

**“SYNTHESIS AND CHARACTERISATION OF
Mn₃O₄ – La₂O₃ NANO COMPOSITES FOR THERMISTERS”**

A

Thesis

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Degree of

Doctor of Philosophy

by

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..... to the Almighty

Declaration

I hereby certify that the work which is presented in thesis entitled “**Synthesis and characterisation of $\text{Mn}_3\text{O}_4 - \text{La}_2\text{O}_3$ nano composites for Thermistors**” in the partial fulfillment of the requirement for award of the degree of DOCTOR OF PHILOSOPHY in the School of Physics and Materials Science, Thapar University, Patiala, is an authentic record of my own work carried out under the supervision of Dr M.L.Singla of CSIR-CSIO Chandigarh and Prof. K. K. Raina of Thapar University patiala. The matter embodied in this report has not been submitted in part or full to any other university or institute for the award of any degree.

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This is to certify that the above statement made by the candidate is correct and true to the best of my knowledge.

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ABBREVIATIONS

STM	Scanning, Tunneling Microscope
CNT	Carbon Nano-tubes
SWCNT	Single Walled Carbon Nanotubes
PCR	Polymerase Chain Reaction
UV-VIS	Ultra Violet - Visible
MRI	Magnetic Resonance Imaging
DMF	N, N-dimethylformamide
NTC	Negative Temperature Coefficient
CTAB	N-Cetyl-N,N,N,Trimethylammonium Bromide
TBAB	Tetrabutylammonium Bromide
PANI	Polyaniline
PAA	Polyacrylate
TEM	Transmission Electron Microscope
SEM	Scanning Electron Microscope
NIR	Near Infra-Red
CCD	Charged Coupled Devices
XRD	X-Ray Diffraction
ICDD	International Centre Diffraction Data
JCPDS	Joint Committee on Powder Diffraction Standards
FTIR	Fourier Transform Infra Red
TGA	Thermo Gravimetical Analysis
DSC	Differential Scanning Calorimetry

PREFACE

In the present study, Synthesis of nano materials of Mn_3O_4 , $\text{La}(\text{OH})_3$ and $\text{Mn}_3\text{O}_4 - \text{La}(\text{OH})_3$ nanocomposite have been carried out following bottom up approach (reduction Process) by selecting several combinations of precursors, reducing agent and stabilization agents. Reaction conditions have worked out for synthesis to have monodisperse nanomaterials of nearly uniform dimensions. $\text{Mn}_3\text{O}_4 - \text{La}(\text{OH})_3$ nanocomposite was transformed into $\text{Mn}_3\text{O}_4 - \text{La}_2\text{O}_3$ following sintering process. These materials have been characterized for their morphology, crystalline structure, composition and optical properties using, TEM, XRD, FTIR, UV-Visible. Thermistors from these ceramic powder were fabricated in the form of thin wire compacted in a stainless steel tube having two sensing wires encapsulated parallel to each other have been fabricated. To work out the negative temperature coefficient (NTC) and NTC cut off temperature each thermistor was kept in temperature controlled furnace for measuring resistivity values with respect to change in temperature. From these results parameters such as thermistor constant, activation energy and temperature coefficient of each thermistor were derived. Such thermistors will find applications to monitor and control the critical systems like aero engine, armor tank and other strategic devices from overheating and fire conditions. The complete work of the thesis is presented in the **six chapters**.

Chapter 1 deals with challenges and applications of nanotechnology, properties of nanoparticles, type of thermistors.

Chapter 2 covers literature which defines a number of methods used for the preparation of Mn_3O_4 , $\text{La}(\text{OH})_3$ and $\text{Mn}_3\text{O}_4 - \text{La}(\text{OH})_3$ nanocomposite and also defines scope of the present work.

Chapter 3 deals with methodology followed for synthesis and characterisation of Manganese Oxide (Mn_3O_4) Nanoparticles, Lanthanum Hydroxide Oxide ($\text{La}(\text{OH})_3$) nanomaterials, $\text{Mn}_3\text{O}_4 - \text{La}(\text{OH})_3$ nanocomposites and Conversion of $\text{Mn}_3\text{O}_4 - \text{La}(\text{OH})_3$ into $\text{Mn}_3\text{O}_4 - \text{La}_2\text{O}_3$. It also covers experimental details on various techniques used for characterisation of these nanomaterials.

Chapter 4 covers the detail description of results and discussions on synthesis and characterisation of nanomaterials, their composite for crystal structure, morphology, chemical structure, thermal stability and light interaction with radiations.

Chapter 5 covers the electrical characterisation of nano materials and their nano composite, negative temperature coefficient (NTC) parameters has been worked out Mn_3O_4 alongwith composite of $\text{Mn}_3\text{O}_4 - \text{La}_2\text{O}_3$ (La_2O_3) for thermistor applications.

Chapter 6 includes the conclusion, summary of the results and significance of the study.

CHAPTER-1

INTRODUCTION

INTRODUCTION

1.1 NANOTECHNOLOGY

Nanotechnology is the design, fabrication and use of nanostructured systems, and the growing, shaping or assembling of such systems either mechanically, chemically or biologically to form nanoscale architectures, systems and devices. The word 'nano' in nanotechnology comes from the Greek word 'nanos' that means dwarf. Scientists use this prefix to indicate 10^{-9} or one-Billionth. One nanometer is one Billionth of a meter that is about 100,000 times smaller than the diameter of a single human hair. "There's plenty of room at the bottom", the 1959 dream statement of the legendary Richard Feynman has been realized in less than half a century by consistent efforts and significant contributions from the scientific community across the globe. Progress made in past few decades has proven the abysmal nature of matter as a whole and the ability to achieve exciting technological advancement for the benefit of mankind. From the invention of carbon fullerene structures, carbon nanotubes by Ijima and the equally important discovery of inorganic fullerene structures; there have been numerous reports that discussed the fundamental and technological importance of novel nanostructured materials. The original vision of Richard Feynman was of the 'bottom-up' approach of fabricating materials and devices at the atomic or molecular scale, possibly using methods of self-organization and self- assembly of the individual building blocks. An alternative 'top-down' approach is the ultra miniaturization or etching/milling of smaller structures from larger ones. Nanoparticles are of great scientific interest as they are effectively a bridge between bulk materials and atomic or molecular structures.

A bulk material should have constant physical properties regardless of its size, but at the nano-scale this is often not the case. Size-dependent properties are observed such as quantum confinement in semiconductor particles, surface plasmon resonance in some metal particles and super-paramagnetism in magnetic materials. The field of nanoscience and technology has under gone explosive growth during the last decades both in terms of new materials and engineering applications as materials in nanometer scale exhibit physical properties distinctively different from that of bulk. Challenges in nanotechnology include the integration of nanostructures and nanomaterials with macroscopic system that can interface with people. Due to vast surface area, all

nanostructured materials possess huge surface energy and thus thermodynamically unstable or metastable.

During fabrication and processing of nanomaterials is to overcome surface energy and prevent the nanomaterials from growth in size. The size distribution of nanoparticle is dependent on the growth process of nuclei which involves generation of growth species, diffusion of the growth from bulk to growth surface, adsorption of the growth species onto the growth surface and surface growth through irreversible process onto the solid surface. A reduction in the spatial dimension of particles or quasiparticles in a particular crystallographic direction within a structure generally results in changes in physical properties of the system in that direction. The small length scales present in nanoscale systems directly influence the energy band structure and can lead indirectly to changes in the associated atomic structure. Such effects are generally termed quantum confinement.

