CHAPTER-1
INTRODUCTION

1.1 Microporous Material:

The class of molecular sieves has been greatly extended during the fifteen years by the discovery of zeolite like silica-based microporous materials; their common feature is three-dimensional, low-density, and open-framework structure consisting of AlO$_4$, PO$_4$, SiO$_4$ or other metal oxygen tetrahedral, linked to each other through bridging oxygen atoms. The network cavities, cages and channels of alumino-silicate zeolites gives numerous commercial applications as ion exchangers, molecular sieves, absorbents and as shape selective catalysts in the petrochemical industry$^{1,2}$. The useful properties of these inorganic “host-guest” structures are closely related to the topologies of the host frameworks, because they define the size and shape of the pore openings (absorption and molecular sieving), and the dimensions of the cages and channels (space available for reactant intermediates in catalysis). The most common zeolites are silicalite-1, ZSM-5, zeolite X, Y, A, zeolite beta, and sodalite. Zeolites are generally crystalline alumino-silicate with a three-dimensional rigid body consisting of interconnected tunnels and cages. In the crystalline structure of zeolite, the metal atoms (mainly Si and Al) are surrounded by four oxygen atoms to form an approximate tetrahedral structure$^3$. The resulting alumino-silicate structure, which is generally highly porous, possesses three-dimensional pores the access to which is through molecular sized windows. Most zeolites contain exchangeable extra framework cations in their channels and cavities, as needed to balance the anionic charge of their frameworks. They may also contain easily replaceable guest molecules such as water or organic molecules. Zeolites can show high selectivity
towards adsorbates and can be used as selective sorbents for gas and liquid phase separations. A general chemical formula of zeolites represented as

\[ \text{M}_{2n} \text{O} \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2 \cdot y\text{H}_2\text{O} \]

where, \( M \) is the exchangeable cation with a valancy \( n \), the value of \( x \) is equal to or greater than 2 because \( \text{Al}^{3+} \) does not occupy adjacent tetrahedral sites and \( y \) is the number of water molecules adsorbed on the zeolite. Mainly alkali and alkaline earth cations are present in the zeolites in the form of exchangeable cations. The pore or channel openings range from 3 to 10 Å, depending on the zeolite type.

Zeolite contains microscopically small channels, so sometimes they are referred to as a molecular sieve. Zeolites are amazing materials because of their physical and chemical properties and the crystal structure of zeolites can be varied easily by changing the chemical composition. Due to the porous structure, zeolites can accommodate different types of cations, such as \( \text{Na}^+ \), \( \text{K}^+ \), and \( \text{Ca}^{+2} \), etc., and are loosely bound so that they can easily be ion-exchanged. The uniform microcrystalline structure of zeolites has always driven researchers toward their catalytic applications. Several changes of the surface and the framework were attempted by incorporating transition metal ion or acidity of the matrix. The substitution of \( \text{Al}^{3+} \) in place of the tetrahedral \( \text{Si}^{4+} \) silica requires the presence of an added positive charge. Due to the shape-selective property of zeolites, they can provide an effective solution for environmental pollution by minimizing the formation of pollutants. Variation of the silica-alumina ratio, incorporation of transition metal ions, surface area, pore sizes, pore architecture, and cations produces a wide spectrum of zeolites to act as catalysts or adsorbents. The simple mechanism behind the formation of porous structures is the hydrolysis of the
silica precursor followed by condensation. Zeolites that are classified under advanced materials show a higher demand in worldwide market, reaching around USD 2.15 billion per year in 2001 and is expected to increase to more than $4 billion by 2012. The utilization of zeolite as catalysts in industrial processes occupies 40% followed by the oxides, complex oxides and ion-exchange resins. The average utilization worldwide for zeolite in fine chemicals industries is thought to be around 60% of its uses worldwide, either as a parent form or after its modification. Nowadays, zeolites are employed as alternative heterogeneous catalysts to substitute homogeneous catalysts in many organic processes because of its more efficient and environmentally-friendly which can eventually reduce plant corrosion and eliminate environmental problems. The synthetic zeolites give alternative sources for natural zeolites in which it exists in minor quantity and always in the mixture of other constituents makes natural zeolites unfavorable and uneconomical to be used for specific applications such as catalysts. Based on these observations, the research in the synthesis of zeolites and other mesoporous materials has been widely explored by researchers all around the world. Studies including the choice of raw materials, optimization of experimental condition for synthesis and the modifications of zeolites structure are the step to increase the potential of zeolite in order to fulfill the market demand.

1.2 Zeolite History:

The name “zeolites” originates from the Greek words “zeo” means boiling and “lithos” means stone because when gently heated, the stones evolved water vapor. There are 40 types of natural zeolites that have been found and to date, the number of synthetic zeolites has increased more than 200. Nowadays, the research in this area of science is
still expanding, resulting to the discovery of synthetic zeolite with new topologies and new catalytic, sorption and separation properties. The history of zeolites began with the discovery of stilbite in 1756 when the Swedish mineralogist Cronstedt discovered the first zeolite mineral. He recognized zeolites as a new class of minerals consisting of hydrated alumino-silicates of the alkali and alkaline earths. Because the crystals exhibited intumescence when heated in a blowpipe flame, Cronstedt called the mineral a “zeolite”. From 1777 through about the 1800s various authors described the properties of zeolite minerals, including adsorption properties and reversible cation exchange and dehydration. In 1862, Deville reported the first hydrothermal synthesis of a levynite. In 1896 Friedel developed the idea that the structure of dehydrated zeolites consists of open spongy frameworks after observing that various liquids such as alcohol, benzene and chloroform were occluded by dehydrated zeolites. Grandjean in 1909 observed that dehydrated chabazite adsorbs ammonia, air, hydrogen and other molecules, and in 1925 Weigel and Steinhoff reported the first molecular sieve effect. They noted that dehydrated chabazite crystals rapidly adsorbed water, methyl alcohol, ethyl alcohol and formic acid but essentially excluded acetone, ether or benzene. In 1927 Leonard described the first use of X-ray diffraction for identification in mineral synthesis. Taylor and Pauling described the first single crystal structure of zeolite minerals in 1930. In 1932 McBain established the term “molecular sieve” to define porous solid material that act as sieves on a molecular scale. Barrer began his pioneering work in zeolite adsorption and synthesis in the mid-1930s to 1940s. He presented the first classification of the known zeolites based on molecular size considerations in 1945 and in 1948 reported the first definitive synthesis of zeolites, including the synthetic analog
of the zeolite mineral mordenite\textsuperscript{20} and a novel synthetic zeolite\textsuperscript{21,22} much later identified as the KFI framework. Barrer’s work in the mid - to late 1940s inspired Robert M. Milton of the Linde Division of Union Carbide Corporation to initiate studies in zeolite synthesis in search of new approaches for separation and purification of air. Some natural zeolites and its year of discovery are summerised in Table 1.1.

