EFFECT OF THERMAL TRANSFORMATION ON THE STRUCTURAL AND ELECTRICAL PROPERTIES OF DODECYLALKYLAMMONIUM INTERCALATED SODIUM-MONTMORILLONITE

M. Phil. Thesis

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A dissertation submitted to the Department of Physics, Bangladesh University of Engineering and Technology (BUET) in Partial fulfillment of the requirement for the degree of

MASTER OF PHILOSOPHY (M. Phil.) in Physics

by

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CANDIDATE’S DECLARATION

It is hereby declared that this thesis or any part of it has not been submitted elsewhere for the award of any degree or diploma.

Md. Kamal Hossain
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Dedicated to

My beloved Parents who have inspired and influenced me for higher study
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Abstract

In the present investigation Dodecylalkylammonium intercalated montmorillonite (DDA-MMT) has been synthesized by intercalating Dodecylalkylammonium into the interlayer spaces of Na-montmorillonite (Na-MMT) by ion exchange reaction at 80°C. Thermal transformation of DDA-MMT has been investigated by Thermogravimetric analysis and Differential Thermogravimetric analysis. X-ray Diffraction analysis and Scanning Electron Microscopy and Fourier Transform Infrared analysis of pre-heat-treated DDA-MMT samples were performed to understand the thermal transformation mechanism. Different microstructural parameters such as crystallite size, r.m.s. strain ($<\varepsilon^2>^{1/2}$) and layer disorder parameters such as variation of interlayer spacing ($g$), proportion of planes affected by variability defect ($\gamma$) have been calculated using X-ray line profile analysis of DDA-MMT pre-heat-treated at 30, 80, 120, 200, 300, 400 and 500°C. The value of basal spacing ($d_{001}$), FWHM, number of silicate layers stacked to form individual crystallite ($N$) have also been used for understanding the thermal transformation of DDA-MMT. Alternating Current electrical properties of DDA-MMT at room temperature and pre-heat-treated at different temperatures have also been investigated.
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<td>Association International Pour l’Etude des Argiles</td>
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<tr>
<td>ASA</td>
<td>1-Ascorbic Acid</td>
</tr>
<tr>
<td>CMS</td>
<td>Clay Minerals Society</td>
</tr>
<tr>
<td>CEC</td>
<td>Cation Exchange Capacity</td>
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<td>DDA</td>
<td>Dodecylalkylammonium</td>
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<td>R.D.F.</td>
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<td>r.m.s.</td>
<td>Root Mean Square</td>
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CHAPTER ONE

GENERAL INTRODUCTION

1.1 Definition of Clays and Clay Minerals
1.2 Properties of Clay Minerals
1.3 Structure and Classification of Clay Minerals
1.4 Structure of Montmorillonite
1.5 Characteristics of Montmorillonite
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1.1 Definition of Clays and Clay Minerals

The geologist, mineralogist, agronomist and engineers use the term ‘clay’ in different ways. However, the nomenclature committee of the Association International Pour l’Etude des Argiles (AIPEA) and the Clay Minerals Society (CMS) define the „Clay“ in following way [1].

"The term 'clay' refers to a naturally occurring material composed primarily of fine-grained minerals, which is generally plastic at appropriate water contents and will harden when dried or fired. Although clay usually contains phyllosilicates, it may contain other materials that impart plasticity and harden when dried or fire. Associated phases of clay may include materials that do not impart plasticity and organic matter."

The term “clay mineral” refers to phyllosilicate minerals and to minerals which impart plasticity to clay and which harden upon drying or firing. Minerals known to produce the property of plasticity are phyllosilicates. Because minerals are not defined according to their crystallite size, appropriate phyllosilicates of any grain size may be considered „clay minerals“. Likewise, clay minerals are not restricted, by definition, to phyllosilicates. If research reveals that a non phyllosilicate mineral imparts plasticity to clay and hardens upon drying or firing, this mineral is a „clay mineral”.

Generally, clays are composed of extremely small crystalline particles of one or more numbers of groups of minerals, known as clay minerals which can develop plasticity in combination with water. Most of the clay minerals are predominantly hydrous aluminium silicates. The aluminium atoms in some cases are replaced either wholly or partly by Mg, Na or Fe. Sometimes alkali and alkaline earth metals are also found to be present in some clay minerals.

Clay is a term used to describe a group of hydrous aluminium phyllosilicate (phyllosilicates being a subgroup of silicate minerals) minerals, that are typically less than 2µm in diameter. Clay consists of a variety of phyllosilicate minerals rich in silicon and aluminium oxides and hydroxides which include variable amounts of structural water. Clays are generally formed by the chemical weathering of silicate-bearing rocks by carbonic acid but some are formed by hydrothermal activity. Clays are distinguished from other small particles present in soils such as silt by their small size, flake or layered shape, affinity for water and high plasticity index. Clay is an abundant raw material which has an amazing variety of uses and properties that are largely dependent on their mineral structure
and composition. Other than the clay structure and composition, there are several additional factors which are important in determining the properties and applications of a clay. These are the non-clay mineral composition, the presence of organic material, the type and amount of exchangeable ions and soluble salts, and the texture [2].

1.2 Properties of Clay Minerals

Clay minerals are characterized by certain properties which includes [3] -

- a layer structure with one dimension in the nanometer range; the thickness of the 1:1 (TO) layer is about 0.7nm, and that of the 2:1 (TOT) layer is about 1nm,
- the anisotropy of the layers or particles,
- the existence of several types of surfaces: external basal (planar) and edge surfaces as well as interlayer surfaces,
- the ease with which the external, and often also the internal, surface can be modified (by adsorption, ion exchange, or grafting),
- Plasticity and hardening on drying or firing; this applies to most clay minerals.

1.3 Structure and Classification of Clay Minerals

It is well known that layer structured clay minerals are formed by the assemblage of tetrahedral sheets of composition $T_2O_5$ (where $T =$ tetrahedral cations, normally $Si^{4+}$, $Al^{3+}$, or $Fe^{3+}$) and octahedral sheet which consist of octahedral cations $Mg^{2+}$, $Al^{3+}$, $Fe^{2+}$, etc. In tetrahedral sheet, the individual tetrahedral are linked with neighboring tetrahedral by sharing three corners each (the basal oxygen) to form a hexagonal mesh pattern (Fig.1.1) [2]. The fourth tetrahedral corner (the apical oxygen) points in a direction normal to the sheet and at the same time forms part of an immediately adjacent octahedral sheet in which individual octahedra are linked laterally by sharing octahedral edges (Fig.1.2) [2]. The common plane of junction between the tetrahedral and octahedral sheets consist of the shared apical oxygens plus unshared OH groups that lie at the centre of each tetrahedral six fold ring at the same $z$-level as the apical oxygen’s. The smallest structural unit contains three octahedra. If all the octahedra are occupied i.e. have octahedral cations at their centers, the sheet is characterized as trioctahedral. If the two octahedral sites are occupied and the third octahedron is vacant, the sheet is characterized as dioctahedral. The assemblage of tetrahedral and octahedral sheet forms a unit layer and the superposition of
Fig. 1.1: Layer spacing and atomic structure of clays.

Fig. 1.2: Diagrammatic sketch of the structure of smectites.
these unit layers results in an overall structure of clay minerals. If the unit layer is formed
by sandwiching an octahedral sheet between two tetrahedral sheets the structure is known
as 2:1 layer type materials e.g. montmorillonite, vermiculite, palygorskite (Fig. 1.3) [2]. If
the assemblage formed by linking one tetrahedral sheet with one octahedral sheet is known
as a 1:1 layer e.g. kaolinite (Fig. 1.4) [2]. The main difference arises among these minerals
due to the presence of amount of negative layer charges which is generated by the
isomorphous substitution of Mg and Fe for Al in the octahedral sheet and to a lesser
extent, substitution of Si in the tetrahedral sheet by Al. These negative charges on the
layers are balanced by hydrated cations in the interlayer space (usually Mg\(^{2+}\), Na\(^{+}\), Ca\(^{2+}\)
etc). A typical classification of clay minerals is shown in Table 1.1.

1.4 Structure of Montmorillonite

Montmorillonite is a member of the smectic group of clay minerals with 2:1 type of layer
structure. There are several concepts present about the exact structure of montmorillonite.
In 1933 Hofmann et al. [4] first suggested the montmorillonite structure that was modified
by later suggestions of Magdefrau and Hofmann [5], Marshall [6] and Hendricks [7].
According to their suggestion montmorillonite is composed of units made up of two silica
tetrahedral sheets with a central alumina octahedral sheet. All the tips of the tetrahedrons
point in the same direction and toward the center of unit. The tetrahedral and the
octahedral sheets are combined so that the tips of the tetrahedron of such silica sheet and
one of the hydroxyl layers of the octahedral sheet from a common layer. The atoms
common to both tetrahedral and octahedral layer become O instead of OH. The layers are
continuous in a and b directions and are stacked one above the other in the c-direction
(Fig. 1.5).

In the stacking of the silica-alumina-silica units O layers of each unit are adjacent to an
oxygen layer of the neighboring units, with the consequence that it is very weak bond and
there is excellent cleavage between them. The outstanding feature of the montmorillonite
structure is that water and other molecules can enter between the unit layer easily, causing
the lattice to expand in the c-direction. The c-axis dimension of montmorillonite is,
therefore, not fixed but varies depending upon the condition of the surroundings. From
electron diffraction diagrams of oriented samples, Zvyagin and Pinsker [8] concluded that
the structure is monoclinic, with β = 90°54′. Nakahira [9] explained the tailed X - ray
diffraction as due to reason of local orderings, with random displacements of multiples of
Fig. 1.3: Diagrammatic sketch of the structure of palygorskite.

Fig. 1.4: Diagrammatic sketch of the structure of kaolinite.
Fig. 1.5: Layer spacing and atomic structure of montmorillonite.
Table 1.1: Classification of Clay Minerals.

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<thead>
<tr>
<th>Layer Type</th>
<th>Group (x = change per formula unit)</th>
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<td>1:1</td>
<td>Serpentine-kaolin (x≈0)</td>
<td>Serpentines kaolins</td>
<td>Chrysotile, antigorite, lizardite, amesite Serpentine, dictite, nacrite</td>
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<tr>
<td></td>
<td>Tales-pyrophyllit (x≈0)</td>
<td>Talcs</td>
<td>Talc, willemseite</td>
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<td></td>
<td>Smectite (x≈0.2-0.6)</td>
<td>Montmorillonites</td>
<td>Montmorillonite, beidellite, nontronite</td>
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<tr>
<td></td>
<td>Vermiculites (x≈0.6-0.9)</td>
<td>Trioctahedral vermiculities</td>
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<tr>
<td></td>
<td>Mica (x≈1.0)</td>
<td>Trioctahedral Micas</td>
<td>Phlogopite, biotite</td>
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<td></td>
<td>Brittle Mica (x≈2.0)</td>
<td>Micas</td>
<td>Lepidilite</td>
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<td></td>
<td>Chlorite (x variable)</td>
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<td>Clintonite, Anadite</td>
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<td></td>
<td>Sepiolite-palygorskite (x variable)</td>
<td>Sepiolite palygorskite</td>
<td>Sepiolite, Loughlinite palygorskite</td>
</tr>
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</table>
In order to explain cation-exchange capacity of montmorillonite, Marshall [6] and Hendricks [7] suggested the replacement of Al by Mg in the octahedral layer, each replacement creating one unit negative charge. This idea also explains common occurrence of magnesium in montmorillonite analysis. The general chemical formula of an ideal montmorillonite is:

\[(M_y\cdot nH_2O)(Al_{4-y}Mg_y)Si_8O_{20}(OH)_4\]

where M (M = Mg$^{2+}$, Na$^+$, Ca$^{2+}$ etc.) is the interlayer cations balance the negative charges which are by the isomorphous substitution of Mg$^{2+}$ and Fe$^{2+}$ for Al$^{3+}$ in the octahedral sheet; and Al$^{3+}$ for Si$^{4+}$ in the tetrahedral sheet. Besides the interlayer cations, the interlayer space of smectite group of clay minerals contains large amount of water molecules. In the above formula, the number of exchangeable cations have been taken as 2/3 unit per unit cell lateral the real quantity varies between the limits 0.1-0.2 which was shown by Foster [10]. According to Franzen et al. [11] it seems that montmorillonite structure is triclinic. There are still different concepts about the montmorillonite structure present since single-crystal photographs cannot be made to solve the exact structure of montmorillonite. But the generally accepted structure of montmorillonite is that which was suggested by Hofmann et al. [4] and modified by Magdefrau and Hofmann [5], Marshall [6] and Hendricks [7].

### 1.5 Characteristics of Montmorillonites

Important structural, physical and chemical characteristics of montmorillonite include [12-14]:

- 2:1 Layer structure clay
- Variable color, usually tan or greenish-gray
- Considerable lattice substitutions
- High layer charge
- Medium to high cation exchange capacity
- Very fine particle size and High surface area
- High sorptive capacity and viscosity
- Thixotropic
- Very low permeability
- Medium to high swelling capacity
- High green and dry compression strength
1.6 Applications of Montmorillonite

Clay minerals play an important role in various fields of scientific and technological interests. The study of clay minerals is of great interest to the agriculturists and soil scientist. The occurrence and properties of clay minerals govern the soil fertilization, plant nutrition and water retention capacity of the soil to a large extent. Hence such a study of clay minerals present in the soil is of special importance in agriculture. Besides agriculture, such study is also useful to the construction engineers. The physical properties of a soil largely depend on the prevalence and kind of clay minerals present in the soil. Therefore the nature of clay minerals present in the soil and their properties will largely responsible for the stability and strength of structures built on it. Clays are also very important in certain industries. In oil industry, certain clays have catalytic activity. They are also used as drilling muds. It is widely used in foundry industry for molding purposes. But of all industrial uses of clays, the use in ceramic industry stands first. It is the most essential and important raw material of ceramic industry.

Bentonite is clay generated frequently from the alteration of volcanic ash, consisting predominantly of smectite minerals, usually montmorillonite. Bentonite presents strong colloidal properties and its volume increases several times when coming into contact with water, creating a gelatinous and viscous fluid. The special properties of bentonite (hydration, swelling, water absorption, viscosity, thixotropy) make it a valuable material for a wide range of uses and applications. Montmorillonite, in case of industrial applications mainly known as bentonite, possibly was first used in making cosmetics in 1888, as foundry-sand in 1920 and it was first used as drilling mud in the late 1920s or early 1930s. Steel companies start to use bentonite as a bond for pelletized tectonic ore around 1950s. Besides these applications bentonite is used as a filtering agent for clarifying wine, water impedance, ingredients in cosmetics, animal feed, pharmaceuticals, colloidal fillers for certain types of paints, an additive to ceramic materials to increase plasticity, fire retarding materials and for many other purposes.

Besides the application intercalation of montmorillonite and polymer montmorillonite composites montmorillonite is being used in various disciplines in recent years. Oyama et al. [15] reported that it can be used as chemical sensor and backfill material in ground water exploration. Sazarashi et al. [16] have suggested that it can be used in nuclear waste management. Peker et al. have investigated [17] the adsorption of alkyl (C-13-15) benzylidimethylammonium chloride onto montmorillonite clay and suggested that it can be
used in cosmetic applications as well as environmental issues. Montmorillonites commercially known as bentonites have other applications are discussed below in brief:

**Foundry:** Bentonite is used as a bonding material in the preparation of molding sand for the production of iron, steel and non-ferrous casting. The unique properties of bentonite yield green sand moulds with good flow ability, compactability and thermal stability for the production of high quality castings.