The nanostructured materials and systems can be classified into following categories depending on the number of dimensions which lie within the nanometre range:

- a) Systems confined in three dimensions: e.g. Nanoparticles and nanopores
- (b) Systems confined in two dimensions e.g. nanowires, nano-rods, nanofilaments and nanotubes: these could either be amorphous, single-crystalline or polycrystalline (with nanometre-sized grains).
- (c) Systems confined in one dimension e.g., displatelets, ultrathin films on a surface and multilayered materials; the films themselves could be amorphous, single-crystalline or nanocrystalline.

Synthesis and applications of nano-particles with diameter of few nanometers is a subject of intense research owing to the deviation of fundamental properties of a material from those of its bulk form. For instance, opaque substances become transparent (copper); inert materials attain catalytic properties (platinum); stable materials turn combustible (aluminum); solids turn into liquids at room temperature (gold); insulators become conductors (silicon). Materials such as gold, which is chemically inert at normal scales, can serve as a potent chemical catalyst at nano-scale. Much of the fascination with nanotechnology stems from these unique quantum and surface phenomena that matter exhibits at the nanoscale. The behaviour of nano sized materials strongly depends on their size, shape and morphology. Wet chemical methods

have been reported for large scale production of nanomaterials. Solution phase synthesis of nanorods/wires of controlled dimensions is still a challenging task as surface energy favours the spherical particle formation.

Synthesis of nanomaterials has been reported in which shape, size is controlled during synthesis by either deploying surfactants/polymer as capping agent or using templates: But still low dimension system such as nano-crystals, thin films, short aspect ratio rods are getting enormous attention due to their potential applications in nanoelectronics, photonics, data recording, fuel cells and sensors.

1.2 HISTORY

The history of nanotechnology can be and is told in multiple ways, with various points of origin and important milestones. Perhaps the most commonly discussed origin point is a lecture by the famous physicist Richard Feynman called 'There's a Room at the Bottom' in which Feynman speculates about all the possible ways in which miniaturization, computer and information technologies and physics can be used to explore the sub-microscopic world. Feynman laid out a series of things he thought should be easy to accomplish in the near future. About fifty years later, many engineers and scientists were still excited by these predictions – but none of them had yet come true [1].

A related work that is occasionally referenced from the same period is that of John von Neumann's 'General and Logical theory of automata' to propose the creation of autonomous machines though in his case, not at the nanoscale [2]. Neither Feynman nor Von Neumann discussed these possibilities in terms of the word 'nanotechnology' however. The term was popularized in a book written by K. Eric Drexler – an inveterate nanotechnology visionary – in a book of 'future history' called *Engines of Creation*. Drexler used the word to describe his vision of a world where molecular manufacturing would allow people to manufacture anything they might need – from automobiles to pieces of beef – simply by feeding waste material into a box that would use nanoscale assemblers to reconfigure it into the necessary form. Drexler warned that as this technology developed it would be necessary to guard against the accidental release of autonomous self-replicating nanomachines that could – if they spun out of control and started to consume or transform the natural and man-made world – turn the planet into a mass of uninhabitable 'grey goo'. Drexler has played an important role in generating both excitement and fear about nanotechnology over the years [3]. Over the last 40

years, however, a significant number of real scientific and engineering breakthroughs have transformed older scientific questions into new nanotechnological ones. At the top of the list is the invention of the scanning tunneling and atomic force microscopes, which have allowed scientists to visualize, investigate, and ultimately probe and experiment with things at a scale never before possible. Between the late 1970s and 1983, Gerd Binnig and Heinrich Rohrer laid the groundwork for modern Scanning Tunneling Microscopes (STM) for which they shared the 1986 Nobel Prize with Ernst Ruska, who designed the first such microscope. These tools allowed engineers and scientist to create stunning images that display the configuration of atoms and molecules. However, it is not just the ability to see atom that makes these tools so fascinating but the ability to actually manipulate, mover or arrange atoms into artificial configurations [4]. Another very significant scientific development that has contributed to the rising enthusiasm for nanotechnology was the discovery of ‘buckyballs’ or buckminsterfullerenes, which are soccer ball shaped molecules composed of 60 carbon atoms. Buckyballs (C₆₀) as well as other quaspherical carbon structures such as C₇₀ and substituted derivatives are known collectively as fullerenes. Buckyballs are named after the famous architect and futurist Buckminster Fuller, whose geodesic domes share the characteristic soccer ball shape and molecule. They are, like diamond and graphite, composed entirely of carbon, but their shape and molecular structure give them special properties. In 1991, S. Iijima, then working at NEC in Japan, discovered another variation on buckyballs, called nanotubes. Nanotubes come in single and multi-walled forms, and the single-walled form is essentially a long cylinder of carbon with half of a buckyball form, and are estimated by some to be the strongest and most flexible material yet discovered. In addition, they have very high electrical conductivity (rivaling copper and gold, but in a much smaller wire), as well as high thermal conductivity [5].

One of the glamorous disciplines to jump quickly into nanotechnology research has been the polymer sciences, which for over 60 years have been experimenting with processes for making new materials, both natural and synthetic. It has been suggested that carbon nanotubes in particular will make exceptional materials for things like car bumpers or jet fighter wings, but the widespread experimentation on, distribution or exposure of these materials is currently limited by the difficulty of producing a large quantity of them. One of the early areas of commercial investment (and of potential

regulatory and environmental concern) is the large scale production of SWCNTs for use in experiments in universities and corporate labs. Mitsubishi Japan, for instance, has begun a significant effort to create larger volumes of fullerenes. The excitement about buckyballs and nanotubes has come primarily from chemists, chemical engineers and physicists. But electrical engineers and, in particular, engineers who create and refine conductors and micro-electronic devices and components. The humble transistor, which has been around since the late 1940s, has reached proportions so small that engineers are now facing the 'novel properties' that nanoscale materials become essential for smaller, faster, lower power devices. Perhaps the smallest such device that has been developed so far is the 'quantum dot' which is designed to confine a single electric charge that might be used as the basis for a computer.

Quantum dots have been the subject of investigation and experiment since the early 1990s, but are not yet used in commercial computing devices. Quantum dots also have unique photo-physical properties and are being investigated for use in biomedical imaging. In addition to chemistry and electrical engineering, the fields of molecular biology and genetic engineering have become expert over the last 10 to 15 years at manipulating the basic components of cellular life at the molecular nanoscale. Techniques and tools that are available to biochemists and molecular biologists, like recombinant DNA and polymerase chain reaction (PCR) have vastly accelerated the kinds of manipulations and experiments that can be done on DNA, RNA and proteins. As mentioned earlier, some of this work is now being redefined as 'nanotechnology' because it is aimed at exploiting the properties of living organisms or molecules involved in organic life. Since about 2000, nano bio-technology has begun to appear as a research field of its own.

1.3 FUNDAMENTAL CONCEPTS

One nanometer (nm) is one billionth, or 10^{-9} , of a meter. As a convention, nanotechnology is taken as the scale range 1 to 100 nm following the definition used by the size of atoms (hydrogen is the smallest atom with diameter of the order of Å), since nanotechnology must build its devices from atoms and molecules. The upper limit is more or less arbitrary but is around the size that phenomena not observed in larger structures start to become apparent and can be made use of in the nano device. These new phenomena make nanotechnology distinct from devices which are merely miniaturized versions of an equivalent macroscopic device; such devices are on a larger

scale and come under the description of micro technology. To put that scale in another context, the comparative size of a nanometer to a meter is the same as that of a marble to the size of the earth. Or another way of putting it: a nanometer is the amount an average man's beard grows in the time it takes him to raise the razor to his face.