Between 1949 and 1954 Milton and co-worker Donald W. Breck\textsuperscript{3} discovered a number of commercially significant zeolite, types A, X, Y, chabazite, faujasite and sodalite (Fig 1.1). In 1954 Union Carbide commercialized synthetic zeolites as a new class of industrial materials for separation and purification. The earliest applications were the drying of refrigerant gas and natural gas. In 1955 T.B. Reed and D.W. Breck\textsuperscript{23} reported the structure of the synthetic zeolite A. In 1959 Union Carbide marketed the “ISOSIV” process for normal – isoparaffin separation, representing the first major bulk separation process using true molecular sieving selectivity. Also in 1959 a zeolite Y - based catalyst was marketed by Carbide as an isomerization catalyst\textsuperscript{24}. In 1962 Mobil Oil introduced the use of synthetic zeolite X as a hydrocarbon cracking catalyst. In 1967 – 1969 Mobil Oil reported the synthesis of the high silica zeolites beta and ZSM-5. In 1977 Union Carbide introduced zeolites for ion – exchange separations. In 1974 Henkel (merchant who was interested in science) introduced zeolite A in detergents as a replacement for the environmentally suspect phosphates. By 1980 following the discovery by R. M. Barrer, a lot of techniques to synthesize zeolites were established not only to produce zeolites, but also for uses of the materials for industrial purposes.
Table 1.1: Naturally occurring zeolites with the year of discovery

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Name of Natural Zeolite</th>
<th>Year of discovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Stilbite</td>
<td>1756</td>
</tr>
<tr>
<td>2</td>
<td>Chabazite</td>
<td>1772</td>
</tr>
<tr>
<td>3</td>
<td>Sodalite</td>
<td>1806</td>
</tr>
<tr>
<td>4</td>
<td>Faujasite</td>
<td>1842</td>
</tr>
<tr>
<td>5</td>
<td>Mordenite</td>
<td>1864</td>
</tr>
<tr>
<td>6</td>
<td>Erionite</td>
<td>1890</td>
</tr>
<tr>
<td>7</td>
<td>Ferrierite</td>
<td>1918</td>
</tr>
<tr>
<td>8</td>
<td>Cancrinite</td>
<td>1965</td>
</tr>
<tr>
<td>9</td>
<td>Barrerite</td>
<td>1974</td>
</tr>
<tr>
<td>10</td>
<td>Merlionite</td>
<td>1976</td>
</tr>
</tbody>
</table>
Fig. 1.1: Building block sodalite cage in different framework of zeolites
1.3 Structure and Properties:

Zeolites are crystalline alumino-silicates with three-dimensional framework, in which the polyhedral sites, usually tetrahedral, are linked by oxygen atoms, comprises of corner-sharing TO$_4$ tetrahedra (T= Si, Al). The crystalline framework contains cages and channels of discrete size in 3-30 Å in diameter. The oxygen atoms are the connectors between silicon and aluminium atoms, while the tetrahedral are arranged into the n-membered rings, where n = 4 or larger. The framework zeolite is constructed from individual tetrahedral unit called TO$_4$ which refers to as Primary Building Unit (PBU) (Fig.1.2).

![Tetrahedra as a primary building unit, aluminum tetrahedra [AlO$_4$]$^-$, and silicon tetrahedra [SiO$_4$]$^-$](image)

The knowledge about the structure of these materials is essential for the understanding and prediction of their macroscopic physical and chemical properties. Size and connectivity of the channels and cavities determine their molecular sieving capability, and chemical compositions and distribution of the framework and extra-framework (metal) active sites are of importance for catalytic, absorption or ion-exchange capacity, framework topologies have been currently determined using X-ray diffraction method. The topology of all known zeolites framework type can be described in terms of
a finite number of specific combinations of tetrahedra called "Secondary Building Units" (SBU's). All unique and confirmed framework topologies (connectivity of T-atoms without reference to chemical composition) are assigned structure type codes by the Structure Commission of the International Zeolite Association (authorized by IUPAC). These are published on a regular basis in the “Atlas of Zeolite Structure Types”\textsuperscript{25}. \( \text{TO}_4 \) can be combined with various methods to form “Secondary Building Unit” (SBU), where T atom is present at each corner and the oxygen atom is located at the midway between the T. SBUs are linked to each other to form an infinitely extended three-dimensional network forming the zeolite\textsuperscript{26} structure (Fig. 1.3)\textsuperscript{1}. Description of the framework topology of zeolites involves "tertiary" building units corresponding to different arrangements of the SBU's in space and various alternative ways have been proposed. In 1967, Meier\textsuperscript{27} proposed the secondary building units of Fig.1.2 as the smallest unit from which zeolite topologies could be built. In the SBU, Al and Si is present at each corner or termination but oxygens are not shown that are located near the mid-points of the lines joining each pair of T atoms. The framework of some zeolites are constructed using only one repeating units, for example, natrolite and thomsonite are constructed by using the 4-1 units, mordenite and ferrierite are constructed by using the 5-1 unit. Sometimes more than one SBU is involved. Thus faujasite topology can be made from 4- and 6- and 8-ring together with 6-6 hexagonal prisms. Sodalite cages, each having 6 X 4-ring and 8 X 6-ring faces, are stacked in 8-fold co-ordination by sharing 6-ring faces to yield the sodalite structure. The framework may be considered in terms of large polyhedral building blocks forming characteristic cages. For example, sodalite, zeolite A and zeolite Y can all be generated by the truncated octahedron known as the \( \beta \) - cage. An alternative
method of describing extended structures uses the two-dimensional sheet building units. Sometimes various kinds of chains can be used as the basis for constructing a molecular sieve framework\textsuperscript{1}.

Fig. 1.3: The Secondary building units (subs) found in zeolite frameworks
Zeolite pores consist of 8, 10, 12 and 14 membered oxygen ring systems to form tube-like structure and pores that are interconnected to each other. Zeolites can be classified based on their pore size; small pore within 5 Å, such as zeolite A, chabazite and erionite; medium pore, within 4.5 Å to 6.4 Å, such as ZSM-5, ferrierite and TS-1 and large pore within 6.5 Å – 7 Å, such as faujasite, ZSM-12 and beta. The presence of extra framework cations is known to strongly affect the properties of zeolites. Synthetic zeolites can be manufactured uniformly with good purity. They are produced under similar conditions with natural zeolites, but in shorter time and at lower temperatures. The reaction composition is the key point of the synthesis to obtain pure zeolites. Natural zeolites are generally formed by the reaction of mineralizing aqueous solutions with solid alumino-silicates at certain temperature and pressure. Procedures to synthesize zeolites in the laboratory are determined by synthesis parameters such as alkalinity, temperature, crystallization period and gel ratio of the reactants. Porous materials consist of a network of interconnected pores of controllable dimension in the atomic, molecular, and nanometric scale. Porous materials can be grouped into three different categories depending on their pore diameter, such as (1) microporous, where the pore size is less than 2 nm, (2) mesoporous with pore diameters in the range of 2–50 nm, and (3) macroporous, in which the pore size is larger than 50 nm. Nanoporous materials of pore sizes between 1 to 100 nm, generally categorized as bulk materials and membranes, can have open pores and closed pores. Zeolite generally shows following properties:

1. High degree of hydration and the behavior of water in zeolite
2. Low density and large void volume when dehydrated
3. Stability of crystal structure of many zeolites when dehydrated
4. Cation exchange properties
5. Uniform molecular size channels in the dehydrated crystals
6. Various physical properties such as electrical conductivity
7. Adsorption of gases and vapours
8. Catalytic properties

These properties make the zeolite an excellent compounds, especially for industry where they find many applications useful for mankind.