**Cat Litter:** Bentonite is used for cat litter, due to its advantage of absorbing refuse by forming clumps (which can be easily removed) leaving the remaining product intact for further use.

**Pelletizing:** Bentonite is used as a binding agent in the production of iron ore pellets. Through this process, iron ore fines are converted into spherical pellets, suitable as feed material in blast furnaces for pig iron production, or in the production of direct reduction iron (DRI).

**Construction and Civil Engineering:** Bentonite in civil engineering applications is used traditionally as a thixotropic, support and lubricant agent in diaphragm walls and foundations, in tunneling, in horizontal directional drilling and pipe jacking. Bentonite, due to its viscosity and plasticity, also is used in Portland cement and mortars.

**Environmental Markets:** Bentonites adsorption/absorption properties are very useful for wastewater purification. Common environmental directives recommend low permeability soils, which naturally should contain bentonite, as a sealing material in the construction and rehabilitation of landfills to ensure the protection of groundwater from the pollutants. Bentonite is the active protective layer of geo-synthetic clay liners.

**Drilling:** Another conventional use of bentonite is as a mud constituent for oil and water well drilling. Its roles are mainly to seal the borehole walls, to remove drill cuttings and to lubricate the cutting head.

**Oils/Food Markets:** Bentonite is utilized in the removal of impurities in oils where its adsorptive properties are crucial in the processing of edible oils and fats (Soya/palm/canola oil). In drinks such as beer, wine and mineral water, and in products like sugar or honey, bentonite is used as a clarification agent.

**Agriculture:** Bentonite is used as an animal feed supplement, as a pelletizing aid in the production of animal feed pellets, as well as a flow ability aid for unconsolidated feed ingredients such as soy meal. It also is used as an ion exchanger for improvement and conditioning of the soil. When thermally treated, it can be used as a porous ceramic carrier for various herbicides and pesticides. It is used to improve growth performance of piglets.
and fish. Montmorillonite can be calcined to produce arcillite, a porous, calcined clay sold as a soil conditioner for playing fields and other soil products such as for use as bonsai soil.

**Pharmaceuticals and Cosmetics:** Montmorillonite clay is widely used in pharmacology. Bentonite is used as filler in pharmaceuticals, and due to its absorption/adsorption functions, it allows paste formation. Such applications include industrial protective creams, calamine lotion, wet compresses, and anti irritants for eczema. Personal care products such as mud packs, sunburn paint, baby and face powders, and face creams may all contain bentonite. Montmorillonite is widely used in pharmacology for a variety of other applications too, such as stabilization of suspensions and emulsions, viscosizing, adhesion to the skin, and tablet making.

**Medicinal:** For internal use, montmorillonite is effective in the treatment of irritable bowel syndrome. It is also used for the prevention of aflatoxicosis, and in the treatment of constipation. Also, a modified version inhibits intestinal absorption of cholesterol (nanotechnology research) and absorbs uric acid. It ameliorates hyperthyroidism of rats and mice. Montmorillonite is also used in other related research. Montmorillonite is proven to be effective in use as an adsorptive of heavy metals, toxins, and hazardous chemicals. For external use, montmorillonite has also shown its effectiveness. It has also shown itself useful for tissue engineering. In medicine, bentonite is used as an antidote in heavy metal poisoning. It is also used as drug carrier, or as part of a drug delivery system, such as for controlled drug release; including for gene delivery, and for drug targeting to specific tissues. It is also used for stability enhancement in drug and nutrient application.

**Antibacterial:** Antibacterial effects of montmorillonite are well demonstrated.

**Detergents:** Laundry detergents and liquid hand cleansers/soaps rely on the inclusion of bentonite, in order to remove the impurities in solvents and to soften the fabrics.

**Paints, Dyes and Polishes:** Due to its thixotropic (Thixotropy is the property of certain gels or fluids that are thick (viscous) under normal conditions, but flow (become thin, less viscous) over time when shaken, agitated, or otherwise stressed) properties, bentonite and organoclays function as a thickening and or suspension agent in varnishes, and in water and solvent paints. Its adsorption properties are appreciated for the finishing of indigo dying cloth, and in dyes (lacquers for paints & wallpapers).

**Paper:** Bentonite is crucial to paper making, where it is used in pitch control, i.e. absorption of wood resins that tend to obstruct the machines and to improve the efficiency of conversion of pulp into paper as well as to improve the quality of the paper. Bentonite
also offers useful de-inking properties for paper recycling. In addition, acid-activated bentonite is used as the active component in the manufacture of carbonless copy paper.

**Catalyst:** Chemically-modified clay catalysts find application in a diverse range of duties where acid catalysis is a key mechanism. Most particularly, they are employed in the alkylation processes to produce fuel additives. For instance, in the nucleophilic substitution, montmorillonite is utilized as solid Bronsted Acid.

**Removal of Lead:** For the efficient removal of Lead (ii), acid activated montmorillonite type of clay is widely demonstrated [18].

### 1.7 Organomodified Montmorillonite

As mentioned earlier that the structure of montmorillonite established by Hofmann et al. [4], Magdefrau and Hofmann [5], Marshall [6] and Hendricks [7], Hofmann and Hansdorf [19], MacEwan [20] consists of octahedrally co-ordinated cation-hydroxyl sheet (O) between two tetrahedrally co-ordinated cation oxygen sheets (T) (Fig.1.6) [2]. The montmorillonite layer consists of negative charges which are generated by the isomorphous substitution of Mg and Fe for Al in the octahedral sheet and to a lesser extent by substitution of Si in the tetrahedral sheet by Al. These negative charges are balanced by hydrate cations in the interlayer spaces and the most commonly associated interlayer exchangeable cations are K, Ca, Na etc. It is well known that the forces between the montmorillonite layers are very weak, and due to these weak interlayer forces free water molecules are highly present between the layers. Basically the distinct types of water molecules are present within the layer (i) free water molecules (ii) water molecules coordinated to the exchangeable cations and (iii) water molecules which is hydrogen bonded to the silicate surface [21]. The interesting feature of montmorillonite structure is that the interlayer cations can be replaced easily by either organic or inorganic molecules through a process called intercalation, which allows a continent method for making new composites suitable for different applications such as catalyst [22, 18], cosmetics [23], nuclear waste treatment [18] etc.

The intercalation of organic species into the interlayer galleries of montmorillonite has proved to be a fruitful area since it has many applications in different fields, for example, cosmetics, inks, polishes, chromatography [24], catalysis [2] etc. The literature has been extensively reviewed in this respect by Weiss [24] and Theng [25]. Hence here some important works and some recent development of montmorillonite intercalation...
Fig. 1.6: Intercalation process and cation exchange of montmorillonite.
compounds have been taken care of. Organophilic clay can be produced from normal hydrophilic clay by ion exchange with an organic cation such as an alkyl ammonium ion. For example, in montmorillonite, the sodium ions in the clay can be exchanged for an amino acid such as 12-aminododecanoic acid (ADA).

\[
\text{Na}^+\text{-CLAY} + \text{HO}_2\text{-R-NH}_3^+\text{Cl} \rightarrow \text{H}_2\text{OC-R-NH}_3^+\text{-CLAY} + \text{NaCl}
\]

Intercalation of alkylammonium ions into montmorillonite interlayers are reported since many years for the characterization of montmorillonites and determination of their layer charge [26-28]. According to Jordan[26], Brindley and Hofmann[27] and Lagaly and Wesis [26] short chain alkylammonium ions are arranged in monolayers and long-chain alkylammonium ions in bilayers into the montmorillonite interlayers. Bala et al. [29] have synthesized some organophilic montmorillonites from Na-montmorillonite using ammonium salts of methyl, propyl and butyl amine.

Lagaly et al. [30] reported that alkyl chain can be intercalated in a fashion of three layer kinked structures into highly charged Montmorillonite. Their investigations also reveal that monolayer has a basal spacing of ~13.6Å and the bilayer a spacing of ~17.7Å. Lagaly [31] investigated the large number of montmorillonite sample and by the intercalation of Alkylammonium, thereafter. He concludes that interlayer cation density of montmorillonite is not constant in all interlayer spaces and it varies from interlayer spaces to interlayer spaces within certain limit. His studies validity the assumption of charge heterogeneity reported by Mortland [32], Tettenhorst and Grim [33].

Vasofsky and Slabaugh[34], McAtee and Robbins [35], Stul and Uytterhoeven [36] have reported the quarternary Alkylammonium intercalated Montmorillonites and found them as adsorbents in gas-solid chromatography. Favre and Lagaly [37] intercalated the diethyl dioctadecylammonium, trimethyl tetradecylammonium and alkylammonium into Montmorillonite interlayers and determined the layer charge density. Their study shows that Montmorillonite develops certain selectivity against distinct quarternary alkylammonium ions when reacted with mixtures of such surfactants and the extent of selectivity depends on particle size. Montarges et al.[38] have intercalated Al-13-polyethyleneoxide complexes into montmorillonite clay.
Ohashi and Nakazawa [39] prepared an organo-clay composite by contacting Na-montmorillonite and humic acid in aqueous solution. Rutherford et al. [40] have calculated micropore volume of two montmorillonite (Saz-1 and SWy-1), each exchanged with Ca, Na, K, Cs and tetramethylammonium (TMA) ions and it was found that micropore volumes and surface areas of the samples increased with the size of exchanged cation TMA>Cs>K>Ca>Na. Han et al.[41] have prepared a new microprous sol pillared clay by the ion-exchange of the inter layer Na$^+$ ions of Montmorillonite with SiO$_2$-Fe$_2$O$_3$ mixed sol particles. Guiu et al. [42] have synthesized tantanium pillared montmorillonite family (Ta-PILC) from Na-montmorillonite clay. Salmon et al. [43] have prepared a super acid sulfonic clay (SASC) from trifluoromethanesulfonic and Montmorillonite type clays.

Breen et al. [44] prepared a range of organoclays containing tetramethylammonium, dodecyltrimethyl-ammonium, or octadecyltrimethyl-ammonium cations at the 25, 50 or 100% exchange level by acid leaching procedures. They have investigated the catalytic ability of acid-activated organoclays which provide reasonable levels of acidity, hydrophobicity and swelling ability for use with nonpolar reagents. Co-polymer intercalation was studied by Myung et al. [45]. They prepared nanocomposites by emulsion co-polymerization of styrene and acrylonitrile in the presence of sodium ion exchanged montmorillonite. This direct and one – step polymerization technique yielded nanocomposites intercalated with styrene – acrylonitrile co-polymer without occurrence of significant delamination of montmorillonite. The infrared spectra (IR) obtained from the purified products revealed the characteristics absorbances due to styrene, acrylonitrile and Montmorillonite. The X-ray diffraction pattern of the purified product also exhibited the increased basal spacing $d_{001}$ about 1.60nm. The transmission electron microscopy micrograph of unpurified products confirmed that the 1-2 nm sized silicate layers are arranged in good order.

Mandal et al. [46] reported the preparation of indium intercalation compounds of tantalum diselenide. These compounds have been studied for microstructural characterization using X-ray line profile analysis to find out information about crystallite size, r.m.s. strain, dislocation density, variability of interlayer spacing, fraction of planes affected by such defects, stacking fault probability, crystallite size anisotropy etc. To find out the information about the interatomic distances and coupling constants for different pairs of atoms, radial distribution function analysis (R.D.F.) has been used.
Aminopropyl - functionalized Magnesium phyllosilicate clay was synthesized by Patil et al. [47] and used as an exfoliated precursor for the intercalation of Myoglobin (Mb), Hemoglobin (Hb) or Glucose Oxide (GOx). Intercalation was achieved by exfoliation of the as synthesized organoclay in water followed by room temperature. X-Ray diffraction data of the resulting nanocomposites showed an expansion of the interlayer $d_{001}$ spacing from 1.6 nm in the parent organoclay to 4.3 and 6.4 nm for samples prepared with Mb and GOx, respectively, indicating that these biomolecules were successfully incorporated into the gallery regions. In both cases, FTIR and circular dichroism spectroscopies showed that secondary structures of the intercalated biomolecules were preserved. In addition, the redox and CO/O$_2$ binding properties of the intercalated Mb, and as well as the enzymatic activity of Gox, were retained in the protein-Organoclay nanocomposites was revealed by UV-vis spectroscopy. Bingxin et al.[48]for the first time has been intercalated the anti-inflammatory drug fenbufen into layered doubled hydroxides (LDHs) consist of cationic brucite-like layers and exchangeable interlayer anions. Because of their biocompatibility, some LDHs, such as Mg/Al, Zn/Al, Fe/Al and Li/Al-LDH, can be used as host materials for drug. The product has been characterized by powder X-ray diffraction (XRD), FTIR spectroscopy, element analysis and thermogravimetry (TG) and shows an expended LDH structure, indicating that the drug has been successfully intercalated into LDH. The dependence of the nature of the fenbufen intercalation process on conditions such as pH value, and chemical composition of the host has been systematically investigated. The interlayer distance in the intercalated materials increases with increasing pH value, resulting from a change in the arrangement of interlayer anions from monolayer to interdigitated bilayer.

Vreysen and Maes [49] have studied the sorption mechanism of Laurentian fulvic acid (FA) onto these poly (hydroxo aluminium) intercalated bentonites which was investigated at different pH values and at different ionic strengths (NaCl or CaCl$_2$)[42]. First two poly (hydroxo aluminium) intercalated Wyoming bentonites were prepared starting from two different aluminium pillaring solutions and then three mechanics contribute to the FA adsorption, depending on the pH and the nature (NaCl or CaCl$_2$) and ionic strength of the background electrolyte. In the presence of NaCl the FA sorption onto poly (hydroxo aluminium) intercalated bentonites can be mainly ascribed to ligand exchange between the amphoteric poly (hydroxo aluminium) hydroxyl groups and the deprotonated carboxylic groups of the FA. The FA adsorption due to ligand exchange reactions decreases with
increasing pH. Perez [50] examined the removal of the heavy metals from aqueous solution by chelating process using hydrotalcite-like compound $[\text{Zn}_2\text{Al(OH)}_6\text{edta.nH}_2\text{O}](\text{ZnAl-edta})$ was obtained from the precursor $[\text{Zn}_2\text{Al(OH)}_6\text{NO}_3\text{nH}_2\text{O}](\text{ZnAl-NO}_3)$, by the anion exchange method. The amount of Cu$^{2+}$, Cd$^{2+}$ and Pb$^{2+}$ adsorbed was monitored by atomic absorption technique at different contact time, pH and metal concentrations. The results indicate the very fast adsorption of the metal cations by ZnAl-edta reaching the equilibrium of the uptake reaction in two hours for Cu and Pb and 24h for Cd.

Aisawa et al. [51] have investigated the intercalation behaviour of nucleotides (AMP, ADP, ATP, CMP, GMP, and UMP) for the NO$_3$/Zn-Al and Mg-Al LDHs by ion-exchange reaction as well as the thermal stability of the AMP and CMP/LDHs. In the experiments for thermal stability of the AMP and CMP/LDHs, 80 - 90% of the intercalated nucleotide were stable at 100˚C, whereas 80-90% of the pure nucleotides were decomposed. The thermal stability of nucleotide, therefore, were found to be improved by the intercalation for the LDH interlayer space. According to XRD and FTIR, the solid products were found to have the layered double hydroxide (LDH) structure. The basal spacing (003) of the nucleotides/LDH was expanded to 1.38-1.67nm, and the absorption peak of NO$_3^-$ at 1385 cm$^{-1}$ was decreased with increasing the amount of nucleotides intercalated, indicating that nucleotides were intercalated for the LDH.