Two main approaches are used in nanotechnology. In the "bottom-up" approach, materials and devices are built from molecular components which assemble themselves chemically by principles of molecular recognition. In the "top-down" approach, nano objects are constructed from larger entities without atomic level control. Areas of physics such as nanoelectronics, nanomechanics, nanophotonics and nanoionics have evolved during the last few decades to provide a basic scientific foundation of nanotechnology.

1.4 CHALLENGES IN NANOTECHNOLOGY

Challenges in nanotechnology include the integration of nanostructures systems that can interface with people. Challenges include the building and demonstration of novel tools to study at the nanometer level what is being manifested at the macro level. The small size and complexity of nanoscale structures make the development of new measurement technologies more challenging than ever. New measurement techniques need to be developed at the nanometer scale and may require extremely sensitive instrumentation, while the noise level must be kept very low.

As the dimensions of materials shrink from centimeters or millimeter scale to nanometer scale, the system properties would change accordingly and mostly decrease with the reducing dimensions of the sample materials. Doping in semiconductors has been a very well established process. Random doping fluctuations become extremely important at nanometer scale, since fluctuations of doping concentration would be no longer tolerable in the nanometer scale. Any distribution fluctuation of dopants will result in a totally different functionality of device in such a size range. Location of dopant atoms also matter. Following are the challenges.

- To overcome huge surface energy due to very large surface to volume ratio.
- To prevent nanomaterial from agglomeration with time.

1.5 APPLICATIONS OF NANOTECHNOLOGY

With nanotechnology, a large set of materials and improved products rely on a change in the physical properties when the feature sizes are shrunk. Nanoparticles, for example, take advantage of their dramatically increased surface area to volume ratio. Their optical properties, e.g. fluorescence, become a function of the particle diameter. When brought into a bulk material, nanoparticles can strongly influence the mechanical properties of the material, like stiffness or elasticity. For example, traditional polymers can be reinforced by nanoparticles resulting in novel materials which can be used as lightweight replacements for metals. Therefore, an increasing societal benefit of such nanoparticles can be expected. Such nanotechnologically enhanced materials will enable a weight reduction accompanied by an increase in stability and improved functionality. Practical nanotechnology is essentially the increasing ability to manipulate (with precision) matter on previously impossible scales, presenting possibilities which many could never have imagined – it therefore seems unsurprising that few areas of human technology are exempt from the benefits which nanotechnology could potentially bring. Some of these major benefitted areas and applications of nanotechnology are mentioned below:

- Medicine
 - Diagnostics
 - Drug Delivery
 - Tissue Engineering
- Chemistry and environment
 - Catalysis
 - Filtration
- Energy
 - Reduction of energy consumption
 - Increasing the efficiency of energy production
 - Recycling of batteries
- Information and communication
 - Memory Storage
 - Novel semiconductor devices
 - Novel optoelectronic devices

- o Displays
 - o Quantum computers
- Heavy Industry
 - o Aerospace
 - o Construction
 - o Nanotechnology and constructions
 - o Nanoparticles the steels
 - o Nanoparticles in glass
 - o Nanoparticles in coating
 - o Nanoparticles in fire protection and detection
 - o Vehicle manufacturers
- Consumer goods
 - o Food
 - Nano foods
 - o Household
 - Optics
 - o Textiles
 - Cosmetics

1.6 NANOMATERIALS

1.6.1 Definition

Nanomaterials is field that takes a materials science-based approach to nanotechnology. It studies materials with morphological features on the nanoscale, and especially those that have special properties stemming from their nanoscale dimensions. Nanoscale is usually defined as smaller than a one tenth of a micrometer in at least one dimension though this term is sometimes also used for materials smaller than one micrometer.

1.6.2 Preparation of Nanomaterials

There are two approaches to the synthesis of nanomaterials and the fabrication of a nanostructure: top down and bottom-up. Bottom-up approach is the collection, consolidation and fashioning individual atoms and molecules into the structure. This is carried out by a sequence of chemical reactions controlled by catalysts. It is a process that is widespread in biology. The top-down approach is preparation of nanostructures by starting from bulk material and breaking it down to nano-size. Attrition or milling is

a typical top down method of making nanoparticles, whereas the colloidal dispersion is a good example of bottom up approach of synthesis of nanoparticles. Lithography may be considered as a hybrid approach, since growth of thin film is bottom up whereas etching is top-down. The biggest problem with top down approach is the imperfection of the surface structure. Top down techniques such as lithography can cause significant crystallographic damage to the processed patterns.

Typical bottom up approach is to build atom by atom on a very large scale. In crystal growth, growth species such as atoms, ions and molecules, after impinging onto the growth surface, assemble into crystal structure one after another. Tools required for top-down approach are too big to deal with nano-ranged objects; hence bottom up approach has a clear advantage. Bottom up approach also promises structures with less defects, and better short and long ordering. The original vision of Richard Feynman was of the 'bottom-up' approach of fabricating materials and devices at the atomic or molecular scale, possibly using methods of self-organization and self-assembly of the individual building blocks. An alternative 'top-down' approach is the ultra-miniaturization or etching/milling of smaller structures from larger ones.

- (i) **Bottom up Synthesis:** In the bottom-up approach, atoms, molecules and even nanoparticles themselves can be used as the building blocks for the creation of complex nanostructures; the useful size of the building blocks depends on the properties to be engineered. By altering the size of the building blocks, controlling their surface and internal chemistry, and then controlling their organization and assembly, it is possible to engineer properties and functionalities of the overall nanostructured solid or system. These processes are essentially highly controlled, complex chemical syntheses.
- (ii) **Top down Synthesis:** top down processes involve the removal or reformation of atoms to create the desired structure. Top-down approaches are inherently simpler and rely either on the removal or division of bulk material, or on the miniaturization of bulk fabrication processes to produce the desired structure with the appropriate properties. When controlled, both top-down and bottom-up methods may be viewed as essentially different forms of microstructural engineering. The two approaches are schematically represented in figure 1.1.