1.4 Synthesis of Zeolite:

The reaction mixture for the preparation of zeolite is monitored by its gel chemistry. In zeolite synthesis, the usual sources of aluminium is aluminium hydroxide or sodium aluminate. For certain purpose aluminium isopropoxide is used. Amorphous silica, sodium silicate, sodium metasilicate, silica glass, silicic acid and various concentrations of silica sol are the common silica sources. Besides the commercially available silica, the uses of high silica content of low cost and waste materials as the silica sources are desirable. Rice husk ash and fly ash were known as a silica sources for synthesizing zeolites of the type Y, mordenite, ZSM-5 and beta. Crystallization of zeolite involves three basic steps. First is the reaching of supersaturation, second is the formation of nucleus and finally the growth of crystal. Saturation solution can be defined as when the solution is in equilibrium with solid and supersaturation solution is achieved when the solution contains more dissolved solid than at its saturation state. After supersaturation was achieved, the nucleation takes place. Before crystallization can occur, a number of
nucleons must exist in solution. Nucleation may occur spontaneously from solution or it may be formed by impurities or contaminants in the reactor walls. The formation of nucleus occurs step-by-step leading to the formation of short chains, flat monolayers and eventually the crystalline nucleus. As soon as stable nucleus has formed in a supersaturated solution, the process of crystal growth starts to occur. Many types of inorganic and organic template are regularly used to synthesize zeolite. Pyrrolidine and piperidine are commonly used in the synthesis of ferrierite. The template functioned as the structure directing agent either in organic or inorganic compound will be the cations neutralized for the anionic framework charge. The role of organic template can be found in the synthesis of siliceous zeolites. In sodalite synthesis template effect plays an important role as it will determine the properties of synthesized material such as pore architecture, channels, windows, extra framework cations. There are four main factors influencing zeolite crystallization, the gross composition, time of crystallization, temperature and pressure. All components in initials reaction mixture play their own role in influencing the crystallization of zeolite. The type of silica phase will determine the rate of solubility of the silica. The rate of solubility decreases from amorphous silica to crystalline silica (consist tridymite, cristobalite and quartz). Another factor to zeolite crystallization is the concentration of hydroxyl ion. The high concentration of hydroxyl ion will increase the alkalinity of the solution and the crystalline phase obtained might differ from the lower concentration of hydroxyl. Alkaline solution will facilitate the solubility of silica which in turns increases the crystallization rate. At higher silicate ratio ($\text{SiO}_2$/Na$_2$O), it will produce unstable solution due to the lack of charge compensation.
This gradually results the formation of colloidal particles of silica instead of polymeric silicate anion which facilitate the production of zeolite.\textsuperscript{28}

The crystallization period of zeolite formation decreases rapidly with increasing temperature. At the same temperature, different phases of zeolite will be formed depending on the crystallization period. The transformation of zeolite phase is due to the existence of metastable phase with respect to another. For example, the formation of zeolite A from metakaolin obtained in the first hour of reaction followed by the transformation of zeolite A to JBW type of zeolite.\textsuperscript{29}

1.5 Uses of Zeolite:

Zeolites have many important industrial applications. The regular network of channels and cavities provide an excellent means of separating species (hence their other name “molecular sieves”). Important applications are summarized below.

1.5.1 Catalysis:

The large internal surface area of zeolites can be exploited for catalytic purposes and they can be highly selective, especially when the pore sizes are manipulated, for example by ion exchange. The role of zeolites in catalysis encompasses three different areas of selectivity which make use of the pore size a) reactant selective catalysis, b) product selective catalysis, and c) transition state catalysis.

There are many advantages of zeolite over other high surface area catalysts: they can be made to be very selective (and hence give fewer by-products and a purer product), have a large number of catalytic sites per unit volume, and a more regular structure, which produces more reproducible results. Zeolite Y (FAU) is used as a
catalyst in the petrochemical industry. It is also used in Fluid Catalytic Cracking (FCC) processes due to their high activity levels, low coke forming tendency, high organic nitrogen and NH$_3$ resistance, regenerability, and molecular shape selectivity.

1.5.2 Ion exchange:

Zeolites can also function as ion exchangers$^{3,26}$. As previously mentioned, the cations associated with the tetrahedral aluminium ions are not part of the framework, and are available for exchange. This principle is applied in water filters, water softeners and detergents, where Na$^+$ ions in zeolite A are exchanged with Ca$^{2+}$ and Mg$^{2+}$ ions from the hard water. Ion exchange is also applied to clean up the nuclear waste. Ion exchange is limited by the pH of the solution, as below pH 3-4 the aluminium in the framework is attacked, and the structure is destroyed. Hence high Si/Al ratios are more stable at low pH.

1.5.3 Other uses:

Dehydrated zeolites can be used as drying agents because they absorb moisture. This is a result of the cation, which is co-ordinated to the water, having moved to a less stable, lower co-ordination site. The zeolite drying agent can be re-dehydrated and reused. When dehydrated, zeolites can also act as adsorbents$^{30}$, with hydrophobic zeolites having the potential ability to remove organic molecules from aqueous solutions$^{31}$. Zeolites have found many agricultural applications$^{32,33}$, the majority using the natural zeolite, clinoptilolite. These include removing harmful heavy metals and PCBs (polychlorinated biphenyls) from soil on farmland. The use of zeolites as slow release fertilisers has been reported. The fertilizer is stored within the zeolite and is applied to the area required. During rain or watering the fertilizer is released from the zeolite into
the soil gradually over a period of time. This prevents the sudden release of fertiliser into
the environment, which can then result in its being washed away into rivers and
groundwater, causing pollution. The same principle can be applied to weed killers and
insecticides. Zeolites can also be used as part of animal litter, and can then be used as
fertilisers to release the beneficial nutrients evenly into the soil. The addition of 1–2% by
weight of zeolites to animal feed has been shown to provide benefits. It is reported that
the zeolites in the feed can degrade natural toxins formed by fungus in the crop being fed
to the animals. This led to better health and an increase in animal body mass. Zeolite
shows some more unusual potential uses in electrical and optical applications, such as
lasers, batteries and sensors.34

1.6 Sodalites:

Sodalite [SOD] framework is considered as an archetype zeolite
framework. Sodalite17 belongs to a class of crystalline microporous tetrahedral network
structures which span a 3D framework enclosing voids of at least 2.5 Å diameters.
Sodalites are encapsulated with anion containing frame work27 consisting of β-cages
(Fig. 1.4a), formed from (Be, Al, Si, Ga, Ge, Zn or P) tetrahedra, directly linked through
the six membered rings, with centrally placed anion co-ordinated tetrahedrally to four
cations. The composition of sodalite is very diverse, and may be expressed by the
general formula Ms[AlSiO₄]₆X₂ (where, X= Cl⁻, Br⁻, I⁻, NO₃⁻, SO₄²⁻, MnO₄⁻, ClO₄⁻ ClO₃⁻,
SCN⁻……etc, and M represents mono or divalent cations of overall charge 8⁺). The
compositional flexibility of the sodalites results from the ability of the structure to vary
the dimensions of the sodalite cage by changes in the intertetrahedral bond angle along
the Si-O-Al direction in the range 120-150°. This permits satisfactory co-ordination by
oxygen to a range of different sized cations, which can in turn form reasonable tetrahedral co-ordination geometry around the anion which is located at or near cage centre.