The intercalation of 1-ascorbic acid (ASA) into three kinds of layered double hydroxides, such as the Mg-Al, Mg-Fe and Zn-Al LDHs, has quantitatively been investigated by the calcination-rehydration (reconstruction) and coprecipitation methods by Sumio Aisawa[52]. The amount of ASA intercalated was considerably different by the LDH system that was estimated to be ca. 0.40 mol/mol-M$^{3+}$ for the Mg-Al and Mg-Fe system by the reconstruction method. The Zn-Al system was hardly restored to the LDH system by the rehydration reaction with the intercalation of ASA. ASA was also intercalated into the Mg-Al and Zn-Al LDHs by the coprecipitation method, while the intercalation of NO$_3^-$ was observed in the Mg-Fe LDH. The basal spacing of the solid products were found expended by the reconstruction method and also by the coprecipitation method which suggest that ASA was intercalated into the LDHs. Furthermore, the authors also observed that the intercalated ASA was easily deintercalated from the LDH interlayer space by the ion exchange method using CO$_3^{2-}$. It is expected that LDHs will be good host material for safe storage of vitamins.
1.8 Thermal Transformation of Organomodified Montmorillonite

The structure and composition of clay minerals are modified by heating. The concomitant changes in properties can be exploited for practical purposes. The actual temperatures at which changes occur vary greatly from one clay mineral to another, and even for different specimens within a given group. These temperatures also depend on the particle size and on the heating regime. Four principal temperature ranges in which significant changes occur in the structures of clay minerals may be distinguished.

- Temperatures sufficiently low to cause partial freezing of clay suspensions or pastes (−5°C): in this temperature range some of the water is converted into ice. However, even at a temperature as low as −60°C a significant amount of water remains in a liquid or semi-liquid state, forming a film that separates the mineral surfaces from the ice.

- Temperatures above dehydration but below dehydroxylation: when the temperature is raised from ambient to that of the onset of dehydroxylation, clays lose adsorbed and hydration water. As a result, the interlayer spaces collapse, while pore space in changed, and the acidity of the clay mineral surfaces and interlayers in substantially altered.

- Temperatures above dehydroxylation, but below those leading to complete destruction of the structure: the change occurring in this temperature range vary for different clay mineral groups. Dehydroxylation destroys the layer structure of trioctahedral, 2:1 type (T-O-T) minerals, whereas that of their dioctahedral counterparts is preserved. Kaolinite group minerals become amorphous to X-rays although some features of the structural framework are preserved.

- Temperatures at which new phases crystallise: dehydroxylated clays that do not turn amorphous to X-rays may become so on further heating, before high temperature phases crystallize. With trioctahedral caly minerals and palygorskite the interval between stages (3) and (4) is very short. Thus intermediate phases, if formed, may escape detection. When new phases crystallize, clay minerals lose their original identity although the crystallographic orientation of the products is frequently related to that of the starting material.

Clay minerals can be heated in different forms: (i) without any admixtures or pretreatment; (ii) mixed with various reagents before heating; (iii) after pretreatment such as acid-activation; and (iv) after preheating and pretreatment, for example, by acid-activation, and
subsequent reheating. In view of the great variety of starting materials and the many variables involved in the heating regime, a range of options is available for the thermal modification of clays. The ubiquitous impurities in natural clays may also play a part. The pre activation temperatures repaired to develop desirable properties, or prevent undesirable properties from developing very with different clay minerals. Some minerals are preferably used in the dehydrated, others in the dehydroxylated form. The following discussion is concerned with some properties of clay minerals are changed or modified by thermal treatment [53].

Exploiting the intercalation behavior of montmorillonite, it is being used in preparation of different types of polymeric clay nano-composites and hybrid materials with better physical, mechanical and thermal properties [54-62]. It is important to note that in the preparation of montmorillonite based materials and their suitability in different applications are predominantly govern by their physicochemical properties such as strength, plasticity, compressibility, pore structure etc. which are highly sensitive on the thermal variation [63-66]. Thus the thermal stability of organo-modified montmorillonite have been considered an important area of investigations to many researchers such as: Gao et al [67] have investigated the trimethyloctadecyl quaternary ammonium intercalated montmorillonite, Bala et al. [68] have investigated alkylammonium intercalated montmorillonite, Onal and Sarikaya [69] investigated methyltributylammonium, methyltriocytalammonium and di(hydrogenatedatallow)dimethylammonium intercalation compounds, Yermiyahu et al. [70, 71] have investigated napthylazonapthylammonium and napthylamonium-montmorillonite compounds. Along with other analysis thermal transformation studies of montmorillonite organically modified with amphiphilic octadecylalkylammonium [72], benzimidazole [73], chlorhexidine acetate [74], tributylammonium [74] have also been reported. Khan et al. [76] have intercalated Glycine ethylester with Na-montmorillonite and their thermal transformation, Lapides et al. have investigated hexadecyltrimethylammonium-montmorillonites [77], Abdallah and Yilmazer have investigated thermally stable phosphonium and imidazolium organo-montmorillonites [78].

1.9 Alternating Current Electrical Properties

Among the physical properties, the dielectric constant and electrical conductivity constitute the two most significant parameters in determining the electrical behavior of
clay minerals. These two structural sensitive properties depend on the chemical composition, structural disorders, and the presence of various types of impurities which are invariably present in the minerals. Hence the values of these properties may be used in the identifications and characterization of various clay minerals. Among the various clay minerals, montmorillonite have diverse commercial applications for peculiarity of structure and the existence of several useful physico-chemical properties, like microporosity, large surface area etc. These properties change considerably during dehydration due to the removal of various types of water present in them. However, it appears that no intensive attempt has been made so far to make an in-depth study of the electrical properties of clay minerals in general and of these two minerals and especially the organophilic clay minerals in particular.

Calvert [79] studied the variation of dielectric properties of montmorillonite saturated by diavalent cations in the temperature range -150°C to +30°C at frequencies ranging from 300 Hz to 10 kHz. His results show that the dielectric behavior depends on the nature of the compensating cations and on the water contents and seems to be closely related to swelling characteristics. The results of the study by Weiler and Chaussidon [80] on montmorillonite gels show that the conduction below 0°C is protonic while above 0°C the conduction is essentially due to absorbed cations. The dielectric behavior of the layer silicate clay minerals like kaolinite, montmorillonite, illite and hallosite was studied by Ficai [81] within the frequency range $3 \times 10^4$ Hz to $3 \times 10^6$ Hz following heating at 75°C, 140°C and 220°C. His results show that in this frequency range the dielectric properties are characteristics of the clay minerals. Bidadi et al. [82] investigated the dielectric behavior of Na-montmorillonite and Li-montmorillonite at frequencies <100 kHz. Their study revealed that dielectric constant depends on the frequency. They observed high dielectric constant for hydrated clays and ascribed to the Maxwell-Wagner effect. The results of Spauszus [83] who studied the changes in the dielectric constants of ethylene chloride, benzene and chlorobenzene upon addition of solids containing montmorillonite and kaolinite observed that two clay minerals gave characteristic values, with the change for air-dried montmorillonite being larger than that of kaolinite because of the interlayer water.

Some investigations on dielectric and electrical behavior of other clay minerals are also found in literature. Such as, Freund [84] attempted to follow the changes in the electrical resistance of metakaolin to the subsequent phases over a temperature range 700°C to
1300°C. Toussaint [85] and Fripiat and Toussaint [86] have studied the dehydroxylation process of kaolinite by measuring the changes in the ac conductivities in vacuum as well as under various water pressure, together with parallel infrared observations. They have put forward a concept of proton delocalization to explain their experimental results. The results of Nakahira [87], who studied the dc conductivities of kaolinite and serpentain, show that the temperature variation of resistivity of serpentain proceeds in an orderly way as compared to that of kaolinite. However, in general, his results for kaolinite are largely consistent with those of Fripiat and Toussaint [86]. Foldvari [88] in his review article on dielectric properties of various clay minerals has concluded that dielectric properties arise from different types of structural changes. The results of Bhattacherjee [89], who studied the variation of dielectric and loss of kaolinite and hallosite during dehydration, are found to be independent of frequency. The variation of dielectric constant with temperature was initially appreciable but at higher temperature the variation was found to be negligibly small. Chatterji [90, 91] based on his data on electrical conductivity of kaolinite has proved that it behaves like a p-type semiconductor. However, the results of Maiti and Freund [92] show that kaolinite exhibit marked proton conductivity at predehydration temperatures. Their conductivity results were supported by IR spectroscopic measurements.

Rizvi and Shakoor [93] studied the frequency dependent ac conductivity ($\sigma_{ac}$), dielectric constant ($\varepsilon'$) and loss factor ($\varepsilon''$) have been measured in the frequency range $10^0$–$10^6$ Hz in polyprrole/Na$^+$–montmorillonite (PPy/Na$^+$–MMT) clay nanocomposites. The nanocomposites were synthesized by in situ polymerization of pyrrole with varying amounts of Na$^+$–MMT from 0.2 to 1.0 wt% in the presence of FeCl$_3$·6H$_2$O in an aqueous medium. All three measured quantities; $\sigma_{ac}$, $\varepsilon'$ and $\varepsilon''$ increased with the increase in MMT content in the composites at all frequencies. The frequency dependence of $\sigma_{ac}$ displayed a low frequency region of almost constant conductivity below $10^4$ Hz, while above this frequency a rapid rise in $\sigma_{ac}$ was observed with the increase in frequency obeying a power law of frequency dependence with an exponent equal to 1. Both real and imaginary parts of the permittivity exhibited a low frequency dispersion which has been attributed to hopping of polarons and bipolarons in PPy and its composites.

Sengwa et al. [94] studied the dielectric dispersion behaviour of montmorillonite (MMT) clay nanoparticles colloidal suspension in poly(vinyl pyrrolidone)-ethylene glycol (PVP-EG) blends were investigated over the frequency range 20 Hz to 1 MHz at 30°C. The 0, 1,
2, 3, 5 and 10 wt% MMT clay concentration of the weight of total solute (MMT+PVP) were prepared in PVP-EG blends using EG as solvent. The complex relative dielectric function, alternating current (ac) electrical conductivity, electric modulus and impedance spectra of these materials show the relaxation processes corresponding to the micro-Brownian motion of PVP chain, ion conduction and electrode polarization phenomena. However, it is observed that there is a sharp difference in the dielectric behavior of clay minerals which do not have any interlayer water with that of the minerals containing interlayer water. The literatures further show that the dielectric constants are dependent on the interlayer water, and as amount of water varies on drying, corresponding dielectric constant also changes.

1.10 Microstructure and Layer Defects

Most of the studies concerning the thermal transformation of organo modified montmorillonite as discussed in earlier section mainly deal with the thermal stability of intercalated organic species and their decomposition mechanism. However, the physical and chemical properties such as rheology, surface area, cation exchange capacity, etc. of a substance may strongly depend on microstructural parameters such as crystallite size, strain and different structural defects. It appears that having the knowledge on microstructure and structural defects can give better insight for understanding the structure, properties and modeling the applications of the materials. So, the studies on microstructure and structural defects and their variation in different physiochemical environment are considered an important area of investigations [95-99].

The microstructure and structural defects of clays and clay based materials are highly sensitive on their thermal variation. Thus the variation of microstructural parameters such as crystallite size, r.m.s. strain and structural defects of clay minerals with variation of temperature have been studied by many researchers. The variability defects of kaolinite and their variation with temperature have been studied by Mitra and Bhattacherjee [100] and De et al. [101]. Lokanatha and Bhattacherjee have studied the variation of crystallite size and layer disorder of palygorskite [102]. Bala et al. have investigated the thermal variation of microstructural and layer disorder parameters of vermiculite [103], and montmorillonite [104, 105]. However, the studies on the variation of microstructure and structural defects of organoclays during thermal transformation are still lack in literatures. Thus in the present study an organoclay termed as DDA-MMT has been synthesized and
different microstructural parameters such as crystallite size, variation of interlayer spacing ($g$), proportion of planes affected by variability defect ($\gamma$) and r.m.s. strain ($<e^2>^{1/2}$) have been investigated. The XRD line profile technique has been used to calculate these parameters. The value of basal spacing ($d_{001}$), FWHM, number of silicate layers stacked to form individual crystallite (N) have also been used for understanding the thermal transformation of DDA-MMT.

### 1.11 Aim and Objectives of the Present Work

Potential uses of MMT are the consequence of their properties such as plasticity, swelling, ion exchange, density, compaction etc. which are mainly governed by the presence of interlayer materials. The interlayer materials interact with the environment and determine its suitability and stability for various applications. In most of the industrial uses of these clays, they are either subjected to heat treatment or to simple dehydration at ordinary atmospheric condition. In view of these facts, the effect of heat treatment on clay minerals as well as clay-based products is considered to constitute an important field of investigation. Thus the stability of interlayer materials and knowing interlayer environment and the consequent changes in their structure and physical properties are of great importance to the users of MMT clay. Therefore the study of thermal transformation and consequent changes in their structural and physical properties are of considerable value to the users of clays. The results of such investigations are very much important in understanding the thermal behavior of the clays and interpreting them to adjust the industrial operations involved in their applications. The review in the previous sections shows MMT usually form intercalation compounds with various aliphatic amines in the formation of organophilic nature mainly known as organophilic MMT. These organophilic compounds are used in different areas as mentioned earlier. However, the thermal stability of intercalated species plays an important role to determine their proper uses. Thus the present work attempts to intercalate Na-montmorillonite using dodecylalkylammonium (DDA)to produce organophilic compound and studying their thermal transformation mechanism. Based on the literatures, the present work therefore aims at the following objectives –

- Intercalation of DDA into Na-MMT interlayers by ion exchange reaction.
Investigations on thermal transformation of intercalated compound by thermal analysis techniques such as thermogravimetric analysis (TGA) and differential thermogravimetric (DTG) analysis.

Studies by X-ray diffraction line profile analysis of DDA-MMT heat treated at 80, 120, 200, 300, 400 and 500°C to explore the thermal transformation mechanism of the compound.

Analysis of the XRD Profile on the variation of different microstructural parameters like crystallite size, interplanar spacing, microstructural strain, variation of interlayer spacing during thermal transformation of intercalated compound.

Investigation of the decomposition of interlayer organic species of DDA-MMT heat treated at different temperature by FTIR and SEM techniques and correlation of results with other studies.

Investigations of the Alternating electrical properties of intercalated compounds and their variation with decomposition of interlayer dodecylammonium of DDA-MMT.
References


CHAPTER TWO
THEORETICAL BACKGROUND

2.1 X-ray Diffraction
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2.1 X-ray Diffraction

2.1.1 General Principle

X-ray diffraction (XRD) is the versatile, non-destructive analytical method to analyze material properties like phase composition, structure, texture and many more of powder samples. Identification of phases is achieved by comparing the X-ray diffraction pattern obtained from an unknown sample with patterns of a reference database. The main analysis in the material science is microstructural of the material, including properties like crystallite size, phase, preferred orientation effects and residual stress in polycrystalline engineered materials, optimization of fabrication parameters for wear resistant ceramics and biomaterials, etc.