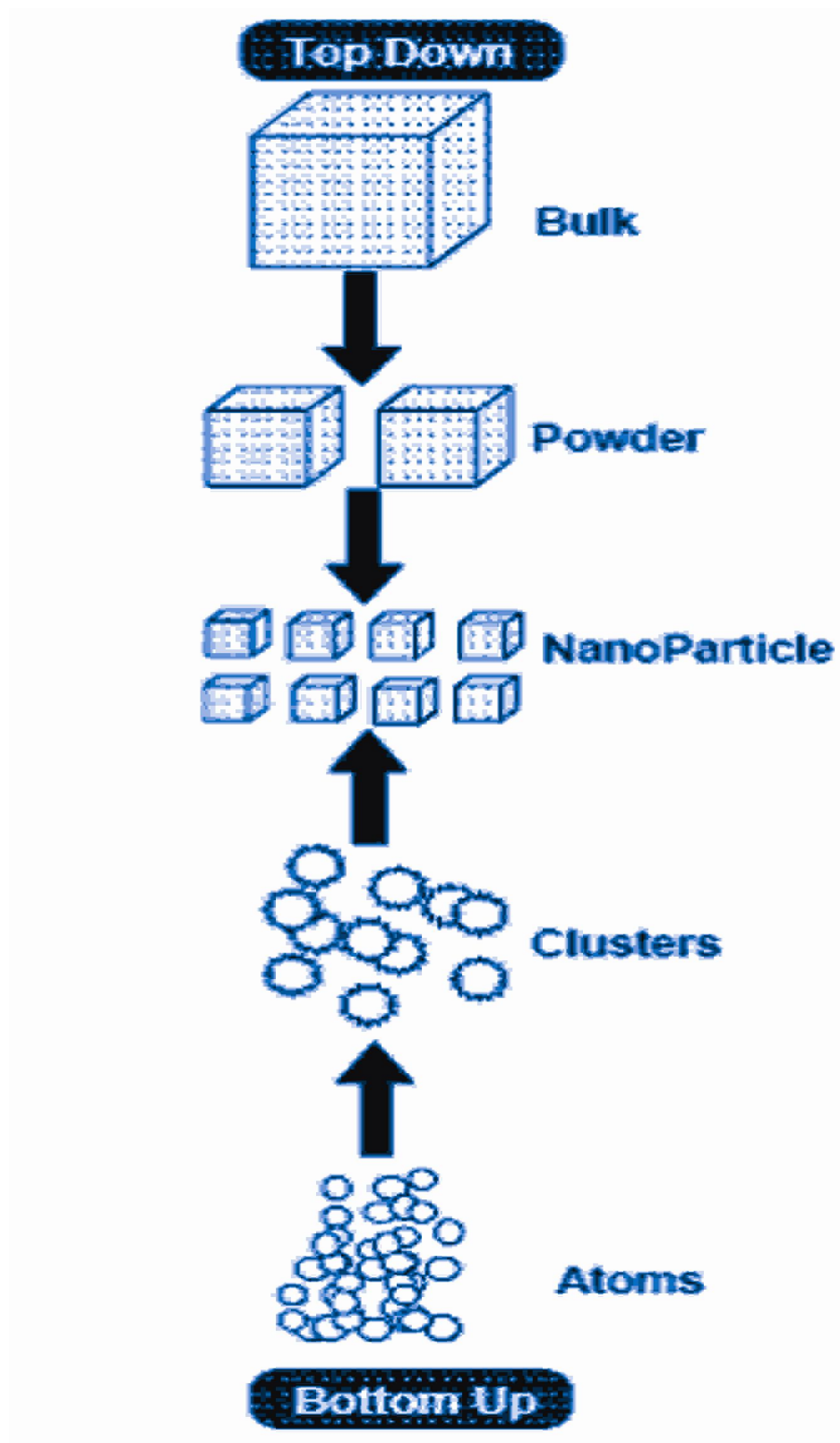


Fig 1.1 : Top down and Bottom up approach

1.6.3 Properties of Nanoparticles

One of the most compelling factors for exhaustive research in nanotechnology is that the nanomaterials have properties markedly different than their bulk counterparts. Many interesting novel effects are observed when the bulk material is reduced to nanometer size regime [6]. These include systematic variation in the electronic properties with size, enhanced catalytic activity as well as exciting current voltage profiles. Materials in nanometer dimensions also exhibit anomalous metal to nonmetal transition as well as markedly different catalytic properties. Magnetic materials in the nanometer dimension exhibit properties like superparamagnetism and has important applications in fields as varied as electronics, MRI and drug delivery [7].

1.6.3.1 The Quantum Effect

One reason for enhanced properties of nanomaterials is quantum confinement. Quantum confinement is the restriction on the mobility of the electrons inside the physical dimensions of nanomaterials. In nanomaterials, when one or more dimensions become so small that it approaches several times the spacing between the atoms in the lattice, the delocalization is impeded. These configurations are usually referred as a quantum well. A quantum wire and a quantum dot are two examples of quantum confinement phenomena. Density of states differs with difference in nano dimensions. Various electronic and other properties depend on density of states. Nature of the dimensionality associated with a nanostructure has effect on its properties.

1.6.3.2 High Surface Area-to-Volume Ratio

Surface area of a given mass of material when subdivided into equal-sized particles increases in inverse proportion to the linear dimensions of the particle. Due to their extremely minute size, nanoparticles have a considerable large fraction of atoms on surface. These atoms have unsatisfied coordination. This gives nanoparticles high surface energy and consequently makes them thermodynamically unstable. The high surface area of the nanoparticles also has an important implication. Catalysis is an important surface phenomenon. The high surface area-to-volume ratio also imparts novel catalytic properties to the nanoparticles [8]. Nano-sized particles of platinum, palladium and rhodium have thus been extensively used with tremendous success in catalyzing a variety of organic transformations, the increased surface area of nanoparticles also influence the sensing properties.

1.6.3.3 Optical Properties

The quantum restrictions on the electronic movement in a nanoparticle are borne in the optical and electronic properties of nanoparticles. Nanoparticles exhibit optical properties that can be suitably fine-tuned according to the particle size. This is true for both metal and semiconductor nanoparticles. The nanoparticles of metal chalcogenides (CdS, CdSe, PbS etc. to name a few) show the property of quantum confinement in their spectroscopic profiles. Thus, for these nanoparticles below their Bohr radius, the UV-vis and fluorescence peaks get systematically blue-shifted as the size of the particles is decreased. This property has been exploited in preparation of materials whose fluorescence covers the complete range of visible spectrum. An interesting commercial application of fluorescent nanoparticles has been their use in the sun screen lotions and creams. Small nanoparticles that are transparent to visible light but absorb in the UV region allow the preparation of lotions that do not leave visible marks on the body upon usage.

1.6.3.4 Electron Conduction Properties

Nanoparticles exhibit properties intermediate of isolated atom and bulk material. This is also true for the electron conduction properties. The electron conduction of nanoparticles of metals is altered due to the reduced density of states in the valence and conduction bands for these systems. The continuous density of state in the bulk state of metal is modified to the formation of discrete energy levels. The separation between these levels can be comparable or larger than thermal energy kT as the particle size is reduced; ' k ' being the Boltzmann constant and ' T ' is the temperature in Kelvin. This separation can be measured in the terms of the average spacing between the successive quantum levels and given by

$$\delta = \frac{4 E_f}{3 n}$$

Where E_f is the Fermi level energy and n is the number of valence electrons in the cluster.

Due to the presence of discrete levels of energy the electron conduction is not continuous in the case of metal nanoparticles. In fact, nanoparticles exhibit discrete charging events [9]. During electron conduction, the electrons have to overcome the

cluster charging energy (E_c) before it can tunnel through the cluster. This occurs only at fixed bias voltage and thus results in incremental increase in the current at potentials where the electron addition to the system is energetically favorable. This results in the current-voltage (I-V) graph exhibiting equally spaced steps. This is commonly known as the "Coulomb staircase" phenomenon [10].

1.6.3.5 Magnetic Properties and Superparamagnetism

Magnetic nanoparticles like different oxides of iron as well as nanoparticles of nickel and manganese have also been successfully synthesized in size-controlled manner. They have important implications in the information storage magnetic materials and as phase contrast reagents for magnetic resonance imaging (MRI). They have already proved to be much better than the currently utilized phase contrast reagents. Due to quantum effects, they also exhibit superparamagnetism. It implies that their magnetic susceptibility is intermediate between a paramagnetic material and a ferromagnetic material.

1.7 NANOCOMPOSITES

1.7.1 Introduction to Nanocomposites

A nanocomposite is as a multiphase solid material where one of the phases has one, two or three dimensions of less than 100 nanometers (nm), or structures having nano scale repeat distance between the different phases that make up the material. In the broadest sense this definition can include porous media, colloids, gels and copolymers, but is more usually taken to mean the solid combination of a bulk matrix and nano-dimensional phases differing in properties due to dissimilarities in structure and chemistry. The mechanical, electrical, thermal, optical, electrochemical, catalytic properties of the nanocomposite will differ markedly from that of the component materials [11]. Size limits for these effects have been proposed, <5 nm for catalytic activity, <20 nm for making a hard magnetic material soft, <50 nm for refractive index changes, and <100 nm for achieving superparamagnetism, mechanical strengthening or restricting matrix dislocation movement [12].