Well known ultramarines contain the polysulphide anion radicals \( \text{S}_3^- \) and \( \text{S}_2^- \) and the corresponding selenium analogues are widely used as pigments, like zeolites, sodalite may be natural or synthetic. The synthetic counterparts are produced at industrial scale for specific uses or prepared in laboratory in the attempt to explore their crystal chemistry and properties. The structural diversity of the sodalite framework such as alumino-silicate, alumino-germanate, gallosilicate,…etc. has been demonstrated by the number of group’s, world wide\(^{35-60} \). Sodalite framework consists of cubo-octahedra, Al-O-Si cages, “\( \beta \) cages”, arranged in a body centered cubic configuration (Fig. 1.4 b ). The unit cell has 42 atoms forming two cages that contain six Na atoms, the latter giving up their electrons to the frame. Sodalites consists of cage of twelve tetrahedron \( \text{AlO}_4 \) or similar unit and twelve tetrahedral \( \text{SiO}_4 \) unit and similar five units; linked together by oxygen bridges in an alternating pattern to form a truncated octahedron with eight single \( \{6\} \)-ring openings and six single \( \{4\} \)-rings typically the cage has a diameter of 6.6Å. Hexagonal six membered ring opening is between 2.2-2.6Å and four membered ring opening is between 1.5-1.6 Å. Different types of micro porous materials, including SOD, LTA, FAU and EMT consist \( \beta \)-cages as a building unit. Some of naturally occurring alumino-silicate sodalite is shown in Fig. 1.5. Investigations on the salt enclathration inside the sodalite alumino silicate matrix and its effect on the thermo chemical properties of sodalite have recently become an area of special interest\(^{62-65} \).
Fig. 1.4: Sodalite cage and sodalite structure by staking cage assembled.
Fig. 1.5: (a-c) naturally occurring alumino-silicate sodalites, and (d) ultramarine sodlite\textsuperscript{61}
Especially, the incorporation of guest anion of different types seems to be a new aim of research, since such materials can be regarded as a model system for waste gas immobilization due to their potential high temperature intra-cage reaction behaviour. This was recently demonstrated for basic nitrate sodalite. The simplicity of sodalite makes them an ideal system to study phenomenon such as host-guest interaction and variation in structural parameters as a function of composition. The vibrational and electronic interactions with each other and with sodalite framework may be controlled by selecting appropriate guest ions and varying their concentration, and carrying out physical or chemical manipulation on the guest species.

The sodalite framework is used as a host material to synthesize sodalite structure with a variety of guest anions. By encapsulating such materials inside a sodalite host matrix, one can create clusters of the guest components. Depending on the degree of interaction between clusters, it may be possible to create extended cluster lattices in various size regimes whose physical properties may be different from both individual clusters and the bulk material composed of the guest ions.

Sodalites have been studied mainly as model compounds for large zeolite systems. The close inspection leads to the realization that the sodalite lattice forms a convenient matrix for a variety of encapsulated guests. The sodium cations inside the sodalite cages are exchangeable by small as well as large cations. The regular space filling framework of sodalite provides a temperature stable homogeneous 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. Six membered rings of sodalite only allow smaller cations and molecular size nearly equal to
water. Sodalites are unique due to the presence of guest anions, which can be used not only as internal reagents but also, provide great flexibility in the composition and space filling properties of trapped species. Substitutions may change substantially the delicate equilibrium of interactions between the partial structures of sodalite (the SOD framework, a virtual lattice spanned by the guest cations and the guest anions) and hence result in complex symmetry relations and phase transitions. It happens quite often that the symmetry of the guest species and the site symmetry in the overall space group do not match, resulting in static or dynamic disorder of the guests. The symmetry of sodalite is cubic with space group P43n. Sodalites can be modified to produce a range of materials with specific and industrially attractive properties. A modification is possible in sodalite framework by isomorphous substitution of germanium in place of silicon gives alumino-germanate sodalite framework. Among all the sodalite groups of materials, the replacement of the framework Al and Si by the larger Ge and Ga affects the structure, the introduction of larger framework atoms may also allow the enclathration of larger anions which can’t be normally incorporated into alumino-silicate sodalites. Germanium based sodalite has been obtained owing to its potential attractive optical properties as nanocomposites in quantum electronics and nonlinear optics. Alumino-germanate sodalites may be represented by the general formula M₈ [AlGeO₄]₆X₂, where M = Na, Li, Ag, …, and X = Cl, Br, ClO₄⁻, ClO₃⁻ ….. The sodalite framework consists of alternating GeO₄ and AlO₄ corner sharing tetrahedra forming four and six rings, which make up the basic β-cage unit. The replacement of the framework Al and Si by the larger Ga and Ge affects the structure, the introduction of larger framework atoms may also
allow the enclathration of larger anions which can’t be normally incorporated into alumino-silicate sodalites.

1.6.1 Uses of sodalite:

Sodalites have a wide range of applications in the field of adsorption, catalysis, ion exchange etc. Due to the shape selective properties, sodalites are used in molecular sieving applications. They can be used to separate molecules on the basis of size, shape and polarity. Sodalites have high affinity for water and have the capability of adsorbing and desorbing property without damage to the crystal structure. They can be used in removal of water and carbon dioxide from gaseous hydrocarbons.

Sodalites are also used as cluster components in insulator, semiconductor material and nano composites in non linear optics or for host matrix of semiconductor quantum super lattice. Sodalite shows electrochemical properties and is used as potential ion selective membrane. They can also be used for waste gas immobilization and seem to be a versatile tool for material science and waste management.

The cations in the sodalite are loosely bound to the sodalite framework and can readily exchange with other cations in aqueous media. This property enables sodalites to exchange ions and can be used for the exchange of heavy metals as well as storage of radioactive wastes. Sodalites can be used to exchange harmful metal ions like Cd$^{2+}$, Pb$^{2+}$, As$^{3+}$, Zn$^{2+}$ etc., from the waste water and industrial effluent. Due to the porous nature of sodalites, they can trap colloidal and suspended particles from organic and mineral origin. Sodalites are also used as pigments, gas storage materials, photochromic and cathodochromic sodalites for information storage, display and filter optics, and as a material for field emission displays.
1.6.2 Sodalite as an ion exchanger:

In case of sodalite the replacement of cations present in their alumino-silicate anion framework by ions in external solutions or melts has been extensively studied for a variety of reasons. The introduction of cations, usually by ion exchange, has been used to modify the catalytic or molecular sieving, actions of the parent sodalite. The theory of ion exchange is given below. Facile exchange between cation $A^{zA}$ initially in solution and $B^{zB}$ initially in sodalite, may be given as

$$
SOD_B A^{zA} + SOD_A B^{zB} \leftrightarrow SOD_B A^{zA} + SOD_A B^{zB}
$$

$SOD_A, B$ are the valencies of the ion and the characters with a bar relation to cation inside the sodalite crystal.

$$
SOD-Na^+ + K^+ \leftrightarrow Na^+ + SOD-K^+
$$

For monovalent exchange

$$
SOD-2Na^+ + Ca^{2+} \leftrightarrow 2Na^+ + SOD-Ca^{2+}
$$

Sodalites have the critical advantages as model cation exchangers in that, their swelling is not significant and salt imbibitions is usually very small under the concentration conditions commonly used to study their exchange properties.