In an ideal crystal, the atoms or molecules arrange themselves in a regular three dimensional pattern which can be obtained by a three dimensional repetition of a certain unit pattern. This simplest volume which has all the characteristics of the whole crystal and which completely fills space is called the unit cell. Since x-rays were electromagnetic waves of wavelength about equal to the inter-atomic distance in crystals, then it should be possible to diffract x-rays by means of crystals. When a beam of monochromatic x-ray of wavelength $\lambda$ falls on a crystal, at an angle $\theta$, called Bragg angle, it is scattered by the individual atoms which are arranged in sets of parallel layers. Each atom becomes a source of scattered radiations and there are certain sets of planes which are particularly rich in atoms. The combined scattering of X-rays from these planes can be looked upon as reflections from these planes. It is due to the presence of such sets of parallel that a crystal acts as reflection grating. For certain glancing angles, reflections from these sets of parallel planes are in phase with each other and produce diffraction pattern. In fact the angle at which the Bragg’s law (Eq.2.1) is satisfied diffraction pattern is produced.

\[
2dsin\theta = n\lambda
\]  

Bragg’s Law: \hspace{1cm} (2.1)

Here, $d = \text{interplanar spacing}; \theta = \text{Bragg’s angle}; \lambda = \text{wavelength of the X-ray used}; n = \text{order of diffraction}. \hspace{1cm}$

The schematic diagram of Bragg’s reflection and diffractometer where the Bragg’s reflection is materialized has been shown in Fig. 2.1 and Fig. 2.2 respectively [1].

2.1.2 X-ray Line Profile Analysis

There are different types of factors which affect the intensity profile recorded by a diffractometer. Some of them related to the inherent structural properties and defects of the
Fig. 2.1: An incident radiation is reflected by the lattice structure of a crystal and will interfere constructively if the Bragg law is obeyed.

Fig. 2.2: A simple representation of Bragg Brentano Diffractometer.
materials and others are purely different types of errors. Thus it is necessary to take proper
care not only to record the observed reflection but also to correct the observed profile for
the various factors to cover the pure defect profile. The problem now is to separate the
effects due to different types of defects and then to identify as well as estimate the extent
and distribution of each type of defect. Assuming the defects to be unrelated to one
another, the observed diffraction profiles due to individual defects in that case become
problem of deconvolution. The different mathematical parameters of a profile and the
methods used to separate the contribution of individual defects in these parameters are
described below:

(a) **Centroid** (< 2θ >)

Wilson [2] introduced centroid or first moment as a measure of the position of an X-ray
diffraction line which is defined as

\[
< 2θ > = \frac{\int (2θ) I(2θ) d(2θ)}{\int I(2θ) d(2θ)}
\]  
(2.2)

The advantage of using this parameter is that it follows simple additivity law i.e. the
centroid C of a profile generated by the effect of N aberrations or physical functions C₁, C₂, ..., C₇ is their sum i.e.,

\[
C = \sum_{i=1}^{N} C_i
\]  
(2.3)

(b) **Half Intensity Width (β₁/₂)**

It is defined as the width of a diffraction profile at points of half maximum
intensity. Scherrer [3] was the first to observe a dependence of half intensity width β₁/₂ of a
diffraction profile on the crystallite size P of the diffracting crystallites and obtain the
relations for β₁/₂ in radians as

\[
β_{1/2} = \frac{K}{P \cos θ_0}
\]  
(2.4)

where  is the wavelength of the X-rays used and θ₀ the Bragg angle. K is a constant
which depends on the shape of the crystallite. Warren [4], Bragg [5] and other workers
have calculated the values of K for different cases. Brindley [6], Stokes and Wilson [7],
Megaw and Stokes [8] and others investigated relationships between lattice strain and the
half intensity width and observed in many cases a linear relationship between β₁/₂ and
tanθ₀ instead of secθ₀ as determined by Scherrer's equation for crystallite size only.
(c) Integral Breadth (\(\beta\))

Laue [9] introduced the idea of integral width defined by

\[
\beta = \frac{\int I(2\theta)d(2\theta)}{I_{\text{max}}} \quad (2.5)
\]

where \(I(\theta)\) is the intensity at angle \(\theta\) and \(I_{\text{max}}\) is the maximum value of the intensity distribution curve. Stokes and Wilson [8] showed that \(K\) in Eq. 2.4 becomes equal to unity if \(\beta_{1/2}\) is replaced by the integral width of \(\beta\) and \(P = \frac{1}{V} \int_{-T}^{T} V(t) dt\). Here \(V(t)\) is the volume common to the crystallite and its 'ghost' displaced by a distance 't' in the \((hkl)\) direction, \(\pm T\) are the limiting values of 't' when \(V(t)=0\). Thus \(\beta = \frac{\lambda}{p \cos \theta}\) for crystallite size only.

(d) Fourier Coefficient \([A(t)]\)

Warren and Averbach [10] have introduced the method of Fourier coefficients for studying line profile analysis. On a suggestion due to Stokes and Wilson [7], Warren and Averbach [10] considered a \((hkl)\) reflection as \((001)\) reflection when referred to another set of axes. As the intensity distribution is a function in reciprocal space, its Fourier transform is then a function in Patterson's space and hence related to some real length in the crystal. Warren and Averbach [10] identified such real length 'l' with 'na' where \(n\) is the order of the Fourier transform and 'a' the lattice distance in the 001 direction. When the observed profile is due to both small crystallite size and strain, the observed Fourier coefficient \(A(t)\) will be a product of crystallite size term \(A^0(t)\) and the strain term \(A^S(t)\). Warren and Averbach [10] derived an expression for the strain term assuming Gaussian distribution as

\[
A^S(t) = \exp[-2\pi^2t^2 <Z^2_i>] \quad (2.6)
\]

Where \(<Z^2_i>\) is the mean square displacement of unit cells 'na' apart along perpendicular to the reflecting planes. Thus

Z

\[>L<K_{\text{sd}}=4\]

\[A(t) = A^0(t)\exp[-2\pi^2t^2 <Z^2_i>] \quad (2.7)\]

If the strain distribution is of Cauchy type then the relation is as -

\[A(t) = A^0(t)\exp[-2\pi^2t^2 <\frac{Z^2_i}{lc}>] \quad (2.8)\]

Where \(c\) is the cut off strain in Cauchy strain profile.
(e) Variance \((W)\)

Touranie [11] introduced the second moment as a measure of line broadening. He showed that variance of the crystallite size profiles has the physical significance of being the harmonic mean of the crystallite size. The most important and advantageous property of this method is that variance are additive and therefore the variance of the line profile can be taken simply as the sum of those due to defect, crystallite size and geometrical broadenings. That the variances are additive, has been noted by other workers. They have used standard deviation as a measure of the line broadening.

In a series of papers Wilson [12-14] has discussed the physical significance of variance or the second moment about the mean, defined by

\[
W_{\phi \theta} = \int \frac{(2 \theta - 2 \bar{\theta})^2 I(2 \theta) d(2 \theta)}{I(2 \theta) d(2 \theta)}
\]

as a measure of line broadening due to crystallite size, strain, mistake and dislocations. He derived a relation for variance in terms of the diffraction angle for crystallite size as

\[
W_{\phi \theta} = \frac{K \lambda \sigma}{2 \pi^2 P \cos \theta} - \frac{L^2}{4 \pi^2 P^2 \cos^2 \theta_0}
\]

where \(\sigma\) is the angular range over which the intensity distribution is applicable, \(P\) is the crystallite size, and \(K, L\) are constant for a given crystallite shape.

For strain, \(W = 4 \tan \theta\) (variance of strain) \(2.11\)

The variance like the centroid possesses the advantage of mathematical additivity. From the property of convolution it can be shown that the mean-square breadth of the resultant line profile is simply equal to the algebraic sum of the mean square breadth of the component profiles.

2.1.3 Microstructural and Layer Disorder Parameters

Layer disorder like variability of interlayer spacing is best identified by asymmetrical broadening of reflections of type \((00l)\). These types of disorder are studied mainly for layer structured materials like clay minerals [15], dichalcogenides [16, 17], etc.

Assuming the line profile to be due to crystallite size, strain and faulting of the type of interlayer spacing the variance of the line profile is given by

\[
W = W_p + W_d
\]

(2.12)
where $W_p, W_s$ and $W_D$ are the second moments of the above three effects respectively. Substituting of the results of Mitra and Bhattacherjee [15] yields

$$W_{(2\theta)} = \frac{\Delta(2\theta)}{2\pi^2 p' \cos \theta} + \frac{S^2}{\cos^2 \theta}$$  \hspace{1cm} (2.13)

where

$$S = \frac{[<e^2> - \frac{\beta_d^2}{\pi^2}]}{d^2}$$  \hspace{1cm} (2.14)

and $p'$ is the apparent crystallite size which is obtained by the method of variance and $p$ is the true crystallite size as determined by the method of Fourier analysis and both are related as

$$\frac{1}{p'} = \frac{1}{p} + \frac{\beta_d}{d}$$  \hspace{1cm} (2.15)

and $\beta_d$ is the integral width of the defect profile. Thus a plot of $W_{(2\theta)}$ versus $\Delta(2\theta)$ will be linear and the slope will give apparent crystallite size and the intercept $[<e^2> - \frac{\beta_d^2}{\pi^2}]$. Using the Fourier line shape analysis technique true crystallite size $p$ is determined. Thus knowing the values of $p$ and $p'$ the value of $\beta_d$ can be obtained.

If $g$ be the mean fractional change in the interlayer distance in the direction of $d(00l)$ and $\gamma$ be the transition probability i.e. the proportion of the planes affected by such disorder, then defect profile from a layer structure as shown by Wilson is given by

$$I(\omega) = NF^2 \left[ \frac{2\gamma(1 - \cos 2\pi lg)}{\gamma^2(1 - \cos 2\pi lg)^2 + (2\pi\omega + \gamma \sin 2\pi lg)^2} \right]$$  \hspace{1cm} (2.16)

where $F$ is the structure amplitude of a layer for the given direction and $N$ is the number of layers. The intensity is measured at a point in the reciprocal space corresponding to a non integral index.

It follows from the above equation that the intensity maximum will be shifted ($\Delta$) from the middle of the $\omega$ interval i.e. centroid by amount

$$\Delta = \left(\frac{\gamma}{2\pi}\right) \sin 2\pi lg$$  \hspace{1cm} (2.17)

Moreover the integral width $\beta_d$ is given by

$$\beta_d = \left(\frac{\gamma}{2}\right)(1 - \cos 2\pi lg)$$  \hspace{1cm} (2.18)

From these equations one can write

$$g = \frac{1}{\pi d \cot^{-1} \frac{\pi \Delta}{\beta_d}}$$  \hspace{1cm} (2.19)
and \[ \gamma = \frac{\beta_d}{\sin^2(\pi \lambda g)} \]  

(2.20)

The peak shift \( \Delta \) in this case is determined following the method followed by Srivastava et al. [17, 18].

### 2.2 Thermal Analysis

One of the widely used thermal analysis techniques is thermogravimetric analysis (TGA) technique. Thermogravimetric analysis is a technique in which the mass of a substance is monitored as a function of temperature or time as the sample specimen is subjected to a controlled temperature program in a controlled atmosphere. It is a technique in which, upon heating a material, its weight increases or decreases. TGA measures a sample’s weight as it is heated or cooled in a furnace.

Thermogravimetry (TG) is the branch of thermal analysis which examines the mass change of a sample as a function of temperature in the scanning mode or as a function of time in the isothermal mode. There are some very important exceptions which include desorption, absorption, sublimation, vaporization, oxidation, reduction and decomposition. TG is used to characterize the decomposition and thermal stability of materials under a variety of conditions and to examine the kinetics of the physicochemical processes occurring in the sample. Thermogravimetric curves are characteristic for a given polymer or compound because of the unique sequence of the physiochemical reaction that occurs over specific temperature ranges and heating rates and are function of the molecular structure. TG curves are normally plotted with the mass change (\( \Delta m \)) expressed as a percentage on the vertical axis and temperature (\( T \)) or time (\( t \)) on the horizontal axis. A schematic representation of a TGA instrument has been shown in Fig.2.3 [19].

### 2.3 Fourier Transform Infrared Spectroscopy

#### 2.3.1 General Principle

IR spectroscopy is an extremely effective method for determining the presence or absence of a wide variety of functional groups in a molecule. It measures the different IR frequencies by a sample positioned in the path of an IR beam and it reveals information about the vibrational state of molecule. The main goal of IR spectroscopic analysis is to determine the chemical functional groups in the sample. Different functional group
Fig. 2.3. Schematic diagram of a TGA instrument.
absorbs characteristic frequencies of IR radiation and its absorption results due to the changes in vibrational and rotational status of the molecules. Actually a molecule when exposed to radiation to produce by the thermal emission of a hot source (a source of IR energy), absorbs only at frequencies corresponding to its molecular modes of vibration in the region of the electromagnetic spectrum between visible (red)and short waves (micro waves). These changes in vibrational motion give rise to bands in the vibrational spectrum; each spectral band is characterized by its frequency and amplitude. The absorption frequency depends on the vibrational frequency of the molecules, whereas the absorption intensity depends on how effectively the infrared photon energy can be transferred to the molecule, and this depends on the change in the dipole moment that occurs as a result of molecular vibration. As a consequence, a molecule will absorb infrared light only if the absorption causes a change in the dipole moment. Thus all compounds except for element diatomic gases such as N\textsubscript{2}, H\textsubscript{2}, and O\textsubscript{2} have infrared spectra and most components present in a flue gas can be analyzed by their characteristic infrared absorption. Furthermore, using various sampling accessories, IR spectrometers can accept a wide range of sample types such as gases, liquids and solids. Thus, IR spectroscopy is an important and popular tool for structural elucidation and compound identification.

### 2.3.2 Infrared Frequency Range

Infrared radiation spans a section of the electromagnetic spectrum having wave numbers from roughly 3000 to 10 cm\textsuperscript{-1} or wavelength from 0.78 to 1000 \( \mu \text{m} \). IR absorption positions are generally presented as either wavenumbers \( \bar{v} \) or wavelengths \( \lambda \). Thus, wavenumbers are directly proportional to frequency, as well as the energy of the infrared (IR) absorption. In the contrast, wave lengths are inversely proportional to frequencies and their associated energy. Wavenumbers and wavelengths can be inter-converted using the following equation:

\[
\bar{v}(\text{cm}^{-1}) = \frac{I}{(\mu \text{m})} \times 10^4
\]  
(2.21)

\[
A = \log_{10}\left(\frac{I}{I_0}\right) = \log_{10}\left(\frac{T}{T_0}\right)
\]  
(2.22)

Where, \( A = \) Absorbance, \( T = \) Transmittance, \( I_0 = \) Intensity of incident light and \( I = \) Intensity of emerged light.
The IR region is commonly divided into three smaller areas: near IR, Mid IR and far IR. The region of most interest for chemical analysis is the mid-infrared region (4000cm\(^{-1}\) to 10 cm\(^{-1}\)) which corresponds to changes in vibrational energies within molecules. The far infrared region (400cm\(^{-1}\) to 10cm\(^{-1}\)) is useful for molecules containing heavy atoms such as inorganic compounds but requires rather specialized experimental techniques. The far and near IR are no frequently employed because only skeletal and secondary vibrations (overtones) occur in these regions producing spectra that are difficult to interpret.