Nanosize powder particles (a few nanometres in diameter, also called nanoparticles) potentially important in ceramics, powder metallurgy, the achievement of uniform nanoporosity and similar applications. Nanoparticles or nanocrystals made of metals, semiconductors, or oxides are of particular interest for their mechanical, electrical,

magnetic, optical, chemical and other properties. Nanocomposites are found in nature, for example in the structure of the abalone shell and bone.

The use of nanoparticle-rich materials long predates the understanding of the physical and chemical nature of these materials. From the mid 1950s nanoscale organo-clays have been used to control flow of polymer solutions (e.g. as paint viscosifiers) or the constitution of gels (e.g. as a thickening substance in cosmetics, keeping the preparations in homogeneous form). By the 1970s polymer/clay composites were the topic of textbooks, although the term "nanocomposites" was not in common use. In mechanical terms, nanocomposites differ from conventional composite materials due to the exceptionally high surface to volume ratio of the reinforcing phase and/or its exceptionally high aspect ratio. The reinforcing material can be made up of particles (e.g. minerals), sheets (e.g. exfoliated clay stacks) or fibres (e.g. carbon nanotubes or electrospun fibres). The area of the interface between the matrix and reinforcement phase(s) is typically an order of magnitude greater than for conventional composite materials. The matrix material properties are significantly affected in the vicinity of the reinforcement. Ajayan et al. note that with polymer nanocomposites, properties related to local chemistry, degree of thermoset cure, polymer chain mobility, polymer chain conformation, degree of polymer chain ordering or crystallinity can all vary significantly and continuously from the interface with the reinforcement into the bulk of the matrix.

The general class of nanocomposite organic/inorganic materials is a fast growing area of research. Significant effort is focused on the ability to obtain control of the nanoscale structures via innovative synthetic approaches. The properties of nano-composite materials depend not only on the properties of their individual parents but on their morphology and interfacial characteristics.

This rapidly expanding field is generating many exciting new materials with novel properties. The latter can derive by combining properties from the parent constituents into a single material. There is also the possibility of new properties which are unknown in the parent constituent materials. This large amount of reinforcement surface area means that a relatively small amount of nanoscale reinforcement can have an observable effect on the macroscale properties of the composite. For example, adding carbon nanotubes improves the electrical and thermal conductivity. Other kinds of nanoparticulates may result in enhanced optical properties, dielectric properties, heat

resistance or mechanical properties such as stiffness, strength and resistance to wear and damage. In general, the nano reinforcement is dispersed into the matrix during processing. The percentage by weight (called mass fraction) of the nanoparticulates introduced can remain very low (on the order of 0.5% to 5%) due to the low filler percolation threshold, especially for the most commonly used non-spherical, high aspect ratio fillers (e.g. nanometer-thin platelets, such as clays, or nanometer-diameter cylinders, such as carbon nanotubes).

1.7.2 Classification of Nanocomposites

1.7.2.1 Ceramic-matrix nanocomposites

In this group of composites the main part of the volume is occupied by a ceramic, i.e. a chemical compound from the group of oxides, nitrides, borides, silicates etc. In most cases, ceramic-matrix nanocomposites encompass a metal as the second component. Ideally both components, the metallic one and the ceramic one, are finely dispersed in each other in order to elicit the particular nanoscopic properties. Nanocomposite from these combinations was demonstrated in improving their optical, electrical and magnetic properties as well as tribological, corrosion-resistance and other protective properties. The binary phase diagram of the mixture should be considered in designing ceramic-metal nanocomposites and measure have to be taken to avoid a chemical reaction between both components. The last point mainly is of importance for the metallic component that may easily react with the ceramic and thereby lose its metallic character. This is not an easily obeyed constraint, because the preparation of the ceramic component generally requires high process temperatures. The safest measure is thus is to carefully choose immiscible metal and ceramic phase. A good example of such a combination is represented by the ceramic-metal composite of TiO_2 and Cu, the mixtures of which were found immiscible over large areas in the Gibbs' triangle [13]. The concept of ceramic-matrix nanocomposites was also applied to thin films that are solid layers of a few nm to some tens of μm thickness deposited upon an underlying substrate and that play an important role in the functionalization of technical surfaces. Gas flow sputtering by the hollow cathode technique turned out as a rather effective technique for the preparation of nanocomposite layers. The process operates as a vacuum-based deposition technique and is associated with high deposition rates up to some micron and the growth of nanoparticles in the gas phase. Nanocomposite layers in the ceramics range of composition were prepared from TiO_2 and Cu by the hollow cathode technique that showed a high mechanical hardness, small coefficients of friction and a high resistance to corrosion.

1.7.2.2 Metal-matrix nanocomposites

With the advent of nanomaterials, nanocomposites are envisioned, and are being developed, with properties that overcome the limitations for metals or composites that contain micron scale reinforcements [14]. Metal matrix composites reinforced with metal or ceramic nanoparticles have superior performance to conventional materials in terms of stiffness as well as creep and wear resistance. [15] Another kind of nanocomposite is the energetic nanocomposite, generally as a hybrid sol-gel with a silica base, which, when combined with metal oxides and nano-scale aluminium powder, can form superthermite materials [16].

1.7.2.3 Polymer-matrix nanocomposites

In the simplest case, appropriately adding nanoparticulates to a polymer matrix can enhance its performance, often in very dramatic degree, by simply capitalizing on the nature and properties of the nanoscale filler (these materials are better described by the term nanofilled polymer composites) [17] as per figure 1.2.

This strategy is particularly effective in yielding high performance composites, when good dispersion of the filler is achieved and the properties of the nanoscale filler are substantially different or better than those of the matrix, for example, reinforcing a polymer matrix by much stiffer nanoparticles of ceramics, clays, or carbon nanotubes. Alternatively, the enhanced properties of high performance nanocomposites may be mainly due to the high aspect ratio and/or the high surface area of the fillers [18-19], since nanoparticulates have extremely high surface area to volume ratios when good dispersion is achieved.

Nanoscale dispersion of filler or controlled nanostructures in the composite can introduce new physical properties and novel behaviours that are absent in the unfilled matrices, effectively changing the nature of the original matrix (such composite materials can be better described by the term genuine nanocomposites or hybrids). Some examples of such new properties are fire resistant or flame retardancy and accelerated biodegradability [20].