1.7 Sodalite Synthesis:

Alumino-silicate sodalite has been synthesized in the past starting from various kinds of materials such as gels, mullite, quartz, zeolite A, and kaolinite. Tomisaka and Eugster have reported of sodalite synthesis from metakaolin under high temperature and in the absence of water. Alumino-germanate sodalites are synthesized from germanium dioxide, beryllonite phase, sodium metagermanate (germanium source) and alumina or sodium aluminate (aluminum source).
Alumino-germanate and alumino-silicate sodalite encapsulated with different anions such as Cl\textsuperscript{−}, Br\textsuperscript{−}, I\textsuperscript{−}, ClO\textsubscript{3}\textsuperscript{−}, ClO\textsubscript{4}\textsuperscript{−}, SCN\textsuperscript{−} may be synthesized hydrothermally. The investigation of new materials for hydrogen storage is of potential interest for future energy management. Beside metal hydrides being well established up to now, new concepts were discussed like the use of nanotubes and nanoscale frameworks developed by molecular design. Since the pioneering work of Barrer\textsuperscript{19-22} on the synthesis of sodalites, the hydrothermal synthetic technique has become the basic route for sodalite synthesis.

Methods used in mineral synthesis have in part imitated natural processes of change by sintering reactions; by crystal growth from melts or hydrothermal magmas; or by pneumatolysis in which reactions proceed not in the presence of excess water as in hydrothermal chemistry, but at high temperature in the presence of small amounts of reactive volatile components as gas or super critical fluid (e.g. H\textsubscript{2}O, H\textsubscript{2}S, CO\textsubscript{2}, or HF). Table 1.3 summarizes the various methods for crystal growth\textsuperscript{99}. In the laboratory some of these have been used to grow large single crystals as near perfect as possible.
Table 1.3: Methods of growing crystals\textsuperscript{99}

<table>
<thead>
<tr>
<th>Growth form</th>
<th>Conditions</th>
<th>Variants</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aqueous solution or magma</td>
<td>Below 100\degree C at ambient pressure or at high temperature (hydrothermal process)</td>
<td>Isothermal temperature gradient Temperature lowering precipitation</td>
</tr>
<tr>
<td>High temperature mixed melts and solutions</td>
<td>Ambient pressure and high temperature</td>
<td>Temperature lowering Evaporation of solvents composition change in melt.</td>
</tr>
<tr>
<td>Pure melt</td>
<td>High temperature and pressure depends on substance</td>
<td>Temperature lowering crystal pulling, Flame fusion</td>
</tr>
<tr>
<td>Solid state</td>
<td>Temperature and pressure depends on circumstances</td>
<td>Sintering, Hot pressing Diamond forming process</td>
</tr>
</tbody>
</table>

During crystallization of a natural multi-component magma at depth anhydrous crystals are formed. This causes volatiles such as water to accumulate in the subterranean crystallization zones, which has been suggested as one cause of volcanism and of the upwelling of lavas\textsuperscript{100}. The accumulation of the volatiles may in turn also lower the viscosity of the remaining magma by dissolving in it and breaking Si-O-Si or Si-O-Al bonds. At high temperature, great pressure can develop which in turn can speed the crystallization process and accelerate the build-up of the pressure of the volatiles. Generally there are three processes used to produce zeolite. These are as below:
1. Preparation of molecular sieve zeolites as high purity crystalline powders.
2. The conversion of clay minerals into zeolites.
3. Processes based on the use of other naturally occurring raw materials.

Due to the industrial importance of this mineral, much effort is made to unravel the mechanism responsible for its formation from its precursors. The art of creating zeolite synthesis has become a scientific interest because this concept may be derived for tailor-made zeolite synthesis. As we know, alumino-silicate zeolites synthesis involves mixing together Si and Al species, metals cations, organic molecules and water, which are then treated hydrothermally or other method and the mixture is then converted into a microporous crystalline alumino-silicate. This process can be denoted as zeolitization.

Sodalites occur as minerals in various forms, they can be synthesized from natural starting materials as well as pure reagents by a variety of methods. These methods are briefly discussed below

1.7.1 Solid state synthesis:

In this method sodalite is synthesized by sintering alumina (or sodium aluminate and sodium hydroxide), silica and sodium salts with the appropriate anions at temperatures rang from 800 °C to 1300 °C in air using stoichiometric amounts of all components. Ultramarine is very good example of solid state synthesis in which the alumino-silicate source (kaolinite, fly ash) are mixed with elemental sulphur, sodium carbonate and reducing agent such as carbon, sodium acetate in mechanical grinder. This mixture is heated in a non oxygen atmospeare at 800°C for certain time results in formation of coloured sodalite. The product obtained may be irregularly shaped grains

101, further Van Doorn et al.102 described slight variation in the method. Instead of using
untreated starting materials, they have used precursors. A gel of sodium aluminate, silica and sodium bromide in water which was evaporated to dryness before being fired in air at 1100 °C with excess NaBr. Using solid state synthesis Neurgaonkar and Hummel\textsuperscript{103} prepared range of sodalite analogues of the type \( M_2N_6(T`T``O_4)_6(XO_4)_2 \), \( M = \text{Ca, Cd, Sr, Mn, Pb; } N = \text{Na, K, Li, Ag; } T` = \text{Al, Ga, Fe, and } T`` = \text{Si or Ge; } X = \text{S, W, Mo, Cr, Te, Se} \).

The solid state method has been used frequently in the production of photochromic and cathodocromic sodalites\textsuperscript{102,104-109}. Variety of dopants are used which shows colour change when excited by an electron beam or UV light, for example, sulphur (\( S^{2-} \))\textsuperscript{101}, oxygen (\( O^{2-} \))\textsuperscript{101}, manganese (\( Mn^{+2} \))\textsuperscript{110}, and iron (\( Fe^{3+} \))\textsuperscript{111,112} are the most common dopants, but \( Co^{2+} \), \( Ni^{2+} \) and \( Cr^{3+} \) have also been used\textsuperscript{102}.

\textbf{1.7.2 Structure conversion:}

Sodalites are also obtained by structure conversion of zeolites. In a method proposed by Chang\textsuperscript{81} a molecular sieve containing β-cages as building units (eg. Zeolite 13X or 4A) is mixed with excess alkali halide and heated to 850 °C in a flowing reducing gas. Williams et al.\textsuperscript{101} described a similar method to produce photocromic and cathodochromic sodalites from faujasite that had been dehydrated at 400 °C, mixed with NaCl dried under vaccum and then exposed to \( H_2S \) of \( SO_2 \) at 200 °C to incorporate sulphide; the product is converted to the sodalite structure.