2.3.3 Infrared Absorption

At temperatures above zero, all the atoms in 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. For a molecule to absorb IR, the vibrations or rotations within a molecule must cause a net change in the dipole moment of the molecule. The alternating electrical field of the electromagnetic radiation interacts with fluctuations in the dipole moment of the molecule. If the frequency of the radiation matches the vibrational frequency of the molecule then radiation will be absorbed, causing a change in the amplitude of molecular vibration. The energy of a molecule consists of transnational, rotational, vibrational and electronic energy

\[ E = E_{\text{electronic}} + E_{\text{vibrational}} + E_{\text{rotational}} + E_{\text{translational}} \]  \hspace{1cm} (2.23)

Translation energy of a molecule is associated with the movement of the molecule as a whole, for example in a gas. Rotational energy is related to the rotation of the molecule, whereas vibrational energy is associated with the vibration of atoms within the molecule. Finally, electronic energy is related to the energy of the molecule’s electron.

Like radiant energy, the energy of a molecule is quantized too and a molecule can exist only in certain discrete energy levels. Within an electronic energy level a molecule has many possible vibrations energy levels. The vibration energy of a molecule is not determined by the orbit of an electron but by the shape of the molecule, the masses of the atoms and eventually by the associated vibrational coupling. For example, simple diatomic molecules have only one bond allowing only stretching vibrations. More complex molecules may have many bonds, and vibrations can be conjugated. The atoms in a CH\(_2\) group, commonly found in organic compounds, can can vibrate in six different ways:
symmetrical and antisymmetrical stretching, scissoring, rocking, wagging and twisting. The major types of molecular vibrations are stretching and bending. Infrared radiation is absorbed and the associated energy is converted into these types of motions. The absorption involves discrete, quantized energy levels. However, the individual vibrational motion is usually accompanied by other rotational motions. These combinations lead to the absorption bands, not the discrete lines, commonly observed in the mid IR region.

The IR spectrum of a clay mineral is sensitive to its chemical composition, isomorphous substitution and layer stacking order. This makes Fourier Transform Infrared (FTIR) spectroscopy, the most informative single technique for assessing the mineralogy and crystal-chemistry of a clay mineral sample. The absorption of IR radiation by clay minerals depends critically on atomic mass, and the length, strength and force constants of interatomic bonds in the structures of these minerals. Absorption is also influenced by the overall symmetry of the unit cell, and the local site symmetry of each atom within the unit cell. Since theory alone gives only limited crystallo-chemical information, the interpretation of IR spectra is generally done by empirically assigning the observed signals to vibrational modes. Structural investigations of well-characterized families of natural and synthetic clay minerals played an essential role in relating spectral features to mineral structures. The monograph by Farmer [20] provides one of the most useful texts on the IR spectra of clay minerals.

2.4 Alternating Current Electrical Properties

The capacitance of parallel plate capacitor having a dielectric medium is expressed as

\[ C = \frac{\varepsilon_0 \varepsilon' A}{d} \]  

(2.24)

where \( \varepsilon_0 \) is the permittivity of free space, \( \varepsilon' \) is the dielectric constant of the medium, \( A \) is the surface area of each of the plates or electrodes and \( d \) is the thickness of the dielectric.

A real capacitor can be represented with a capacitor and a resistor. The parameters such as angular frequency (\( \omega \)) of the applied field, the parallel resistance \( R_p \), Parallel capacitance \( C_p \) and the series resistance \( R_s \) and series capacitance \( C_s \) are related to the dielectric constant \( \varepsilon' \), dielectric dissipation factor \( \varepsilon'' \) and loss tangent as :

\[ \varepsilon' = \frac{C_p}{C_0} \]  

(2.25)
The ac conductivity $\sigma_{ac}$ was calculated using eq \(\text{a}\).

$$\sigma_{ac} = \frac{G_p d}{A}$$  \hspace{1cm} (2.28)

The dependence of ac conductivity $\sigma_{ac}$ on frequency may be described by the power law \[26\]:

$$\sigma_{ac}(\omega) = A\omega^n$$  \hspace{1cm} (2.29)

where $A$ is a proportionality constant and $\omega$ ($= 2\pi f$, $f$ is the linear frequency) is the angular frequency and is the exponent, which generally takes the value less than unity for Debye type mechanism and is used to understand the conduction/relaxation mechanism in amorphous materials.

The dielectric behavior of a material is usually described by Debye dispersion equation \[21, 22\]:

$$\varepsilon^*(\omega T) = \varepsilon' - i\varepsilon''$$  \hspace{1cm} (2.30)

Where $\varepsilon'$ is the complex dielectric permittivity, $\varepsilon'$ (energy dissipated per cycle) is the real part of complex dielectric permittivity and $\varepsilon''$ (energy stored per cycle) is the imaginary part of the complex dielectric permittivity.

$$\varepsilon' = \varepsilon_s + \frac{\varepsilon_s - \varepsilon_{\infty}}{1 + \omega^2 \tau^2}$$  \hspace{1cm} (2.31)

$$\varepsilon'' = \frac{(\varepsilon_s - \varepsilon_{\infty})\omega\tau}{1 + \omega^2 \tau^2}$$  \hspace{1cm} (2.32)

where $\varepsilon_s$ is the static dielectric constant, $\varepsilon_{\infty}$ is the high frequency dielectric constant and the quantity $\tau$ is a characteristic time constant, usually called dielectric time relaxation time, it refers to a gradual change in the polarization following an abrupt change in applied field.

The dielectric loss tangent is expressed by

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'}$$  \hspace{1cm} (2.33)

The graphs of $\varepsilon'$ and $\varepsilon''$ against frequency of the applied field (logarithmic scale) through the dispersion regions show that the maximum loss value occurs when $\omega\tau = 1$, ...
corresponding to a critical frequency $\omega_{max} = \frac{1}{T}$, and location of this peak provides the easiest way of obtaining the relaxation time from the experimental results.

2.5 Scanning Electron Microscopy

2.5.1 General Principle

The scanning electron microscope (SEM) is the most widely used type of electron microscope as electron beam instruments. It examines microscopic structure by scanning the surface of materials. An SEM image is formed by a focused electron beam that scans over the surface area of a specimen. Perhaps the most important feature of an SEM is the three-dimensional appearance of its images because of its large depth of field. For example, the depth of field can reach the order of tens of micrometers at $10^3 \times$ magnifications and the order of micrometers at $10^4 \times$ magnifications. SEM owes its popularity to the versatility of its various modes of imaging, the excellent spatial resolution of its images, the ease with which the micrographs that are generated can be interpreted, the modest demands that are made on specimen preparation, and its user-friendliness.

The SEM is a mapping, rather than an imaging, device and so is a member of the same class of instruments as the facsimile machine, the scanning probe microscope, and the confocal optical microscope. The sample is probed by a beam of electrons scanned across the surface. Radiations from the specimen, stimulated by the incident beam, are detected, amplified, and used to modulate the brightness of a second beam of electrons scanned, synchronously with the first beam, across a cathode ray tube display (Fig. 2.4). If the area scanned on the display tube is $A \times A$ and the corresponding area scanned on the sample is $B \times B$ then the linear magnification $M = A/B$. The magnification is therefore geometric in origin and may be changed by varying the area scanned on the sample. The arrangement makes it possible for a wide range of magnifications to be obtained, and allows rapid changes of magnification since no alterations to the electron-optical system are required. There is no rotation between the object and image planes, and once the instrument has been focused on a given area the focus need not be changed when the magnification is varied. To a first approximation the size of the finest detail visible in the image will be set by the size of the probe scanning the specimen. Multiple detectors can be used to collect several signals simultaneously which can then be displayed individually, or combined, in perfect register with each other. It is this capability in particular which makes the SEM so
Fig. 2.4. Schematic diagram of an SEM instrument.
useful a tool since multiple views of a sample, in different imaging modes, can be collected and compared in a single pass of the beam.

2.5.2 Instrumentation

An SEM of an electron gun and a series of electromagnetic lenses and apertures as shown in Fig.2.4. In an SEM, the electron beam emitted from an electron gun is condensed to a fine probe for surface scanning. Advanced SEM systems use a field emission gun because of its high beam brightness. Beam brightness plays an even more important role in imaging quality in an SEM. When high-energy electrons strike a specimen, the electrons are scattered by atoms of the specimen. Electron scattering results in a change of direction of travel of electrons under the specimen surface. Electron trajectories during scattering in a specimen are schematically. The interaction between electrons and specimen atoms occurs within a certain volume under the specimen surface. Both SEs and BSEs generated by scattering are used as signal sources for forming SEM. The zone is usually described as pear-shaped, and its size increases with the energy of incident electrons in the probe. SEs are the products of inelastic scattering, and they have an energy level of several kV. In the interaction zone, SEs can escape only from a volume near the specimen surface with a depth of 5–50 nm, even though they are generated in the whole pear-shaped zone. In contrast, BSEs are the products of elastic scattering, and they have an energy level close to that of incident electrons. Their high energy enables them to escape from a much deeper level in the interaction zone, from depths of about 50–300 nm. The lateral spatial resolution of an SEM image is affected by the size of the volume from where the signal electrons escape [23, 24].
References


CHAPTER THREE

EXPERIMENTAL DETAILS

3.1 Sample Source
3.2 Synthesis of Dodecylalkylammonium Montmorillonite
3.3 Thermal Treatment of Dodecylalkylammonium Montmorillonite
3.4 Characterization Techniques
3.4.1 X-ray Diffraction Analysis
3.4.2 Thermogravimetric Analysis
3.4.3 Fourier Transform Infrared Spectroscopic Analysis
3.4.4 Alternating Current Electrical Properties
3.4.5 Scanning Electron Microscopic (SEM) Analysis

References
3.1 Sample Source

Sodium montmorillonite (SWy-2, CEC=74.6 meq per 100 g) sample was supplied by Purdue University, USA. The chemical formulae of the sample were given as

\[ \text{Na}_{0.75} (\text{Al}_{3.06} \text{Fe}^{3+}_{0.30} \text{Fe}^{2+}_{0.02} \text{Mg}_{0.65})(\text{Al}_{0.18} \text{Si}_{7.82})\text{O}_{20}(\text{OH})_4 \]

Dodecylalkylammonium (C\(_{12}\)H\(_{27}\)N) (CEC 1000 meq per 185.36g) was collected from Merck, Germany. The other chemicals used in the experiment were analytical grade and collected from local market.

3.2 Synthesis of Dodecylalkylammonium-Montmorillonite (DDA-MMT)

The intercalation of Dodecylalkylammonium (C\(_{12}\)H\(_{27}\)N) in Na-montmorillonite was carried out following a procedure similar to described by Bala et al. [1] and Khan et al. [2]. For synthesis of dodecylalkylammonium intercalated montmorillonite, 0.86 ml of dodecylalkylammonium was mixed with 2 ml concentrated HCl in a round bottom flask and heated for few minutes at 80 °C. In a beaker, 5 g of Na-montmorillonite was dispersed in 500 ml hot water at 80 °C. The solution of dodecylalkylammonium obtained earlier was then added into the dispersion of Na-montmorillonite and the mixture was stirred vigorously for 60 minutes and dodecylalkylammonium was formed. Then filtered and washed repeatedly to make it free from the chloride ions. The sample was subsequently dried in air atmosphere to afford the product as a powder. The organomodified compounds were termed as DDA-MMT where DDA stands for dodecylalkyl-ammonium and MMT for montmorillonite.

3.3 Thermal Treatment of Dodecylalkylammonium-Montmorillonite

The synthesized product was heat treated in a Muffle Furnace (Carbolite, Bamford, Sheffield, England, S30 2AU). For the purpose of XRD analysis at different temperature, the powder sample was divided into several portions. Each portion was then separately heated in a quartz crucible for 1 hour, at temperature 80, 120, 200, 300, 400 and 500 °C. On completion of heating the sample were cooled and kept in desiccators to avoid subsequent absorption of moisture. The variation of the temperature in the furnace was within ± 5 °C around the expected temperature.
3.4 Characterizations

3.4.1. XRD Analysis

The X-ray diffraction (XRD) intensities of the compounds were recorded with a Philips, X"Pert PRO XRD PW 3040, X-ray diffractometer using monochromatic CuKα (λ =1.542Å) radiation at Materials Science Division, Atomic Energy Center, Dhaka. The unit contains wide range goniometer, programmable divergent slit (PDS), anti scatter slit (ASS) and Geiger-Muller (G. M.) tube. The G. M. tube was connected to an automatic chart recorder arrangement. Copper target and a nickel filter were used. The tube was operated at 60kV and about 55mA current. X-ray diffractometer contain following configurations:

- “Cu-Tube” with maximum input powder of 60 kV and 55 mA.
- “Ni-Filter” to remove CuKα component.
- “Solar Slit” to pass parallel beams only.
- “Programmable Divergent Slit” to reduce divergence of beam and control irradiated beam area.
- “Mask” to get desired beam area.
- “Sample holder” for placing powder sample.
- “Anti-Scatter Slit” to reduce air scattering background.
- “Programmable Receiving Slit” to control the diffracted beam intensity.
- “Solar Slit” to stop scattered beam and pass parallel diffracted beam

In the present investigation X-ray intensities were recorded for the range of 20, 3° to 10° with a step size of 0.02° for pure Na-MMT and DDA-MMT at room temperature and DDA-MMT heat treated at 80, 120, 200, 300, 400 and 500°C and time for each step was 1.0 sec. The data for all the samples were then analyzed by using computer software “X"PERT HIGHSCORE” from which structural parameters was determined. The microstructural and layer disorder parameters were calculated by the methods described in chapter 2 and following the method similar to that described by Mitra[3], Mitra and Bhattacherjee [4], Srivastava et al. [5] and Bala et al. [6, 7].
3.4.2 Thermogravimetric Analysis

Thermal analysis refers to the simultaneous applications of thermo gravimetric (TGA) and differential thermo gravimetric analysis (DTG) to one and the same sample in a single instrument. The test conditions are perfectly identical for the TGA and DTG signals (same atmosphere, gas flow rate, vapor pressure of the sample, heating rate, thermal contact to the sample crucible and sensor, radiation effect, etc.). The thermal stability of DDA-MMT were also investigated by thermogravimetric analysis on TG/DTA 6300 apparatus, Seiko Instruments Inc., Japan in the temperature range 25-1000°C at the heating rate of 10°C/min in an air atmosphere. Crucible was used as the container of samples. It is useful to control the temperature in a predetermined way either by a continuous increase or decrease in temperature at a constant rate or by carrying out a series of determinations at different temperatures. More advanced temperature profiles have been developed which used an oscillating heating rate or modify the heating rate in response to changes in the systems properties.

3.4.3 Fourier Transform Infrared Spectroscopic Analysis

Fourier Transform Infrared (FTIR) spectra of pure compounds are generally so unique that they are like a molecular "fingerprint". While organic compounds have very rich, detailed spectra, inorganic compounds are usually much simpler. For most common materials, the spectrum of an unknown can be identified by comparison to a library of known compounds. We have several infrared spectral libraries including on-line computer libraries. To identify less common materials, IR will need to be combined with nuclear magnetic resonance, mass spectrometry, emission spectroscopy, X-ray diffraction, and/or other techniques. But in this case, we have obtained intensity in the measurement of FTIR analysis for the samples are Na-MMT and DDA-MMT. Appropriate quantity of Potassium Bromide (KBr) and Sample (in the ratio 100 : 0.1) was mixed by grinding in an agate mortar. Pellets were made with about 100mg mixture. FTIR Spectra were recorded with FTIR- 8400S Shimadzu spectrophotometer in the range 4000-400 cm⁻¹.
3.4.4 Alternating Current Electrical Properties

Alternating Current Electrical Properties were carried out by using Hewlett Packart impedance analyzer (HP 4291A). For dielectric measurements, the pellet shaped samples were well polished to remove any roughness and the two surfaces of each pellet were coated with silver paint as contact material.