POLYMER NANOCOMPOSITES

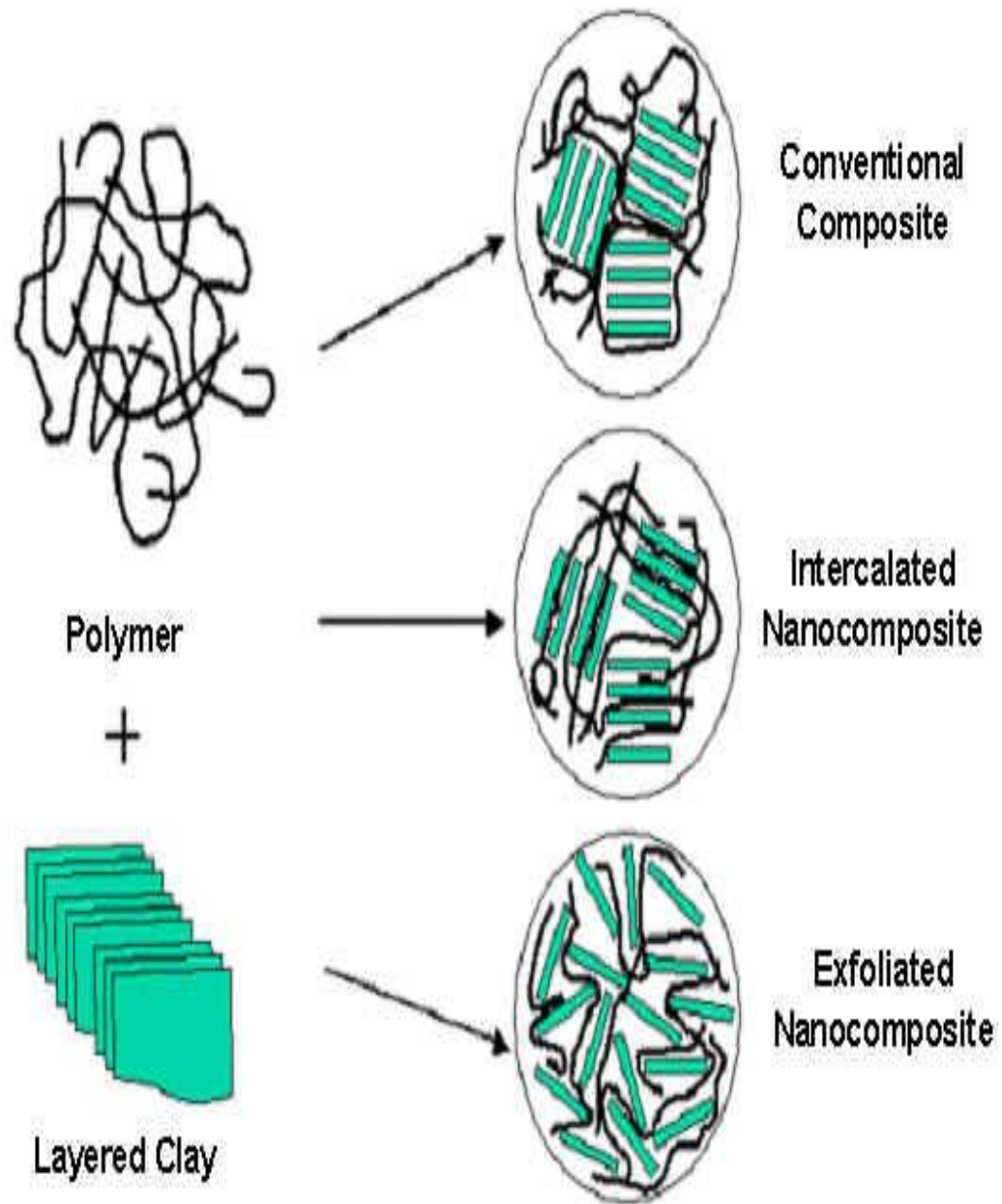


Figure 1.2 : Polymer-matrix nanocomposite

1.7.2.4 Advantages of Nanosized Additions

Several conferences and publications on the Nanocomposites revealed clearly the property advantages that nanomaterial additives can provide in comparison to both their conventional filler counterparts and base polymer. Properties which have been shown to undergo substantial improvements include:

- Mechanical properties e.g. strength, modulus and dimensional stability
- Decreased permeability to gases, water and hydrocarbons
- Thermal stability and heat distortion temperature
- Flame retardancy and reduced smoke emissions
- Chemical resistance
- Surface appearance
- Electrical conductivity
- Optical clarity in comparison to conventionally filled polymers

1.7.3 Particle Loadings

In addition it is important to recognise that nanoparticulate/fibrous loading confers significant property improvements with very low loading levels, traditional microparticle additives requiring much higher loading levels to achieve similar performance. This in turn can result in significant weight reductions (of obvious importance for various military and aerospace applications) for similar performance, greater strength for similar structural dimensions and, for barrier applications, increased barrier performance for similar material thickness.

1.7.4 Areas of Applications

Mechanical property improvements have resulted in major interest in nanocomposite materials in numerous automotive and general/industrial applications. These include potential for utilisation as mirror housings on various vehicle types, door handles, engine covers and intake manifolds and timing belt covers.

More general applications currently being considered include usage as impellers and blades for vacuum cleaners, power tool housings, mower hoods and covers for portable electronic equipment such as mobile phones, pagers etc.

Gas Barriers

The gaseous barrier property improvement that can result from incorporation of relatively small quantities of nanoclay materials is shown to be substantial. Data provided from various sources indicates oxygen transmission rates for polyamide-organoclay composites which are usually less than half that of the unmodified polymer.

Passive barrier characteristics are provided by nanoclay particles incorporated via melt processing techniques whilst the active contribution comes from an oxygen scavenging ingredient (undisclosed). Oxygen transmission results reveal substantial benefits provided by nanoclay incorporation in comparison to the base polymer (rates approximately 15-20% of the bulk polymer value, with further benefits provided by the combined active/passive system).

Food Packaging

The requirement for a non-refrigerated packaging system capable of maintaining food freshness for three years. Nanoclay polymer composites are currently showing considerable promise for this application.

It is likely that excellent gaseous barrier properties exhibited by nanocomposite polymer systems will result in their substantial use as packaging materials in future years. A somewhat more esoteric possibility arising from enhanced barrier performance recently suggested has been blown-films for artificial intestines.

Fuel Tanks

The ability of nanoclay incorporation to reduce solvent transmission through polymers such as polyamides has been demonstrated. As a result, considerable interest is now being shown in these materials as both fuel tank and fuel line components for cars. Of further interest for this type of application, the reduced fuel transmission characteristics are accompanied by significant material cost reductions.

Films

The presence of filler incorporation at nano-levels has also been shown to have significant effects on the transparency and haze characteristics of films. In comparison to conventionally filled polymers, nanoclay incorporation has been shown to significantly enhance transparency and reduce haze. With polyamide based composites,

this effect has been shown to be due to modifications in the crystallisation behaviour brought about by the nanoclay particles; spherulitic domain dimensions being considerably smaller. Similarly, nano-modified polymers have been shown, when employed to coat polymeric transparency materials, to enhance both toughness and hardness of these materials without interfering with light transmission characteristics.

Environmental Protection

Water laden atmospheres have long been regarded as one of the most damaging environments which polymeric materials can encounter. Thus an ability to minimise the extent to which water is absorbed can be a major advantage. Specifically, increasing aspect ratio was found to diminish substantially the amount of water absorbed, thus indicating the beneficial effects likely from nanoparticle incorporation in comparison to conventional microparticle loading. Hydrophobic enhancement would clearly promote both improved nanocomposite properties and diminish the extent to which water would be transmitted through to an underlying substrate. Thus applications in which contact with water or moist environments is likely could clearly benefit from materials incorporating nanoclay particles.

Flammability Reduction

The ability of nanoclay incorporation to reduce the flammability of polymeric materials was a major theme of the paper presented by Gilman of the National Institute of Standards and Technology in the US. In his work Gilman demonstrated the extent to which flammability behaviour could be restricted in polymers such as polypropylene with as little as 2% nanoclay loading. In particular heat release rates, as obtained from cone calorimetry experiments, were found to diminish substantially by nanoclay incorporation. Although conventional microparticle filler incorporation, together with the use of flame retardant and intumescent agents would also minimise flammability behaviour, this is usually accompanied by reductions in various other important properties. With the nanoclay approach, this is usually achieved whilst maintaining or enhancing other properties and characteristics.

1.8 CERAMIC

1.8.1 Introduction to Ceramic

A ceramic is an inorganic, non-metallic solid prepared by the action of heat and subsequent cooling. Ceramic materials may have a crystalline or partly crystalline structure, or may be amorphous (e.g., a glass). Because most common ceramics are crystalline, the definition of ceramic is often restricted to inorganic crystalline materials, as opposed to the non-crystalline glasses. Ceramics are commonly electrical and thermal insulators, brittle composed of more than one element (e.g., two in Al_2O_3).