\textbf{1.7.3 Hydrothermal synthesis:}

Hydrothermal synthesis can be carried out at atmospheric pressures and temperatures from 80 °C to 150 °C in polypropylene or Teflon lined containers or elevated temperature (up to 550 °C) and pressures (up to 175 MPa)\textsuperscript{112} in platinum or silver lined autoclaves. Hydrothermal synthesis of 1:1 alumino-silicate sodalites is carried
out in aqueous solutions of sodium hydroxide, containing source of aluminum or silicon and the sodium salt of the anion to be encapsulated. Figure 1.6 gives general mechanism of the reaction for the growth of sodalites and other zeolites. Hydrothermal synthesis usually refers to reactions occurring under conditions of high temperature-high pressure (>100°C, >1 bar) in aqueous solutions in a closed system. Nowadays, the concept of hydrothermal synthesis covers the entire region above room temperature and 1 bar. Hydrothermal synthetic techniques have been applied not only in the preparation of zeolites and related porous materials, but also in the preparation of most other important inorganic materials, such as superionic conductors, chemical sensors, electronically conducting solids, complex oxide ceramics and fluorides, magnetic materials, and luminescence phosphors.

The increasing interest in hydrothermal synthesis derives from its advantages in terms of high reactivity of reactants, easy control of solution or interface reactions, formation of metastable phases, and unique condensed phases, reduced air pollution, low energy consumption, etc. According to reaction temperature, the hydrothermal synthesis can be classified into subcritical and supercritical synthetic reactions. In subcritical synthesis, the temperature is in the range of 100-240°C, while in supercritical synthesis, the temperature could reach 1000 °C and the pressure may increase up to 3000 bar. Water can act as a mineralizer or a catalyst under elevated pressure-temperature conditions. The solubility of nonpolar species increases whereas that of ionic and polar compounds decreases. Under hydrothermal conditions, the physical and chemical properties of reactants are also changed significantly. High temperature and pressure hydrothermal conditions accelerate the reaction rate among the complex ions, intensify
the hydrolyzation reaction, and significantly change the redox potential of the reactants. Consequently, hydrothermal (high temperature and pressure) conditions can promote the reactivity of reactants with low solubility at ambient temperature. The viscosity of water decreases with the increase in temperature. Consequently, the mobility of molecules or ions in water under hydrothermal conditions is enhanced significantly. The hydrothermal synthesis of zeolite materials is typically performed in sealed vessels. A major safety concern is associated with the high autogenous pressure generated in such sealed vessels at elevated temperatures from the vapor pressure of the reactants. Hydroxide has important role in the synthesis and acts as a mineralizer or solubilizer. Hydroxide ion functions as a structure director by controlling the degree of polymerization of silicates in solution, which also has temperature dependence. It has a nucleation time, crystal growth rates and phase purity, a high pH tends to reduce the length of the induction period\(^1\). Sodalites have been obtained at low concentration of NaOH solutions, but at least 4 M NaOH concentration is normally required\(^{114}\).

Barrer and coworkers\(^{114,115-117}\) and others\(^{118,119}\) have shown that kaolinite (Al\(_2\)O\(_3\):2SiO\(_2\):2H\(_2\)O) is used as starting material for sodalite at low temperature (80-160 °C). Many syntheses have used silica or sodium silicate and alumina or sodium aluminate as starting materials. Other framework ions may be introduced like Ga\(^{102,103,119,120}\), Ge\(^{72,74,76,121-123}\), and Fe\(^{122,123}\). Hydrothermal sodalite syntheses have several advantages over the solid state methods.
Fig. 1.6: General mechanism for sodalite crystal growth
1) Hydrothermal method gives greater choice of incorporated anions and permitting the addition of small quantities of dopant in solid, liquid or gaseous forms.

2) Conditions are less severe so that reagents can sometimes be used that are unstable at the high temperatures of solid state reactions.

3) The final product is often much superior and its properties are more easily controlled.

4) The degree of crystallinity is generally greater than the material grown by solid state sintering.

Crystal growth of a zeolite and sodalite is preceded by the formation of an alumino-silicate gel. The mechanism by which zeolites form from such gels is among the least understood aspect of zeolite chemistry\textsuperscript{124}. Thompson and Dyer\textsuperscript{125} have likened crystallization processes in zeolite synthesis to emulsion polymer synthesis. Learning on this comparison, they modeled zeolite crystallization by aggregation of pseudo–cells coming together to form a large particle. The stable silicate or alumino-silicate anions in the form of the rings and cages characteristic of those found in zeolite and sodalite framework\textsuperscript{126} (i.e. single 4-rings, single 6-rings, double 4-rings, double 6-rings and complex units\textsuperscript{3}). In the mechanism of crystallization (Fig. 1.7) the growth conditions for sodalite, and zeolite-A are same. The initial major product in the sodalite synthesis is zeolite-A, which changes into sodalite. The change in anion type may lead to formation of cancrinite. Mechanism shows cage formation and continued crystallization of sodalite, where the composition between the occlusion of different anions dictates the relative concentrations of anions in the product.
Fig. 1.7: Proposed mechanism for sodalite crystallization
1.8 Characterization Methods:

Following techniques have been used for the characterization of synthesized products.

1.8.1 IR spectroscopy:

Infra red (IR) is one of the most common spectroscopic technique used by organic and inorganic chemists. IR spectroscopy can yield information about the structural details of the material. It is the absorption measurement of different IR frequencies by a sample positioned in the path of an IR beam. Different functional groups absorb characteristic frequencies of IR radiation. The atoms in the molecules are in continuous vibration with respect to each other, when the frequency of a specific vibration is equal to the frequency of the IR radiation directed on the molecule, the molecule absorbs the radiation.

IR spectrum in the range 350 cm\(^{-1}\) to 4000 cm\(^{-1}\) is used to characterize and differentiate the different sodalite structures. The framework vibrations can be classified as structure sensitive (vibrations related to the external linkage of TO\(_4\) units in the structure) and structure insensitive (internal vibrations of framework TO\(_4\)). Sodalites shows three sets of fundamental vibrations due to symmetric stretching vibration \(\nu_s\) (T-O-T), asymmetric stretching vibration \(\nu_a\) (T-O-T) and bending vibration \(\delta\)(O-T-O).

1.8.2 X-ray powder diffraction:

X-ray powder diffraction is one of the most versatile and powerful non-destructive technique used for qualitative and quantitative analysis of the crystalline materials. Crystalline solids have unique X-ray powder pattern and can be used as a finger print for its identification. Using X-ray powder pattern, unit cell parameter, space
group, qualitative phase identification crystal structure analysis, texture analysis, crystallite size, lattice distribution, micro strain etc. can be obtained.

Further, the X-ray powder diffraction can be coupled with powerful technique like Rietveld programs like FULLPROF or GSAS for the crystal structure refinement. Rietveld method\textsuperscript{138} is introduced by H. M. Rietveld\textsuperscript{127} for the crystal structure refinement using neutron powder diffraction and X-ray diffraction data. X-ray and neutron diffraction techniques provide quantitative statistical information on crystal structures and defects averaged over volumes from about $10^{-3}$ to few cm$^3$, respectively. This fact is important for interpreting the nature of the information provided by the different diffraction techniques more accurately.