3.4.5 Scanning Electron Microscopic (SEM) Analysis

The surface roughness of the DDA-MMT at room temperature and heat treated at different temperature were taken by using scanning electron microscopy (Hitachi S-3400N, type-II, Japan). The micrographs were taken on smooth surfaces of the pellet shaped samples after polishing by using a universal polisher.
**Fig. 3.1:** Na-montmorillonite after mixing with HCl and water (before intercalation).

**Fig. 3.2:** Na-montmorillonite intercalated with dodecylammonium at 80°C.
**Fig. 3.3:** Na-montmorillonite intercalated with dodecylammonium at 80 °C (during washing)

**Fig. 3.4:** Dodecylammonium intercalated montmorillonite (DDA-MMT) at the time of drying.
References


CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Introductory Remarks

4.2 Thermal Analysis
4.2.1 Thermogravimetric Analysis
4.2.2 Differential Thermogravimetric Analysis

4.3 X-ray Diffraction Analysis
4.3.1 Nature of X-ray Diffraction Profiles
4.3.2 Variation of Basal Spacing
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4.3.4 Variation in Crystalline Size
4.3.5 Variation of Interlayer Spacing, Proportion of Affected Defect and r.m.s. Strain

4.4 Fourier Transform Infrared Analysis

4.5 Scanning Electron Microscopic Analysis

4.6 Alternating Current Electrical Properties

References
4.1 Introductory Remarks

Montmorillonite belongs to smectite group of clay minerals which has 2:1 type of layer structure. The structure of montmorillonite established by Hofmann et al.[1], Marshall [2], Magdefrau and Hofmann [3], Hendricks [4], Hofmann and Hansdorf [5], MacEwan [6] consists of negatively charged silica sheets which are held together by charge - balancing counterions such as Mg$^{2+}$, Na$^+$ and Ca$^{2+}$ etc. The general chemical formula of the montmorillonite is \((\text{M}^{+}_{y} \cdot \text{nH}_2\text{O})(\text{Al}_{4-y}\text{Mg}_y)\text{Si}_8\text{O}_{20}(\text{OH})_4\), where \(\text{M} (\text{M} = \text{Na}^+, \text{Ca}^{2+}, \text{Mg}^{2+}\text{etc})\) is interlayer cation. These interlayer cations balance the negative charges which are generated by the isomorphous substitution of Mg$^{2+}$ and Fe$^{2+}$ for Al$^{3+}$ in the octahedral sheet and Al$^{3+}$ for Si$^{4+}$ in tetrahedral sheet. The interesting structural feature of montmorillonite structure is that these interlayer cations can be replaced with organic species through a process called intercalation. Intercalations of organic compounds into the interlayer space of montmorillonites and investigating their properties have been a subject of great interest for many years [7-10]. These intercalated compounds which are mainly known as organophilic montmorillonites have many applications in different areas such as thickeners in paints, greases, oil-base drilling muds, and for the purpose of gelling various organic liquids, catalysts [11-13]. Recently organically modified montmorillonites by means of polymer intercalation have been drawn the attention of many researchers because of their interesting behavior [14-20]. It is observed that these new types of polymeric materials show high strength, high modulus, excellent gas barrier properties, and low thermal expansion coefficient [14, 15, 17, 18, 20]. It is important to note that in the preparation of clay based materials and their suitability in different applications are predominantly governed by their physicochemical properties such as strength, plasticity, compressibility, pore structure etc. which are highly sensitive on the thermal variation [21-24]. Thus the thermal stability of organomodified clays has been considered an important area of investigations to many researchers. Thermal stability of organomodified montmorillonites has been investigated by many researchers such as Lapides et al. have investigated hexadecyltrimethylammonium-montmorillonites [25], Abdallah and Yilmazer have investigated thermally stable phosphonium and imidazolium organo-montmorillonites [26], Önal and Sarikaya investigated methyltributylammonium, methyltrioctylammonium and di(hydrogenatedtallow) dimethylammonium intercalation compounds [27], Yermiyahu et al. have investigated naphthylazonaphtylammonium-montmorillonite compound [28], Gao et al. have investigated the
trimethyloctadecylquarternary ammonium intercalated montmorillonite [29]. Most of these studies mainly deal with the thermal stability of intercalated organic species and their decomposition mechanism. However, the physical and chemical properties such as rheology, surface area, cation exchange capacity, etc. of a substance may strongly depend on microstructural parameters such as crystallite size, strain and different structural defects. It appears that having the knowledge on microstructure and structural defects can give better insight for understanding the structure, properties and modeling the applications of the materials. So, the studies on microstructure and structural defects and their variation in different physiochemical environment are considered an important area of investigations [30-34]. The microstructure and structural defects of clays and clay based materials are highly sensitive on their thermal variation. Thus the variation of microstructural parameters such as crystallite size, r.m.s. strain and structural defects of clay minerals with variation of temperature have been studied by many researchers. The variability defects of kaolinite and their variation with temperature have been studied by Mitra and Bhattacherjee [35] and De et al. [36]. Lokanatha and Bhattacherjee have studied the variation of crystallite size and layer disorder of palygorskite [37]. Bala et al. have investigated the thermal variation of microstructural and layer disorder parameters of vermiculite [38] and montmorillonite [39, 40]. However, the studies on the variation of microstructure and structural defects of organoclays during thermal transformation are still lack in literatures. Thus in the present study an organoclay known as DDA-MMT synthesized by intercalating dodecylammonium into the interlayer spaces of Na-montmorillonite and different microstructural parameters such as crystallite size, variation of interlayer spacing (g), proportion of planes affected by variability defect (γ) and r.m.s. strain (<e^2>^1/2) have been investigated. The XRD line profile technique has been used to calculate these parameters. The value of basal spacing (d_001), FWHM, number of silicate layers stacked to form individual crystallite (N) have also been used for understanding the thermal transformation of DDA-MMT. The thermal decomposition of DDA-MMT was also investigated by TGA, DTG. FTIR technique was also been used to investigate the thermal transformation of DDA-MMT pre-heated at different temperatures. SEM studies of the sample were also been done. Dielectric and electrical properties of the samples were also been investigated.
4.2 Thermal Analysis

4.2.1 Thermogravimetric Analysis

The thermal stability behavior of the untreated Na-montmorillonite and DDA-MMT samples has been shown in Fig. 4.1. It is observed from the figure that Na-montmorillonite loses its weight rapidly from 20 to 200°C, thereafter a slower loss is observed up to 500°C and onward this temperature the loss becomes again rapid. It can be mentioned here that interlayer spaces of montmorillonite possesses three types of water molecules, namely, free, coordinated to the interlayer cations and hydrogen bonded to the tetrahedral sheet [39]. Besides these, another type of water molecules are observed which is the constituent of the octahedral sheet. It appears from the present observations that the initial weight loss of about 9.6% between 20°C and 200°C is due to the expulsion of the intercalated water molecules which are almost free or loosely bound and coordinated to the Na⁺ ions and hydrogen bonded to the tetrahedral sheet [41] and 500°C to onward can be assigned to the removal of water molecules from the octahedral sheet [42]. According to Bray et al. [43] TGA of clay minerals do not show any clear end point which implies that some water molecules from octahedral sheet can be removed at lower temperature. Thus the poor weight loss (~1.7%) in the temperature range 200– 500°C may be due to the removal of some of the octahedral and strongly hydrogen bonded water molecules. Though it is difficult to identify from the TGA at which temperature the removal of the particular water molecules present in the interlayer spaces will start and will be finished, but it may not be so illogical to mention that the initial weight loss is governed by the free water molecules and then by coordinated and hydrogen bonded water.

In order to better understanding the thermal stability behavior of DDA-MMT the weight loses in different temperature ranges are recorded in Table 4.1. The first stage of decomposition is confined to 30 - 120°C and weight loss observed in this temperature range is 1.8%. The weight loss observed in this temperature range for Na-MMT itself is associated with relatively much higher weight loss (~8.8%) which suggested the removal of water from the inter layer coordinated to Na⁺. The organophilic properties of the DDA-MMT lead to the conclusion that the alkylammonium ions adsorbed less water. XRD and FTIR analysis also confirmed our view. Shuali et al. [44] also observed similar behavior on pyridine – treated sepiolite and palygorskite. The weight loss in the temperature range 120 - 200°C for Na-MMT is approximately 0.8%. This loss can be incorporated to the decomposition of hydrogen bonded water molecules and some of the OH groups from
Table 4.1. Thermogravimetric data of pure Na-MMT and DDA-MMT

<table>
<thead>
<tr>
<th>Samples</th>
<th>Weight Loss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>30 – 120°C</td>
</tr>
<tr>
<td>Na-MMT</td>
<td>8.8</td>
</tr>
<tr>
<td>DDA-MMT</td>
<td>1.8</td>
</tr>
</tbody>
</table>

Fig. 4.1: Thermogravimetric analysis traces of pure Na-MMT and DDA-MMT.
The corresponding weight loss for DDA-MMT in this range is almost 0. The weight loss observed in the temperature range 200 – 500°C for DDA-MMT is 8.8% and corresponding weight loss for Na-MMT is 1.7%. The weight loss for the DDA-MMT mainly originates from the decomposition and oxidation of intercalated ammonium and partly from the adsorbed water molecules. In the present investigation the greater weight loss for DDA-MMT at the temperature range 200 – 500°C is associated to the decomposition of intercalated ammonium. These observations are in agreement with the reported results for other organomodified – montmorillonite [28, 45, 46]. The weight loss in the temperature range 500 - 1000°C for DDA-MMT and Na-MMT is approximately 4.5% which is close to the ideal value 4.9% related to the dehydroxylation of Na-montmorillonite [47, 48].

4.2.2 Differential Thermogravimetric Analysis

The first derivative of TGA curve (DTG) of DDA-MMT and Na-MMT has been presented in Fig. 4.2. The different peaks observed in DTG curves with their onset, peak position and offset temperature has been shown in Table 4.2. The peaks observed in DTG curve of DDA-MMT assigned as Peak-I, Peak-II, Peak-III and Peak-IV. The first peak is observed between the temperature 30 to 125°C both for DDA-MMT and Na-MMT with some variation in the peak position. This peak is responsible for the removal of free and hydrogen bonded water molecules as mentioned in TGA analysis. The Peak-II and Peak-III having the peak temperature are nearly at 272°C and 344°C are found in DDA-MMT. The onset temperature of Peak-II is around 180°C and the offset temperature of Peak-III is around 430°C. Interestingly, these peaks are absent in Na-MMT which clearly indicate the dodecylalkylammonium has been intercalated into the interlayer spaces and it decomposes within the temperature range 180°C (onset of Peak-II) – 430°C (Offset of Peak-III). Peak-IV obtained at Na-MMT is assigned to the dehydroxylation of octahedral sheet. DDA-MMT shows the Peak-IV like Na-MMT having some variation in the range of temperature which may happens due to local change in interlayer environment due to the intercalation. The remarkable advantage in DTG curve is that it can gives more specific information about the onset and offset temperature of decomposition with the maximum decomposition temperature of organic species of organo-montmorillonite. DTG analysis of DDA-MMT also gives indication two stage decomposition of intercalated dodecylammonium. The results obtained in TGA and DTG analysis are in good agreement with the observation of XRD analysis for decomposition of intercalated organic species.
Fig. 4.2: Differential thermogravimetric (DTG) analysis curves of pure Na-MMT and DDA-MMT.
Table 4.2: Parameters of different peak positions of DTG thermogram of DDA-MMT and Na-MMT.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Parameters</th>
<th>Peak-I (°C)</th>
<th>Peak-II (°C)</th>
<th>Peak-III (°C)</th>
<th>Peak-IV (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DDA-MMT</td>
<td>Onset of the Peak</td>
<td>30</td>
<td>180</td>
<td>298</td>
<td>500</td>
</tr>
<tr>
<td></td>
<td>Top of the Peak</td>
<td>51</td>
<td>272</td>
<td>344</td>
<td>590</td>
</tr>
<tr>
<td></td>
<td>Offset of the Peak</td>
<td>120</td>
<td>298</td>
<td>430</td>
<td>660</td>
</tr>
<tr>
<td>Na-MMT</td>
<td>Onset of the Peak</td>
<td>30</td>
<td>-</td>
<td>-</td>
<td>550</td>
</tr>
<tr>
<td></td>
<td>Top of the Peak</td>
<td>70</td>
<td>-</td>
<td>-</td>
<td>700</td>
</tr>
<tr>
<td></td>
<td>Offset of the Peak</td>
<td>125</td>
<td>-</td>
<td>-</td>
<td>780</td>
</tr>
</tbody>
</table>
4.3 X-ray Diffraction Analysis

4.3.1 Nature of X-ray Diffraction Profiles

Fig. 4.3 shows the XRD profiles of Na-MMT and DDA-MMT for (001) reflection at room temperature (30°C). It is observed that the peak position ($2\theta_p$) corresponding to (001) reflection for Na-MMT with hydrated Na$^+$ ($2\theta_{PNaMMT} = 6.335^\circ$) is shifted towards lower angle region resulting in an increase in basal spacing, when it is intercalated by dodecylammonium ($2\theta_{PDAMMT} = 4.968^\circ$). The basal reflection both for Na-MMT and DDA-MMT were observed to be broad and asymmetrical. The XRD patterns for 001 reflection of DDA-MMT heated at different temperatures have been presented in Fig. 4.4. It is observed that the sample heated at 80°C shows the peak corresponds to $2\theta_p$ at 5.192° which is little bit smaller than the sample at 30°C. Onward 80°C, with increase of temperature $2\theta_p$ does not show any significant variation up to 200°C. The peak position shifted toward higher angle region at considerable amount when the sample heated at 300°C. Again, the peak observed at 300°C is highly diffused in nature. The peak observed at 300°C was deconvoluted into two peaks. The peaks were found to be at $2\theta_p = 5.271^\circ$ and $2\theta_p = 6.388^\circ$. The first peak corresponds to the Phase –I („virgin phase”) and second peak is due to the Phase–I (decomposed phase). Onward 300°C, the peak shifting is less prominent. The asymmetry and broadening of the peak were observed to vary significantly with the rise of heating temperature especially at the temperature of 300°C and 400°C.

4.2.2 Variation of Basal Spacing

In the present investigation the basal ($d_{001}$) spacing of DDA-MMT and Na-MMT at room temperature are found to be 17.723Å and 13.952Å respectively (Table– 4.3). The basal spacing of montmorillonite intercalation compounds mainly depends on the length of chain intercalates and their orientation. The intercalates may be arranged in different ways like monolayer, bilayer and paraffin types. The basal spacing for aliphatic alkylammonium-MMT compounds are $\approx$13.6Å (for monolayer) and $\approx$17.7Å (for bilayer) respectively [7-10]. The increase of basal spacing in DDA-MMT with respect to Na-MMT indicates the intercalation of dodecylammonium into the interlayer spaces of Na-MMT. However, the basal spacing observed in DDA-MMT is greater than that of alkylammonium intercalated monolayer compound and very close to that of bilayer compound. It infers that intercalated dodecylammonium are oriented in bilayer arrangement into the interlayer spaces of Na-MMT.
**Fig. 4.3:** XRD patterns of Na-MMT and DDA-MMT without heat treatment (30°C).
Fig. 4.4: XRD patterns of DDA-MMT heat treated at different temperatures.
**Table – 4.3:** Different Parameters Calculated from 001 Reflection of DDA-MMT and Na-MMT at Room Temperature (30°C).

