalite, shows symmetric and asymmetric (T-O-T) vibrations of the sodalite framework in the mid IR region. For the Na$_8$[AlGeO$_4$]$_6$(ClO$_4$)$_2$ sodalite, the asymmetric stretching vibration $\nu_3$ of ClO$_4^-$ at 1112 cm$^{-1}$ confirms encapsulation of ClO$_4^-$. The absorption band at 620 cm$^{-1}$ is also characteristic for the enclathration of perchlorate in the sodalite cages and in potassium and silver exchanged sodalite, the asymmetric vibration $\nu_a$ for ClO$_4^-$, found at 1114 cm$^{-1}$ and 1108 cm$^{-1}$, respectively confirms the enclathration of perchlorate ion in the alumino-germanate sodalite cage. The spectra shows that, for silver derivative the absorption bands shifted towards lower frequency, while for potassium derivative, the absorption bands shifts towards higher frequencies. This shift in absorption band is may be due to contraction and expansion of sodalite framework. The crystal structure of Na$_8$[AlGeO$_4$]$_6$(ClO$_4$)$_2$, Na$_{3.2}$K$_{4.8}$[AlGeO$_4$]$_6$(ClO$_4$)$_2$ and Na$_{3.9}$Ag$_{4.1}$[AlGeO$_4$]$_6$(ClO$_4$)$_2$ sodalites were refined from X-ray powder data in the space group P$\bar{4}3n$: $a = 9.249$ Å, and Al-O-Ge angle is 140.930° and $a = 9.257$ Å, and Al-O-Ge angle is 141.080°, $a = 9.195$ Å, and Al-O-Ge angle is 139.034°, respectively.

Section-B gives study on synthesis and characterization of chlorate and thiocyanate sodalite. In Na$_8$[AlGeO$_4$]$_6$(ClO$_3$)$_2$ sodalite, the chlorate anion shows absorption bands at 992 cm$^{-1}$, and 486 cm$^{-1}$. Spectrum also shows strong absorption band due to asymmetric Al-O-Ge stretching at ~850 cm$^{-1}$, two symmetric Al-O-Ge stretching vibrations in the region 580 cm$^{-1}$ to 640 cm$^{-1}$ and
bending modes of vibration (O-T-O) in the region 360 cm$^{-1}$ to 400 cm$^{-1}$. In thiocynate sodalite IR absorption at 871.82 (asymmetric), 590.22, 621.08 (symmetric), 378.05 (bending) cm$^{-1}$ confirmed the formation of alumino-germanate sodalite framework. Thiocynate anion absorbs at 2071 cm$^{-1}$. The crystal structures were refined in the space group P$\bar{4}$3n with unit cell 9.169 Å for chlorate, and 9.238 Å for thiocynate sodalite.

Single resonance line in $^{27}$Al MAS NMR spectra of perchlorate, chlorate and thiocynate sodalite confirms the complete ordering of Al and Ge in the alumino-germanate sodalite framework. Due to 3/2 spin the $^{23}$Na nucleus exerts a quadrupole moment interacting with local field gradient and shows quadrupole pattern with two well resolved $^{23}$Na MAS NMR peaks in the sodalite studied. Derivatives of perchlorate sodalites, clearly show the effect of silver, and potassium on $^{23}$Na MAS NMR. Unlike perchlorate sodalite $^{23}$Na MAS NMR spectrum of chlorate sodalite give single line at 3.364 ppm, due to dynamic nature of chlorate anion. Thermogravimetric analysis showed onset decomposition temperature for chlorate enclathrated sodalite at 973K and 1023K for thiocynate sodalite. While for sodium, potassium and silver perchlorate sodalite derivatives the decomposition temperature is 873K, 848K and 873K, respectively.

Section-C deals with short route synthesis of alumino-germanate halide sodalite using organic solvent (50% ethanol). The IR spectra clearly distinguish between chloro, bromo and iodo sodalites. In halide sodalites the anion (Cl$^-$, Br$^-$ and I$^-$) affects the lattice parameter as expected. Unit cell parameters are found to be 8.9502 Å for Cl-SOD, 8.9986 Å for Br-SOD and 9.0779 Å for I-SOD. On
comparison of alumino-silicate sodalite with alumino-germanate sodalites the substitution of Ge instead of Si in the framework, leads to an increase of T-O bond length. In alumino-silicate sodalite the average Al-O distance is ~1.73Å, while in alumino-germanate sodalite it is found to be ~ 1.74 Å. The Ge-O bond length ~1.74 Å exactly matches with the standard Ge-O bond length 1.74 Å. Present study shows slight increase in T-O bond length from chloro to iodo sodalite. The $^{27}$Al MAS NMR study confirms alternating Al and Ge ordering of the sodalite framework. Thermal analysis shows stability of halide anion in the alumino-germanate sodalite framework and the decomposition temperatures are in the range of 800 °C - 900 °C for chloro, bromo and iodo sodalites.