The Rietveld method is based on a least-square approach to refine a calculated powder profile with the observed powder profile. In this method, all factors contributing to the intensity $y_i$ at point $i$ in the powder pattern may be simultaneously refined by a least square procedure until the best fit is obtained between the entire observed powder diffraction pattern and the entire calculated pattern. Since the method is a structure refinement procedure, a reasonably good starting model is required. The quantity that is minimized by the least square procedure is the residual, $S_y$, which is defined as\textsuperscript{127},

$$S_y = \sum \frac{1}{y_i} (y_i - y_{ci})^2$$

where, $y_i$ and $y_{ci}$ are the observed and calculated intensity at the $i^{th}$ step, respectively. The sum is over all data points in the powder pattern. The calculated intensity at point $i$ ($y_{ci}$) is determined according to\textsuperscript{127}
where, $y_{bi}$ is the background intensity, $J,hkl$ denotes the Miller indices for the Bragg reflection $hkl$ of phase $J$, $s_J$ is the scale factor for phase $J$ and $O_{hkl}$ is the preferred orientation function. The refinement includes structural parameters like atomic positions, thermal and site occupancy parameters as well as parameters for the background, lattice constants, instrumental geometrical-optical features, specimen aberrations, scale factor and peak broadening due to the sample microstructure.

X-ray powder diffraction pattern for different synthesized sodalite were studied by Philips, PW-1710, X-ray powder diffractometer using CuKα radiation with wavelength $\lambda = 1.54$ Å. The X-ray machine was operated at 25 KV, 25 mA. The diffraction patterns were recorded with a step size 0.017° and 40 sec/step between 5 to 80°, 2θ range.

Sample preparation:

1. Sample was dried in an oven at 120 °C.
2. Finely ground sample (0.5 gm) was taken on a polymethylmethacrylate (PMMA) sample holder.
3. Sample was placed evenly to cover the sample holder.
4. Sample holder was placed in the cavity using a glass slide.
5. Measurement was done with a step size 0.017° and 40 sec/step between 5 to 80°, 2θ range.
1.8.3 Magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy:

NMR spectroscopy is used for the structural investigations of many nuclei, when a nucleus is placed in a magnetic field; NMR active nuclei absorb at a characteristic frequency and give the signal. The resonance frequency, energy of the absorption and the intensity of the signal are proportional to the strength of the magnetic field. Depending on the local chemical environment different nuclei in a molecule resonate at different frequencies. By using resonance frequency and chemical shift, structural information can be obtained.

In MAS NMR, spin of nuclei interact with the magnetic or electric field. These interactions are orientation dependant. As the powder sample contains all possible orientations, the peak broadening appears. This peak broadening effect can be minimized if the measurement is done at a magic angle (54.7°). The magic angle is a root of a second order Legendre polynomial and so any interaction which depends on this second order Legendre polynomial vanishes at the magic angle. By spinning the sample (usually at frequency 1 to 70 KHz) at the magic angle (54.7°) with respect to the direction of the magnetic field, the normally broad lines become narrower, increasing the resolution for better identification and analysis of the spectrum.

The MAS NMR spectra are used to determine the nature and chemical environment of the atoms. $^{29}$Si MAS NMR spectra provides information on Si/Al ordering, crystallographic equivalent and non-equivalent Si in various sites, framework silica to aluminum ratio, coordination of Si and Al, spectral correlation with Si-O-T bond
angles (T= Al/Ga) and Si-O bond lengths. MAS NMR spectroscopy of $^{23}$Na nuclei is used to study the nature and chemical environment of these nuclei in sodalite cages.

The 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, in a 5 mm probe using tetramethylsilane as a internal standard. The $^{23}$Na MAS NMR spectrums was recorded at 79.39 MHz with 40.5 μsec pulse duration, 1 sec pulse delay and a spinning rate of 7 KHz in a 5 mm probe using sodium chloride is used as a internal standard.

For all the samples $^{27}$Al MAS NMR spectrum were recorded at 130.0 MHz on a Bruker Advance 500 MHz widebore spectrometer with 6.15 μsec pulse duration, 3 sec pulse delay and a spinning rate of 5 KHz in a 4 mm probe (Alumina as a internal standard).

1.8.4 Thermal analysis:

Whenever a material is to be studied, one of the easiest test is the thermal behavior of the material. The observation of the thermal behavior of the material and the quantitative measurement of the changes on heating can yield a lot of useful information on the nature of material. Thermal analysis is a group of techniques in which one or more properties of a sample are studied, when the sample is subjected to a controlled temperature program. Thermal method provides information regarding decomposition, oxidations, phase changes, heat capacity, mechanical changes, expansion phase changes, glass transitions, curie points etc.
Thermogravimetric analysis (TGA) measures changes in weight of material with change in temperature. In Differential thermal analysis (DTA) the material and inert reference undergo identical thermal cycles and changes in material either exothermic or endothermic with relation to inert reference can be studied. Differential scanning colorimetry (DSC) measures the difference in the amount of heat required to increase the temperature of a sample and reference as a function of temperature.

Generally, zeolites are thermally stable, but heating at elevated temperature may lead to structure breakdown and therefore decrease in crystallinity. In this study, thermal analysis is used to study decomposition properties of enclathrated anions and framework structures of sodalites and cancrinites. Simultaneous thermal analysis including TGA/DTA were carried out using Metlor Toledo thermoanalyser with a heating rate of 10 °C/min, in the temperature range, room temperature to 1200 °C.

1.8.5 Scanning electron microscopy (SEM):

The crystal morphology of the synthesized sodalites and cancrinites were studied by SEM technique. SEM is the type of electron microscope that images the material surface by scanning it with a high energy beam of electrons. The electrons are bombarded on the sample and scattered secondary electrons form the image. A thin layer of sample is mounted on a carrier and to prevent the material from thermal damage by the electron beam and surface charging, it is coated with gold film. The ejected secondary electrons are accelerated to photo multiplier tube and the amplified signal is displayed as a two-dimensional intensity distribution that can be viewed as an image. All the scanning electron micrographs were obtained on a JEOL JEM-6360A SEM equipment.
1.8.6 **Raman spectroscopy:**

Raman spectra were recorded at room temperature using Nicolet almega XR dispersive Raman Spectrophotometer (Thermo Electron Corporation) with 780 nm Laser. The sample containing disk was rotated during excitation to minimize heating effects. Raman spectra were recorded in the region 200 to 4000 cm\(^{-1}\).

1.8.7 **UV-Visible spectroscopy:**

The UV-visible spectra were recorded in the region 200 to 800 cm\(^{-1}\) by using UV-VIS-NIR spectrophotometer, Perkin Elmer Precisely, Lambda 950 (Hitachi-model-330).

1.8.8 **Electron spin resonance spectroscopy:**

The ESR spectrum was recorded at room temperature with E-line century series, ESR spectrometer. ESR spectroscopy was used to detect enclathrated paramagnetic cluster present within the sodalite cages.

1.9 **Brief Review on the Earlier Work Done:**

Investigations on the formation and decomposition reactions of salt imbibed sodalites are essential for the understanding of the intra-zeolite chemistry, because the zeolite A, X and Y consists of sodalite cages as basic structural units. From these structural relations sodalites are an attractive model system for members of the zeolite family. Though the zeolite minerals were discovered in 1756, the zeolite science and technology has been greatly extended in the last 50-60 years. The zeolite science and technology became strong enough after the pioneer work of Professor R.M. Barrer\(^\text{27}\).
to increasing number of industrial zeolite-based processes and their rapidly increasing applications as well as the recent progress in zeolite structures and properties, there is a exponential increase of papers and patents in the field of zeolites. Professor R.M. Barrer contributed more than 35 years to the zeolite research and reported thermodynamic analysis of nucleation, crystallization and salt inclusion as well as the preparation of many new materials including new zeolite topologies, new compositions of known structures and several novel post-synthesis approaches to modify zeolite compositions and properties.