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Na-MMT</th>
<th>DDA-MMT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basal Spacing, $d_{001}$ (Å)</td>
<td>13.952</td>
<td>17.723</td>
</tr>
<tr>
<td>FWHM (rad.)</td>
<td>$3.41 \times 10^{-2}$</td>
<td>$1.55 \times 10^{-2}$</td>
</tr>
<tr>
<td>Crystallite Size, $P_V$ (Å)</td>
<td>131</td>
<td>116</td>
</tr>
<tr>
<td>Variability Defect, $g$</td>
<td>0.482</td>
<td>0.389</td>
</tr>
<tr>
<td>Fraction of planes affected by variability defect, $\gamma$</td>
<td>$2.37 \times 10^{-2}$</td>
<td>$6.54 \times 10^{-2}$</td>
</tr>
<tr>
<td>RMS strain, $&lt;e^2&gt;^{1/2}$</td>
<td>$7.51 \times 10^{-3}$</td>
<td>$21.18 \times 10^{-3}$</td>
</tr>
</tbody>
</table>
The variation of basal spacing with temperature has been presented in Fig. 4.5. It is observed from Fig. 4.5 that \(d_{001}\) decreases when the sample is heated at 80°C. In the temperature range 80 – 200°C, it does not show any significant variation. At 300°C, two peaks correspond to the basal spacing of 16.765Å and 13.836Å was observed. Initial decrease in \(d_{001}\) at 80°C may be due to the expulsion of water molecules present at the interlayer spaces as supported by TGA. Nearly the same value of \(d_{001}\) up to 200°C indicates the stability of interlayer species up to this temperature. Two basal spacings observed at 300°C clearly indicate the presence of two phases at this temperature. The two phases are termed as Phase-I and Phase-II. Phase-I corresponds to the „virgin phase“ in which the intercalated dodecylammonium has not been decomposed and Phase-II correspond to the „decomposed phase“ where the intercalated dodecylammonium has been decomposed. It is observed from Fig. 4.5 that Phase - II shows significant decrease in basal spacing than Phase– I. The sharp decrease in basal spacing in Phase - II can be assigned to the decomposition of intercalated dodecylammonium has been supported by the onset and peak temperature of the Peak-II of DTG thermogram of DDA-MMT. It appears that in Phase - II the interlayer species decomposed and expelled from the interlayer galleries resulting a significant decrease in \(d_{001}\) value. This observation is an agreement with that of made by Xie et al. for trimethyldodecyl and trimethyloctadecylalkylammonium intercalated montmorillonite where they concluded that organic compound decomposes in the temperature range 200– 500°C [49]. Again, the value of \(d_{001}\) for DDA-MMT heated at 400°C and 500°C are found to be little bit small to that of Na-MMT at room temperature. It seems that organic species decomposed and expelled along with the residual water molecules from the interlayer galleries.

4.3.3 Variation in Full Width at Half Maximum

The FWHM of Na-MMT and DDA-MMT at room temperature are observed to be \(3.41 \times 10^{-2}\) rad. and \(1.55 \times 10^{-2}\) rad. respectively (Table 4.3). The FWHM of DDA-MMT at room temperature was observed to be 2.2 times larger than that of pure Na-MMT. The change in FWHM represents the change in spatial heterogeneity of silica sheets in the sample [43]. The lower value of FWHM of DDA-MMT with compare to that of Na-MMT at room temperature indicates relatively more homogeneous stacking of the silicate sheets in DDA-MMT. The interlayer galleries of Na-montmorillonite contain hydrated \(\text{Na}^+\) ions together with free and hydrogen bonded water molecules which may vary from one gallery to others [39]. This heterogeneity of interlayer cations and water molecules may play an
Fig. 4.5: Variation of interplanar spacing (d$_{001}$) with heat treatment temperature of DDA-MMT.
important role in the stacking heterogeneity of silicate sheets. It appears in the present investigation that when dodecylammonium ions are being intercalated by exchanging the hydrated Na+ ions, free and hydrogen bonded water molecules from the interlayer spaces are also expelled due to the size effect of intercalate which gives more homogeneous stacking of silicate sheets. The variation of FWHM of (001) reflection of DDA-MMT with temperature has been presented in Fig. 4.6. It is observed that the value of FWHM increases from 30°C to 120°C and then shows a decreasing trend in Phase–I. The variation of FWHM in the temperature range 30 – 300°C in Phase– I may be due to the expulsion of residual water molecules from the interlayer galleries which is expected not to be same for every gallery. Relatively lower value of FWHM at the temperature range 120 – 300°C in Phase – I indicate the expulsion of water molecules from the interlayer spaces of DDA-MMT before 120°C. Interestingly, the FWHM shows a decreasing trend in Phase –II with increase of temperature. Relatively higher values of FWHM at 300°C in Phase – II infers that expulsion of intercalated dodecylammonium is not complete and some of the interlayer galleries have some intercalates which gives a heterogeneous stacking of MMT layers giving a larger value of FWHM. Onward 300°C, it decreases significantly indicating the expulsion of residual dodecylammonium from the interlayer spaces.

4.3.4 Variation in Crystallite Size

In the present investigation the crystallite size ($P_v$) was calculated from (001) reflection using the method of variance. The crystallite size calculated from the X-ray diffraction profile follows the equation

$$W_{2θ} = \frac{αλ}{2π²P_v cos θ} + \frac{S^2}{cos^2 θ} \quad (4.1)$$

Where $W_{2θ}$ is the variance of the profile and $α$ is the angular range over which the intensity distribution is appreciable, $P_v$ is crystallite size, $λ$ is the wavelength of the X-ray used [39]. It is clearly seen from the equation (4.1) that a plot between range ($α$) and variance ($W_{2θ}$) should give a straight line. In the present investigation the plots of range vs. variance of DDA-MMT heated at different temperature have been presented in Fig. 4.7. The straight line nature of the range vs. variance plots are observed clearly. The $P_v$ has been calculated from the slope of these plots. The values of crystallite size obtained for DDA-MMT and Na-MMT at room temperature has been presented in Table– 4.3. The variation crystallite size obtained for DDA-MMT heated at different temperature has been presented in Fig.4.8.
Fig. 4.6: Variation of FWHM with heat treatment temperature of DDA-MMT.
Fig. 4.7: Variance ($W_{2\theta}$) – range ($\alpha$) plots for 001 reflection of DDA-MMT heat treated at (a) 30°C (b) 120°C (c) 500°C.
Fig. 4.8: Variation of crystallite size ($P_v$) calculated by variance method with heat treatment temperature of DDA-MMT.
The values of crystallite size calculated from variance method were observed to be 116 Å and 131 Å for DDA-MMT and pure Na-MMT respectively. It is observed from the figure that crystallite size decreases with increase of temperature up to 300°C in Phase – I. The values of crystallite size observed for Phase – II at 300°C and 400°C is lower than the value of Phase – I. However, at 500°C it shows relatively greater value with compare to that of 400°C but less than that of DDA-MMT at 30°C. However, rate of decrease of crystallite size is relatively small in the temperature range 30–120°C with respect to that of 120–300°C in Phase - I. It appears that the variation of crystallite size at Phase–I is related to the expulsion of water molecules from the interlayer galleries of DDA-MMT and at Phase – II is related to the decomposition and expulsion of dodecylammonium from the interlayer spaces. However, relatively larger values of crystallite size at 500°C may be due to some sort of reorientation of MMT layers. Since montmorillonite is a layer structured material and layers are stacked in c-direction thus the value of crystallite size calculated from 001 reflection indicates the stacking size. Thus, the number of silicate layers stack to form an individual crystallite, \(N = \frac{P_v}{d_{001}} + 1\), have been calculated [50]. The value of \(N\) for DDA-MMT is found to be 7, 7, 6, 6, 6 and 8 at the temperature 30, 80, 120, 200, 400 and 500°C respectively. It is interesting to mention that number of layers stacked to form an individual crystallite does not change significantly with increase of temperature. On an average, it appears that individual crystallites are formed by stacking 7 layers of MMT. The variation of \(N\) generally indicates the growth and break up of crystallites with temperature. In case of decomposition of organo-montmorillonite there is possibility to create cleavage among the layers resulting the breakup of crystallites. It seems in the present investigation that such types of cleavage are not being created in the temperature range 30 – 200°C and 400 – 500°C.

**4.3.5 Variation of Interlayer Spacing (\(g\)), Proportion of Planes Affected Defect (\(\gamma\)) and r.m.s. Strain (\(<e^2>^{1/2}\))**

The values of the variation of interlayer spacing (\(g\)), proportion of planes affected by such defect (\(\gamma\)) and r.m.s. strain (\(<e^2>^{1/2}\)) in DDA-MMT at room temperature were found to be 0.389, 6.54×10^{-2} and 21.18×10^{-3} respectively and that of Na-MMT were observed to be 0.482, 2.37×10^{-2} and 7.51×10^{-3} respectively (Table 4.3). The value of \(g\) is small in DDA than the Na-MMT. It indicates that stacking of silicate layers is more homogeneous in DDA-MMT. The Na-MMT possesses different types of water molecules such free water molecules, water molecules hydrogen bonded to the silicate sheets and co-ordinated to the
Na$^+$ cations. Again, the distribution of water molecules, interlayer cations are not same in every interlayer galleries [7]. It appears that the intercalation of dodecylammonium into the interlayer galleries remove the Na$^+$ cations as well as the water molecules from the interlayer galleries which gives relatively an ordered structure of DDA-MMT [51] showing lower values $g$ with compare to Na-MMT. The fraction of planes affected by variability defect is greater in DDA-MMT than Na-MMT as indicated by the value of $\gamma$. The value of r.m.s. strain $<e^2>^{1/2}$ obtained in DDA-MMT at room temperature is considerably greater than that of Na-MMT. The unmodified Na-MMT contains Na$^+$ ions into the interlayer galleries whereas DDA-MMT possesses dodecylammonium into the galleries. The size of present organic intercalates is greater. Due to this greater size of intercalate the value of r.m.s. strain may be greater in DDA-MMT at room temperature than Na-MMT.

The variation of interplaner spacing ($g$) with temperature has been represented in Fig. 4.9. It is observed from the Fig. 4.9 that $g$ increases with temperature upto $120^\circ$C then almost constant up to $300^\circ$C in Phase-I. However, the value of $g$ increases with increase of temperature in Phase – II. The initial increase of $g$ in Phase-I may be due to the expulsion of water molecules from the interlayer galleries. The sharp decrease at $300^\circ$C in Phase-II is related to the decomposition and expulsion of intercalates from the interlayer galleries. The variation of $\gamma$, proportions of planes affected by variability defect, with temperature has been presented in Fig. 4.10. The value of $\gamma$ shows an increasing trend with the increase of temperature up to $120^\circ$C, then a decrease is observed upto $300^\circ$C in Phase-I. In Phase-II the value of $\gamma$ shows a decreasing trend with increase of temperature. The minimum value of $\gamma$ is observed to be 0.062 at $500^\circ$C. The value of $\gamma$ indicates that more number of planes are affected with variability defect at $120^\circ$C. This relatively large value of $\gamma$ in the temperature range $120 – 300^\circ$C in Phase-I may be considered the indication of onset of decomposition of dodecylammonium into the interlayer galleries. It seems that $\gamma$ can be an important parameter because it gives the quantitative idea on the amount of defect present in the concerned sample. The variation of r.m.s. strain with temperature has been presented in Fig. 4.11. The variation of r.m.s. strain also increases with increase of temperature up to $120^\circ$C and then decreases up to $300^\circ$C in Phase-I. A decreasing trend in r.m.s strain is observed with increase of temperature in Phase-II. The values of $g$, $\gamma$ and $<e^2>^{1/2}$ and their variation can be attributed to the fact of variation of layer charge, interlayer cations distribution and the water molecules being present in the interlayer space [39].
Fig. 4.9: Variation of variability defect ($g$) with heat treatment temperature of DDA-MMT.

Fig. 4.10: Variation of fraction of planes affected by variability defect ($\gamma$) with heat treatment temperature of DDA-MMT.
Fig. 4.11: Variation of r.m.s. strain ($\sqrt{<e^2>}$) with heat treatment temperature of DDA-MMT.
variation of r.m.s. strain in the temperature range 30 – 120°C is more likely to the expulsion of water molecules from the interlayer spaces. The variation observed in Phase-II is associated to the decomposition of intercalated dodecylammonium and their expulsion. It appears that the lower values of r.m.s. strain at 500°C is associated with the completion of decomposition of intercalates and its expulsion from the interlayer spaces.

4.4 Fourier Transform Infrared Analysis

The Fourier Transform Infrared (FTIR) spectra of Na-MMT and DDA-MMT are shown in Fig. 4.12 and positions and the relative intensity of the observed bands together with their assignments to different vibrational modes are recorded in Table 4.4. The common feature in IR for Na-MMT and DDA-MMT is the presence of bands at around 3637 cm⁻¹, 3439 cm⁻¹ and 1640 cm⁻¹ because of OH (free), OH (hydrogen bond) and OH (bending) vibrations respectively. DDA-MMT show the presence of two new bands at around 3274 cm⁻¹ and 2934 cm⁻¹ and are due to NH₃⁺ stretching and CH₃ asymmetric stretching vibrations of intercalated primary aliphatic ammonium respectively [52, 53]. The bands in DDA-MMT were also observed at about 2859 cm⁻¹ and 1470 cm⁻¹ respectively. These bands correspond to the symmetrical CH₃ stretching absorption band (2858 cm⁻¹) and for the –CH₂– scissor vibration band (1471 cm⁻¹) [53]. The presence of transmission bands due to CH₃, CH₂ and NH₃⁺ in DDA-MMT conform the alkylammonium intercalation in the interlayer spaces of Na-MMT and the systematic decrease in intensity of OH (free) and OH (hydrogen bond) bands showed that the DDA-MMT become more and more organophilic.

Fig. 4.13 shows the FTIR spectra of heat treated DDA-MMT and their assignments are shown in Table 4.4. The sample heated at 80, 120 and 200°C do not show any significant variation in their position of OH free and OH hydrogen bonded water molecules but their intensity decreases gradually with respect to the Si-O-Si vibration which is considered as the characteristic frequency of montmorillonite minerals and it is expected that this will not change significantly in these temperature. The interesting feature of heat treated IR spectra is that NH₃⁺ stretching vibration almost disappears at 300°C and the intensity of the bands responsible due to CH₃ asymmetric stretching vibrations decreases. At 500°C, NH₃⁺ stretching vibrations absent and the intensity of CH₃ asymmetric stretching vibration decrease significantly and it turns into shoulder. The variation in NH₃⁺ stretching vibration of confirms the decomposition of intercalated dodecylammonium at 300°C. However, the
**Fig. 4.12**: FTIR spectra of Na-MMT and DDA-MMT at room temperature.
Fig. 4.13: FTIR spectra of DDA-MMT at different heat treatment temperatures.
**Table 4.4.** Important FTIR frequencies and their assignments of Na-MMT and DDA-MMT.