The word ceramic comes from the Greek word "κεραμικός" (keramikos), "of pottery" or "for pottery", from "κέραμος" (keramos), "potter's clay, tile, pottery" which is said to derive from the Indo- unattested), meaning heat. The earliest mention of the word "ceramic" is the Mycenaean Greek ke-ra-me-we, "workers of European word *cheros (ceramics", written in Linear b syllabic script. Ceramic may be used as an adjective describing a material, product or process; or as a singular noun, or, more commonly, as a plural noun, ceramics.

1.8.2 Ceramic Structures

Ceramics comprise crystallites that may vary in structure, perfection and composition as well as in size, shape and the internal stresses to which they are subjected. In addition, the interfaces between crystallites are regions in which changes in lattice orientation occur, often accompanied by differences in composition and attendant electrical effects. As a consequence it is very difficult, if not impossible, to account precisely for the behaviour of ceramics. The study of single-crystal properties of the principal components has resulted in valuable insights into the behaviour of ceramics. However, the growth of single crystals is usually a difficult and time-consuming business while the complexities of ceramic microstructures render the prediction of properties of the ceramic from those of the corresponding single crystal very uncertain. Consequently, empirical observation has usually led to the establishment of new devices based on ceramics before there is more than a partial understanding of the underlying physical mechanisms.

1.8.3 Arrangement of Ions in Ceramics

When atoms combine to form solids their outer electrons enter new states whilst the inner shells remain in low-energy configurations round the positively charged nuclei.

The relative positions of the atoms are determined by the forces between them. In ionic materials, with which we are mainly concerned, the strongest influence is the ionic charge which leads to ions of similar electrical sign having their lowest energies when as far apart as possible and preferably with an ion of opposite sign between them.

The second influence is the relative effective size of the ions which governs the way they pack together and largely determines the crystal structure. Finally there are quantum-mechanical 'exchange' forces, fundamentally electrostatic in origin, between the outer electrons of neighbouring ions which may have a significant influence on configuration. In covalently bonded crystals the outer electrons are shared between neighbouring atoms and the exchange forces are the main determinants of the crystal structure. There are many intermediate states between covalent and ionic bonding and combinations of both forms are common among ceramics, particularly in the silicates.

The following discussion of crystal structure is mainly devoted to oxides, and it is assumed that the ionic effects are dominant. Ionic size is determined from the distances between the centres of ions in different compounds and is found to be approximately constant for a given element in a wide range of compounds provided that account is taken of the charge on the ion and the number of oppositely charged nearest neighbours (the coordination number). It must be realized that the concept of ions in solids as rigid spheres is no more than a useful approximation to a complex quantum wave-mechanical reality. For instance, strong interactions between the outer electrons of neighbouring ions, i.e. covalent effects, reduce the ionic radius while the motion of ions in ionic conduction in solids often requires that they should pass through gaps in the structure that are too small for the passage of rigid spheres. Nevertheless, the concept allows a systematic approach to the relation of crystal structure to composition. Most ceramics usually contain both metallic and nonmetallic elements with ionic or covalent bonds. Therefore, the structure of the metallic atoms, the structure of the nonmetallic atoms, and the balance of charges produced by the valence electrons must be considered. As with metals, the unit cell is used in describing the atomic structure of ceramics. The cubic and the hexagonal cells are most common (Fig 1.3). Additionally, the difference in radii between the metallic and nonmetallic ions plays an important role in the arrangement of the unit cell. In metals, the regular arrangement of atoms into densely packed planes led to the occurrence of slip under stress, which gives metal their characteristic ductility.

In ceramics, brittle fracture rather than slip is common because both the arrangement of the atoms and the type of bonding is different. The fracture or cleavage planes of ceramics are the result of planes of regularly arranged atoms. Ionic bonding is found in many ceramic structures such as NaCl, MgO and Al_2O_3 . Atoms have unlike electrical charges, making them ions, which create an electrostatic attraction between atoms. This causes bonding between atoms. The ions pack into a regular arrangement. The nature of the ceramic depends on the size of the ion charges and the size of the ions. Covalent bonding is found in many ceramic structures such as SiC, BN and diamond. The atoms in these ceramics are arranged so that each pair of nearest neighbour atoms forms a chemical bond by sharing a pair of electrons. The high energy of covalent bonds makes these ceramics very stable with regard to chemical and thermal changes. Unlike ionic and metallic bonding, covalent bonding is directional and as a result, the atoms in many covalently bonded ceramics are arranged symmetrically to give a highly ordered structure. This gives them a very high hardness but also gives them a low toughness as they can be easily fractured along certain crystal planes.

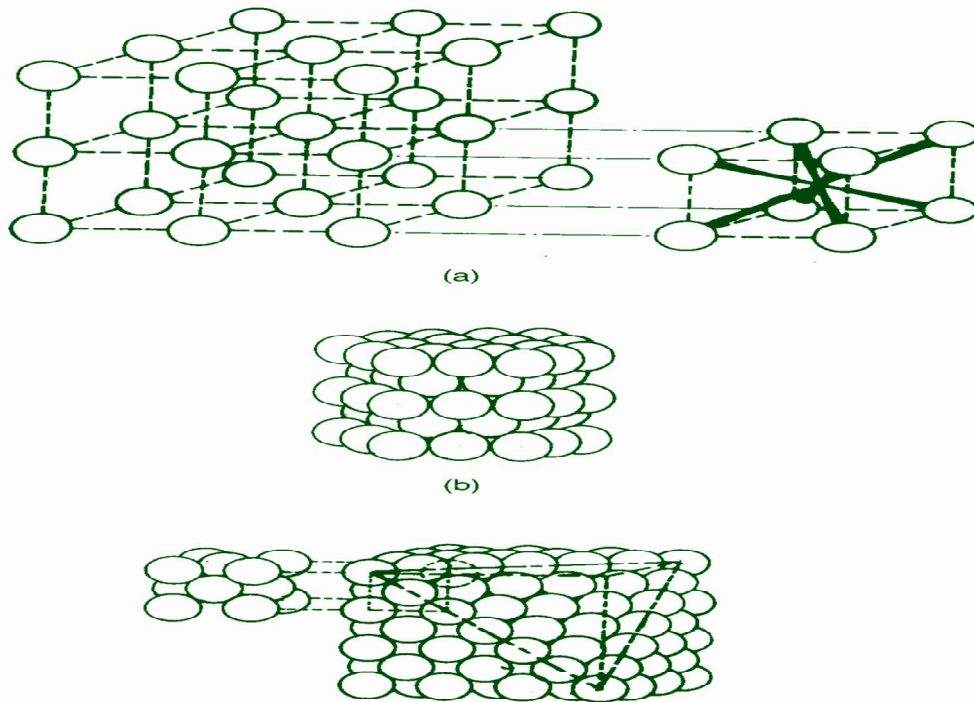


Figure 1.3 Packing of ions: (a) simple cubic packing showing an interstice with eightfold coordination; (b) hexagonal close packing; (c) cubic close packing showing a face-centered cubic cell.

1.8.3.1 Crystal Structures

Ceramic bonds are mixed, ionic and covalent, with a proportion that depends on the particular ceramics. The ionic character is given by the difference of electronegativity between the cations (+) and anions (-). Covalent bonds involve sharing of valence electrons. Very ionic crystals usually involve cations which are alkalis or alkaline-earths (first two columns of the periodic table) and oxygen or halogens as anions.

The building criteria for the crystal structure are two:

- maintain neutrality
- charge balance dictates chemical formula
- achieve closest packing

The condition for minimum energy implies maximum attraction and minimum repulsion. This leads to contact, configurations where anions have the highest number of cation neighbors and vice versa. The parameter that is important in determining contact is the ratio of cation to anion radii, r_C/r_A .