Sodalite of the type $M_8[AlSiO_4]_6(X)_2$ is of fundamental interest to many researchers. Felsche et al. and Kedrick et al. studied hydro sodalites. The synthesis, characterization and thermal properties of nitrite and nitrate containing alumino-silicate sodalite have been discussed by many researchers. Stein et al. studied halo alumino-silicate sodalite and their silver derivaties, Brenchley and others have studied chloride, chlorate and perchlorate sodalite as well as different derivatives of halate sodalites. Alumino-silicate sodalite with thiocyanate, carbonate anion and sodalite containing formate anions in organic solvent, iodate, cyanate, azide, basic and non basic carbonate sodalite and mixed sodalites have been studied in the past. Eiden-Assmann et al. have studied the silver and lead exchanged hydro sodalite and discussed the arrangement of silver and lead in sodalite cages. There are a few reports on structure refinement of single crystal of acetate and formate containing alumino-silicate sodalite.

The framework aluminum from alumino-silicate sodalite can be replaced by germanium to give the alumino-germanate sodalite of the type $M_8[AlGeO_4]_6(X)_2$. 
Alumino-germanate sodalite structure was studied by Neoff et al.\textsuperscript{70} and M.E. Fleet\textsuperscript{39}. There are few reports which show isomorphous substitution of aluminum by germanium\textsuperscript{71,72}, J.-Ch. Buhl et al.\textsuperscript{151,152}, Gesing\textsuperscript{153}, Johnson et al.\textsuperscript{96,154,155} and others\textsuperscript{73,156,157} have reported alumino-germanate sodalite with variety of encapsulated anion and studied their relation with unit cell parameter and MAS NMR shift. Though, these reports are available, the sodalites containing guest species are not studied in detail and literature survey shows the need for more detailed characterization in this field. The isomorphous substitution of tetrahedral atom can be used to modify structural properties. The substitution of framework aluminum by germanium results in modification of the molecular cages and channels of the cancrinite which can be used for further applications.

Sodalites can be used for the removal of heavy metals as well as toxic elements from various effluents. Sodium ion from the sodalite cage can be exchanged with heavy metals. Nowadays, increased thermal power generation has resulted in discharge of an uncontrolled amount of fly ash into the environment. Due to its adverse effects, attributed mostly to its fine structure and toxic elements, regulations for its land disposal are stringent. Development of attractive methods of fly ash disposal or proper utilization with emphasis on resource recovery has thus become an imperative. Class- F fly ash is good source of alumino-silicate sodalite. Sodalite can be synthesized from coal fly ash. There are only few papers presenting alumino-silicate sodalites synthesized from coal fly ash with heavy metal exchange\textsuperscript{88,138,159-162} but report on adsorption of heavy metal on sodalite and correlation of Langmuir\textsuperscript{163} and Freundlich adsorption\textsuperscript{164,165} isotherm are studied. Another type of sodalite, ultramarine blue was applied for manufacturing of the luxury and very expensive pigment used for artistic painting. The ultramarine blue was prized
for its intense deep colour and for the great thermal stability and resistance to fading. The pioneer work on ultramarine has been invented in the 1820s, J.B. Guimet and C.G. Gmelin. Ultramarine is a type of sodalite containing sulphur chromophore with general formula $\text{Na}_8[\text{AlSiO}_4]_6(\text{S}_2\text{S}_3)\text{_2}$. Its synthesis involves the alumino-silicate source as a kaolin, sulfur, sodium carbonate and reductive agents (charcoal, tar, etc.) at high temperature ($800–900 \, ^\circ\text{C}$) for a long time. Both natural and synthetic ultramarine exhibit the SOD structure and the chromophore sulfides (mostly $\text{NaS}_3$ and $\text{NaS}_2$) encapsulated in the $\beta$-cages is responsible for blue colour. Ultramarine and its analogs were obtained from kaolin$^{166-173}$, zeolites$^{174-184}$, and fly ash$^{185}$.

1.10 Scope of the Present Work:

Investigations on the micro-porous materials have recently become an area of special interest. Micro-porous materials can be used for variety of applications in diverse areas such as; ion exchange, catalysis, clusters compounds of insulators, semiconductor, gas separation, removal of heavy metals, adsorption and separation. The properties of these materials vary with the degree of composition. The simplicity of these materials makes them ideal systems to study phenomenon like host-guest interaction and variation in structural parameters as a function of their composition. In order to use these materials for future applications it is very important to characterize and study the structural properties of these materials. Natural sodalite formation takes place over a longer period of time, while the synthetic sodalites can be obtained in few hours or days. Closer inspection of sodalites leads to the realization that the sodalite lattice forms a convenient matrix for a variety of encapsulated guest and can be used for further applications. The
aim of the present work is to study the synthesis, structure and physicochemical properties of the alumino silicate and alumino-germanate sodalites.

The above brief review on earlier work shows that the bulk of work on alumino-silicate sodalite of the type, $\text{Na}_8[\text{AlSiO}_4]_6X_2$ (where $X=\text{Cl}^–, \text{NO}_3^–, \text{ClO}_4^–,…$etc.), is available, while only limited work is available on alumino-silicate mixed halide sodalite of the type $\text{Na}_8[\text{AlSiO}_4]_6\text{Cl}_{2-x}\text{Br}_x$ and $\text{Na}_{8-x}\text{Ag}_x[\text{AlSiO}_4]_6\text{Br}_{2-x}\text{I}_x$. The present studies enabled us to find different relationship among IR absorption band, the Al-O-Si angle and unit cell.

Further, to investigate the effect of substitution of silicon by germanium on structure of sodalite was also studied. Up to now, numbers of alumino-germanate version of zeolite with different framework topologies have been reported in literature. Here we describe our attempt to crystallize the alumino-germanate sodalite in its pure form. The present work was also undertaken to see the effect of organic solvent on crystallization of alumino-germanate halide sodalite. The purpose of this work is to find the experimental conditions under which sodalites can be directly synthesized. To our knowledge, however, no systematic studies of adsorption of heavy metal on the alumino-silicate sodalite have been carried out so far. This study investigated the chemical modification of F-class coal fly ash to an iodate enclathrated alumino-silicate sodalite, and is synthesized by hydrothermal treatment followed by fusion of coal fly ash with NaOH. Sorption behaviour of heavy metals (Cd$^{2+}$, Pb$^{2+}$, and Zn$^{2+}$) from aqueous solution on iodate sodalite was examined. The Freundlich and Langmuir isotherms are evaluated for iodate sodalite.
In the present study emphasizes on synthesis and characterization of intense blue ultramarine using coal fly ash was also carried out. Present work is also undertaken to develop alternative method of coal fly ash disposal or proper utilisation with emphasis on resource recovery. In this context, we have come to the conclusion that, there is need to find a new material that can work in harmony with nature using waste coal fly ash. A solution to this problem is use of coal fly ash for synthesis of intense blue ultramarine by green chemistry approach. The method allows accelerating and facilitating the synthesis process producing negligible gas emission but free from waste pollution.