<table>
<thead>
<tr>
<th>Sample Assignments</th>
<th>Wavenumber (cm⁻¹)</th>
<th>Na-MMT 30 (°C)</th>
<th>DDA-MMT 30 (°C)</th>
<th>DDA-MMT 300 (°C)</th>
<th>DDA-MMT 500 (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH free</td>
<td>3637s</td>
<td>3639m</td>
<td>3638m</td>
<td>3639m</td>
<td></td>
</tr>
<tr>
<td>OH H-bonded</td>
<td>3439s</td>
<td>3438m</td>
<td>3443m</td>
<td>3439m</td>
<td></td>
</tr>
<tr>
<td>OH bend</td>
<td>1640m</td>
<td>1638w</td>
<td>1637w</td>
<td>1638w</td>
<td></td>
</tr>
<tr>
<td>Si-O stretching</td>
<td>1049vs</td>
<td>1051vs</td>
<td>1051vs</td>
<td>1053vs</td>
<td></td>
</tr>
<tr>
<td>NH₃⁺ stretching</td>
<td>-</td>
<td>3274w</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>CH₃ asym. stretching</td>
<td>-</td>
<td>2934m</td>
<td>2932m</td>
<td>2934sh</td>
<td></td>
</tr>
<tr>
<td>CH₃ stretching absorp.</td>
<td>-</td>
<td>2859m</td>
<td>2857m</td>
<td>2859sh</td>
<td></td>
</tr>
<tr>
<td>–CH₂– scissor</td>
<td>-</td>
<td>1470w</td>
<td>1474sh</td>
<td>1470sh</td>
<td></td>
</tr>
</tbody>
</table>

m = medium; s = strong; vs = very strong; b = broad; sh = shoulder; w = weak; a = absent
presence of the bands due to CH$_3$ asymmetric stretching vibration up to 400°C indicate the presence of some carbon moiety in the interlayer spaces of DDA-MMT.

### 4.5 Scanning Electron Microscopic Analysis

The surface morphology and grain size of the presently investigated Na-MMT and DDA-MMT heated at different temperatures were analyzed using scanning electron microscopic (SEM) photographs. Fig.4.14 represents SEM images of unmodified Na-MMT and heat treated DDA-MMT. The SEM micrographs show the roughness of Na-MMT and DDA-MMT. The shape of the grains is not clearly defined. Grain boundaries are not clearly identified with the present magnification stage.

### 4.6 Alternating Current Electrical Properties

Fig. 4.15 represents the variation of dielectric constant ($\epsilon$) of Na-montmorillonite and DDA-MMT with respect to the frequency (log $f$). It is observed from the figure that dielectric constant of Na-MMT is very high at lower frequency and it decreases gradually with increase of frequency (log $f$). The parameter decrease rapidly up to log $f = 5$ and after that it shows a slower decrease. It is well known that when a solid is placed in an electric field, the movement of charge carriers and their accumulation at the interface of the sample and electrodes, in addition to the various types of polarization, which display different types of frequency response, plays a dominant role in deciding the nature of dielectric constant as has been described by Newnham [54]. In fact the variations of $\epsilon$ with frequency will be indicative of the type of polarization operative in the sample. It is more suitable to explain the high dielectric constant of montmorillonite by Maxwell - Wagner effect [55-58]. In case of frequency variation of dielectric constant (Fig. 4.15) in DDA-MMT shows very low value as compared Na-MMT. Bidadi et al. [58] proposed a simpler form of Maxwell - Wagner effect to show the variation of dielectric constant of montmorillonite and the high value of that. They assigned that the high dielectric constant value of montmorillonites is related to the thickness of the silicate layers and the insulating behavior of it. In the present investigation the thickness of the silicate layers for all the montmorillonite are same since we have used same montmorillonite sample for the synthesis of DDA-MMT. Then only variable remains the insulation behavior of silicate layers. It is well known that silicate layers possess some free charges which are generated by isomorphous substitution of some foreign atoms and which are being counter balanced
Fig. 4.14: SEM micrographs of DDA-MMT (a) 30°C (b) 300°C (c) 500°C.
Dielectric Constant, $\varepsilon' \times 10^{-3}$

Frequency, log$f$ (Hz)

![Graph showing variation of dielectric constant with frequency for Na-MMT and DDA-MMT.](image)

**Fig. 4.15:** Variation of dielectric constant with frequency of Na-MMT and DDA-MMT.
by the interlayer cations and water molecules. Now if the water molecules and interlayer
cations are removed, the charges on silicate layers will be free which will ultimately
decrease the degree of insulation of the silicate layers resulting in a decrease of dielectric
constant. This hypothesis can explain the results of low dielectric constant of DDA-MMT
with respect to the high value of Na-MMT clearly. As we observed from our TG and IR
analysis, the DDA-MMT becomes organophilic in nature and less water content is present
in it. Above explanation gives some idea on the variation of dielectric constant when Na-
MMT is intercalated with dodecylammonium at a particular frequency at room
temperature in our experimental range. But the explanation of the variation of dielectric
constant of DDA-MMT with increase of frequency will be more complicated. Since in this
case all the factors like polarizability of the charges, interactions of the alkylammonium
ions with residue water molecules, orientations of the chain and microstructure of the
sample etc. will come to the picture. The variation of dielectric constant with frequency of
different pre-heated DDA-MMT has been shown in Fig.4.16. It is also observed that
dielectric constant of preheated DDA-MMT shows a decreasing trend with increase of
frequency. However, the values of dielectric constant of DDA-MMT heated at 500°C are
observed to be higher. In order to better understanding the variation of dielectric constant
with temperature we plot the preheated temperature vs. dielectric constant of DDA-MMT
(Fig.4.17). It is observed that dielectric constant decreases with increase of temperature
upto 300°C. Onward this temperature the value of dielectric constant increases. It is well
established that montmorillonites are characterized by several types of water, each of
which escape at different temperature ranges as evidenced by TGA and IR data. These
water molecules also play significant roles independently in controlling the thermal
behavior of the electrical properties. The appreciable high value of \( \varepsilon \) at lower frequencies
and at room temperature can be well attributed mainly to dipolar and space charge
polarizations due to presence of free charge carriers inherently present in the minerals (e.g.
water molecules [dipolar], impurity ions) which follow the electric field that is applied and
pile up at the surface of the crystal or at major defect regions inside the sample. Such
accumulation of charge carriers leads to a barrier whose height is a measure of the trapped
charge carrier concentration. It is quite reasonable that in the temperature range 30-300°C
the variation of dielectric constant is related to the expulsion of water molecules which
were present in DDA-MMT as observed in the TGA analysis. However, the variation
**Fig. 4.16:** Variation of dielectric constant with frequency of DDA-MMT heat treated at different temperatures.

**Fig. 4.17:** Variation of dielectric constant with heat treatment temperature of DDA-MMT.
observed in onward 300°C may be related to the decomposition of intercalated dodecylammonium.

The variations of ac conductivity (log\(\sigma_{ac}\)) analysis curve with frequency are shown in Fig. 4.18. The ac conductivity shows an increasing trend with increase of frequency for both Na-MMT and DDA-MMT. However, the variation in initially small and becomes rapid at higher frequency. Again, the values of ac conductivity obtained for DDA-MMT is higher than that of the Na-MMT. As mentioned earlier that intercalation of long chain ammonium into the interlayer spaces removes the different types of water molecules along with the removal of interlayer cations. The removal of these water molecules makes some charges free which may help to increase the conductivity in case of DDA-MMT. The variation of this conductivity with frequency is obviously associated with the various types of polarization, especially space charge and orientational as pointed out by Glushkova and Firsova [59]. The variation of ac conductivity with frequency of preheated DDA-MMT with frequency has been presented in Fig. 4.19. The nature of the variation of ac conductivity with frequency is almost similar for the sample heated at 80 – 300°C. However, the value of ac conductivity obtained for the sample at 30°C is much greater than that of sample heated at higher temperature (Fig.4.20 and Fig. 4.21). Calvet [60] proposed that the conductivity of montmorillonite sample is largely determined by the water molecules which do not take part in the hydration of the compensating charges generated by the isomorphous substitution which was described in previous section as free water molecules. It was also proposed that these water molecules allowed the transfer of the charges both in interlayer spaces and between the aggregates. It seems in present investigation that at lower temperature the presence of these free water molecules is responsible for higher conductivity value and with increase of temperature this water molecules expulsion thus conductivity decreases.
**Fig. 4.18:** Variation of AC conductivity with frequency of Na-MMT and DDA-MMT.
**Fig. 4.19:** Variation of AC conductivity with frequency of DDA-MMT heat treated at different temperatures.
Fig. 4.20: Variation of AC conductivity with temperature of DDA-MMT.

Fig. 4.21: Variation of AC conductivity with temperature (region: 80 – 500°C) of DDA-MMT.
References


CHAPTER FIVE

CONCLUSIONS

5.1 Conclusions

5.2 Scope of Further Work
5.1 Conclusions

In the present investigation an organo clay (DDA-MMT) is synthesized by intercalating dodecylammonium into the interlayer spaces of Na-montmorillonite. It is utmost essential to have sufficient knowledge on thermal stability and different structural and microstructural parameters and their variations on the variation of temperature for tailoring the applications of organoclays. Thus the thermal transformation of synthesized DDA-MMT has been investigated. TGA, DTG, XRD, SEM and FTIR techniques were used to investigate the thermal transformation behavior of DDA-MMT. Dielectric and electrical properties of the DDA-MMT have also been studied.

TGA of DDA-MMT shows 1.8% weight loss in the temperature range 30 – 120°C. At this temperature range, Na-MMT shows 8.8% weight loss. This indicates that water molecules usually present into the interlayer spaces removed along with the interlayer cations due to the size effect of the intercalates. In the temperature range 120 – 200°C, DDA-MMT do not show any significant weight loss indicating thermal stability of the sample. The weight loss observed in the temperature range 200 – 500 °C for DDA-MMT is 8.8% which is much greater than the pure Na-MMT. This implies the decomposition and expulsion of intercalated dodecylammonium in this temperature range. DTG analysis of DDA-MMT gives more precise information on the onset, peak and offset of decomposition temperature. DTG curve of DDA-MMT shows two peak one at 272 °C and other at 344 °C which are absent in pure Na-MMT. These two peaks infer the two stage decomposition of intercalated dodecylammonium in DDA-MMT.

Basal spacing (d_{001}) of DDA-MMT and Na-MMT at room temperature are found to be 17.723Å and 13.952Å respectively. The expansion of basal spacing confirms the intercalation of dodecylammonium into the interlayer spaces of Na-MMT. The value of basal spacing of DDA-MMT suggests bilayer arrangement of alkylammonium into the interlayer. At 300°C, both „virgin phase“ and decomposed phase of DDA-MMT are present. Basal spacing of decomposed phase drops to 13.836Å at 300°C. This happens due to the decomposition and expulsion of dodecylammonium to a greater extent as supported by TGA and DTG analysis. FWHM of Na-MMT and DDA-MMT at room temperature are observed to be $3.41 \times 10^{-2}$ rad. and $1.55 \times 10^{-2}$ rad. respectively. The lower values of FWHM in DDA-MMT indicate the more homogeneous stacking of montmorillonite layers in DDA-MMT. The value of FWHM becomes maximum at 300°C in decomposed phase.
indicating heterogeneity in stacking of MMT layers. This heterogeneity may arise due to the incomplete decomposition of intercalated dodecylammonium. This is supported by the offset temperature of decomposition of third peak in DTG curve which is 430°C. This proposition can also explain the lower value of FWHM at 500°C. The values of crystallite size calculated from variance method were observed to be 116 Å and 131 Å for DDA-MMt and pure Na-MMT respectively. The crystallite size of DDA-MMt decreases with increase of temperature up to 300°C which is related to the decomposition of intercalates of DDA-MMt. The values of the variation of interlayer spacing (\(g\)), proportion of planes affected by such defect (\(\gamma\)) and r.m.s. strain (\(<e^2>^{1/2}\)) in DDA-MMt at room temperature were found to be 0.389, 6.54\(\times\)10\(^{-2}\) and 21.18\(\times\)10\(^{-3}\) respectively and that of Na-MMt were observed to be 0.482, 2.37\(\times\)10\(^{-2}\) and 7.51\(\times\)10\(^{-3}\) respectively. Interlayer variation become relatively small as observed by a sharp decrease in \(g\) at 300°C, just after the temperature of first phase of decomposition and expulsion of dodecylammonium. The proportion of planes affected by this defect is minimum at 500°C as observed from the value of \(\gamma\). The value of r.m.s. strain increases with increase of temperature up to 120°C and then decreases upto 300°C. A decrease in the value of \(<e^2>^{1/2}\) is observed for DDA-MMt heated at 300°C. It decreases drastically at 500°C due to the completeness of decomposition of intercalates.

The FTIR spectra of Na-MMt and DDA-MMt shows the bands at around 3637 cm\(^{-1}\), 3439 cm\(^{-1}\) and 1640 cm\(^{-1}\) because of OH (free), OH (hydrogen bond) and OH (bending) vibrations respectively. DDA-MMt shows the presence of two new bands at around 3274 cm\(^{-1}\) and 2934 cm\(^{-1}\) and are due to NH\(_3^+\) stretching and CH\(_3\) asymmetric stretching vibrations of intercalated primary aliphatic ammonium respectively. The bands in DDA-MMt were also observed corresponding to the symmetrical CH\(_3\) stretching absorption band at 2858 cm\(^{-1}\) and for the –CH\(_2–\) scissor vibration band at 1471 cm\(^{-1}\). The presence of transmission bands due to CH\(_3\), CH\(_2\) and NH\(_3^+\) in DDA-MMt conform the alkylammonium intercalation in the interlayer spaces of Na-MNT. The intensity of the NH\(_3^+\) decreases significantly at 300°C and 400°C and almost disappears at 500°C. This supports the decomposition of DDA-MMt take place at wide range of temperature as observed in thermal and XRD analysis.

The values of dielectric constant decreases significantly when Na-MMt is intercalated with dodecylammonium. Again, Na-MMt at room temperature shows very high value of dielectric constant at lower frequencies. The high value of dielectric constant of Na-MMt
and its reduction with the intercalation of dodecylammonium can be explained by Maxwell-Wagner effect. The values of dielectric constant of DDA-MMT show considerable variation with the heat treatment temperature. At room temperature, the value of dielectric constant for DDA-MMT was found to be 230 and that was at 300°C and 500°C was 180 and 570 respectively. The ac conductivity is observed to be higher for DDA-MMT with compare to Na-MMT at room temperature. The increase of layer charge density during intercalation may responsible for the enhancement of conductivity in case of dodecylammonium intercalation. The ac conductivity decreases significantly when the DDA-MMT is under heat treatment. This may happen due to the loss of residual free water molecules which usually play role to transfer the charges both in interlayer spaces and between the aggregates.

The quantitative information on $d_{001}$, $P_V$, $g$, $\gamma$ and $<e^2>^{1/2}$ and their variations with temperature are expected to be important for tailoring the applications of this material in concerned areas. More precise information on the decomposition temperature of intercalated dodecylammonium may be fruitful for the application of this material especially in clay modified materials. Information obtained from dielectric and electrical analysis in the present investigation will be helpful to understand the behavior and/or interactions of organoclay to other materials.

5.2 Scope of Further Work

In the present investigation, Na-MMT has been intercalated with dodecylammonium. Thermal stability of the sample has been investigated. The variation of different structural and microstructural parameters with the variation of heat treatment temperatures has been investigated along with the dielectric and electrical properties. Use of this material in synthesis of polymer clay composites / nanocomposites and correlating their properties with the microstructure of organoclay could be an interesting effort for further works. Again, in the present investigation aliphatic amine has been used to modify the Na-MMT. Intercalation of aromatic amines into the interlayer spaces of Na-MMT and studies their thermal transformation and variation of microstructural parameters and making a comparison between aliphatic and aromatic amine modified montmorillonite would an interesting area of investigation. This organically modified montmorillonite can be tested for the tailoring the desired properties of other materials such as ceramics, ferrites etc. by the suitable addition of small percentage of material.