The fourth chapter is divided into three sections. Section-A covers synthesis and characterization of halide sodalite from coal fly ash. Synthesis of value added product from waste material plays an important role in protection from environmentally hazards. Coal fly ash is potential alumino-silicate source and can be used for synthesis of halide sodalite. The IR spectra distinguish between chloro, bromo and iodo sodalites. In halide sodalites, change of anion in the sodalite cage affects the lattice parameter as expected. In halide sodalites, size of anion goes on increasing from chloro to bromo and iodo. The unit cell parameter shows linear expansion in size due to expansion in framework structure. Unit cell parameters are found to be 8.859 for Cl-SOD, for Br-SOD is 8.930 and 8.963 Å for I-SOD. On comparison of halide alumino-silicate sodalites with synthesized sodalites from coal fly ash, leads to an increase of T-O bond length. In alumino-silicate sodalite the average Al-O distance is ~ 1.73Å, which is well match with
our synthesized sodalite and is found to be ~ 1.727 Å. The Si-O bond length ~ 1.62 Å, is close to the standard Si-O bond length 1.63 Å. Present study shows increase in T-O bond length from chloro to iodo sodalites.

Section-B covers synthesis and characterization of iodate enclathrated alumino-silicate sodalite obtained from coal fly ash. In IO₃⁻ sodalite, IR spectrum shows νas vibration for the iodate at 800 cm⁻¹. Weak band near 1620 cm⁻¹ and a broad band in the region 3000-3600 cm⁻¹ can be assigned to the bending mode of water molecule that is absorbed in sodalite channels. X-ray diffraction pattern matches well with JCPDS data. ²⁹Si chemical shift, δ, exhibit single sharp resonance line in the spectrum at -89.430, which confirms strictly alternating ordering of Si and Al atoms in the TO₄-sodalite framework, i.e. Si(4Al) units. ²³Na MAS NMR spectrum of iodate sodalite gives sharp single line in the spectrum at -4.363 ppm due to highly symmetrical environment.

In the current work, we have also studied the adsorption capacities of the synthesized sodalite for the removal of lead, cadmium and zinc ions from wastewater. We also wanted to confirm whether sodalite, a dense form of zeolite is cost-effective and is an alternative sorbent that could replace the expensive resins now used for wastewater treatment.

In present study, Langmuir and Freundlich isotherms are evaluated for adsorption of lead, cadmium and zinc metals by iodate sodalite. The effect of temperature on metal retention, for the adsorption of Cd²⁺, Pb²⁺, and Zn²⁺ was carried out at three different temperatures (25, 50, and 75°C). The equilibrium uptake (mg/g) of sodalite increased with temperature elevation for all metals.
studied. The results obtained for iodate sodalite shows that uptake for Pb$^{2+}$, Cd$^{2+}$ and Zn$^{2+}$ increased with temperature, suggests the process to be endothermic.

The Langmuir constants $Q_0$ and $b$ values for the adsorption of Pb$^{2+}$, Cd$^{2+}$ and Zn$^{2+}$ on the iodate sodalite samples are calculated. The values of $R^2$ are in range of 0.912-0.993 indicates that the adsorption data fit the Langmuir isotherm very well. The maximum adsorption capacities ($Q_o$) for all the metal increase and followed the order $75^\circ > 50^\circ > 25^\circ$ C.

Section-C covers solid state synthesis and characterization of ultramarine blue, one of the forms of alumino-silicate sodalite synthesized from coal fly ash. Ultramarine exhibit the sodalite (SOD) structure and the chromophore sulfides (mostly NaS$_3$ and NaS$_2$) encapsulated in the $\beta$-cages is responsible for blue colour. The IR spectrum of the blue ultramarine shows the bands of alumino-silicate sodalite (mostly the asymmetric stretch at $\sim$1000 cm$^{-1}$). The spectrum illustrate the structural changes of the coal fly ash and the structural sensitive bands in the range 800-400 cm$^{-1}$ allow confirming blue ultramarine product formation.

In comparison with coal fly ash, blue ultramarine product shows shift in Al-O-Si vibration from 1097 to 1009 cm$^{-1}$. Bands typical for sodalite structure are clearly visible at 698.23 and 671.24 cm$^{-1}$. Absorbance band corresponds to the $\nu_3$ frequencies from the S$_3^-$ ion chromophore appeared at 582.5 cm$^{-1}$, which confirmed the identity of the product. In the Raman spectrum, the band at 545 cm$^{-1}$ associated with the $\nu_3$ anti-symmetric stretching mode of S$_3^-$ is observed in ultramarine. UV visible and ESR studies also confirmed the evidences of encapsulated S$_3^-$ ion chromophore in ultramarine blue sodalite.