1.8.4 Types of Ceramic Materials

A ceramic material is often understood as restricted to inorganic crystalline oxide material. It is solid and inert. Ceramic materials are brittle, hard, strong in compression, weak in shearing and tension. They withstand chemical erosion that occurs in other materials subjected to acidic or caustic environment. Ceramics generally can withstand very high temperatures such as temperatures that range from 1,000°C to 1,600°C (1,800°F to 3,000°F). Exceptions include inorganic materials that do not include oxygen such as silicon carbide or silicon nitride. A glass is often not understood as a ceramic because of its amorphous (non-crystalline) character. However, glass making involves several steps of the ceramic process and its mechanical properties are similar to ceramic materials. Traditional ceramic raw materials include clay minerals such as kaolinite, whereas more recent materials include aluminium oxide, more commonly known as alumina. The modern ceramic materials, which are classified as advanced ceramics, include silicon carbide and tungsten carbide. Both are valued for their abrasion resistance, and hence find use in applications such as the wear plates of

crushing equipment in mining operations. Advanced ceramics are also used in the medicine, electrical and electronics industries.

1.8.4.1 Crystalline ceramics

Crystalline ceramic materials are not amenable to a great range of processing. Methods for dealing with them tend to fall into one of two categories - either make the ceramic in the desired shape, by reaction in situ, or by "forming" powders into the desired shape, and then sintering to form a solid body. Ceramic forming techniques include shaping by hand (sometimes including a rotation process called "throwing"), slip casting, tape casting (used for making very thin ceramic capacitors, etc.), injection moulding, dry pressing, and other variations. A few methods use a hybrid between the two approaches.

1.8.4.2 Non-crystalline ceramics

Non-crystalline ceramics, being glasses, tend to be formed from melts. The glass is shaped when either fully molten, by casting, or when in a state of toffee-like viscosity, by methods such as blowing to a mold. If later heat-treatments cause this glass to become partly crystalline, the resulting material is known as a glass-ceramic.

1.8.5 Types of Ceramics Products & Applications

For convenience, ceramic products are usually divided into four sectors; these are shown below with some examples:

- Structural, including bricks, pipes, floor and roof tiles.
- Reflectories, such as kiln linings, gas fire radiants, steel and glass making crucibles.
- Whitewares, including tableware, wall tiles, pottery products, and sanitary ware.

1.8.5.1 Classification of technical ceramics

Technical ceramics can also be classified into three distinct material categories:

- Oxides: Alumina, zirconia
- Non-oxides: Carbides, borides, nitrides, silicides
- Composites: Particulate reinforced combinations of oxides and non-oxides.

Each one of these classes can develop unique material properties because ceramics tend to be crystalline.

- Ceramics are used in the manufacture of knives. The blade of a ceramic knife will stay sharp for much longer than that of a steel knife, although it is more brittle and can be snapped by dropping it on a hard surface.
- Ceramics are increasingly used in motor-sports, where a series of durable and lightweight insulatory coatings have become necessary, for example on exhaust manifolds.
- Ceramics such as alumina and boron carbide have been used in ballistic armored vests to repel large-calibre rifle fire. Such plates are known commonly as Small Arms Protective Inserts (SAPI). Similar material is used to protect cockpits of some military airplanes, because of the low weight of the material.
- Ceramic balls can be used to replace steel in ball bearings. Their higher hardness means that they are much less susceptible to wear and can offer more than triple lifetimes. They also deform less under load meaning they have less contact with the bearing retainer walls and can roll faster. In very high speed applications, heat from friction during rolling can cause problems for metal bearings; problems which are reduced by the use of ceramics. Ceramics are also more chemically resistant and can be used in wet environments where steel bearings would rust. The two major drawbacks to using ceramics is a significantly higher cost, and susceptibility to damage under shock loads. In many cases their electrically insulating properties may also be valuable in bearings.
- Work is being done in developing ceramic parts for gas turbine engines. Currently, even blades made of advanced metal alloys used in the engines' hot section require cooling and careful limiting of operating temperatures. Turbine engines made with ceramics could operate more efficiently, giving aircraft greater range and payload for a set amount of fuel.
- Recently, there have been advances in ceramics which include bio-ceramics, such as dental implants and synthetic bones. Hydroxyapatite, the natural mineral component of bone, has been made synthetically from a number of biological and chemical sources and can be formed into ceramic materials. Orthopedic implants

made from these materials bond readily to bone and other tissues in the body without rejection or inflammatory reactions. Because of this, they are of great interest for gene delivery and tissue engineering scaffolds. Most hydroxyapatite ceramics are very porous and lack mechanical strength and are used to coat metal orthopedic devices to aid in forming a bond to bone or as bone fillers. They are also used as fillers for orthopedic plastic screws to aid in reducing the inflammation and increase absorption of these plastic materials. Work is being done to make strong, fully dense nano crystalline hydroxyapatite ceramic materials for orthopedic weight bearing devices, replacing foreign metal and plastic orthopedic materials with a synthetic, but naturally occurring, bone mineral. Ultimately these ceramic materials may be used as bone replacements or with the incorporation of protein collagens, synthetic bones.

- High-tech ceramic is used in watchmaking for producing watch cases. The material is valued by watchmakers for its light weight, scratch-resistance, durability and smooth touch. IWC is one of the brands that initiated the use of ceramic in watchmaking. The case of the IWC 2007 Top Gun edition of the Pilot's Watch Double chronograph is crafted in high-tech black ceramic.

1.9 METAL OXIDES NANOMATERIALS: The emergence of a new generation of smart materials

The ability to control the particle size and morphology of nanoparticles is of crucial importance nowadays both from a fundamental and industrial point of view, considering the tremendous amount of high-tech applications of nanostructured metal oxide material devices such as dye-sensitized solar cells, displays and smart windows, chemical, gas and biosensors, lithium batteries, and supercapacitors. Indeed, further development, improvement, and optimization of such devices will be reached provided that better fundamental understanding of their fascinating and unique physical properties and electronic structure where quantum mechanics prevail will be available, as well as a better match between the materials design and the required device applications for the sake of miniaturization and performance.

In almost all applications of nanomaterials devices, fabrication represents one of the most important challenges to their realization and commercialization. Indeed, to fulfill the great promise and expectation of nanomaterials, scientists and chemists in

particular have developed a plethora of new synthetic techniques and patterning methods, such as self-assembly, mechanochemistry, chemistry by microwave, lithography or template- and membrane-based synthesis. However, to afford the production needs of cheap, clean, reliable, and durable materials with controlled properties for realistic and practical applications of nanotechnology, the request of mass production of thin film devices will probably represent one of the most important issues of the development of future devices. Chemical design of nanomaterials would probably contribute to a great extent. Another crucial issue of nano-scale materials production is the ability to control the purity of the materials.

The basic idea of purpose-built nanomaterials is to model and design materials with the proper morphology, size, shape, and texture in order to probe, tune, and optimize the investigated physical properties. The purpose is to demonstrate that the same material (crystallographic structure and composition) designed in the proper fashion may achieve better performance, overcoming its weakness or even developing new properties.

1.9.1 Manganese Oxide, Lanthanum Hydroxide and Lanthanum Oxide

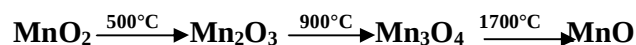
1.9.1.1 Manganese Oxide (Mn_3O_4) Nanoparticles

Manganese (II, III) oxide is the chemical compound with formula Mn_3O_4 . It appears brown in colour and is insoluble in water. It is paramagnetic at room temperature. Mn_2O_3 and Mn_3O_4 have also been used to produce soft magnetic materials such as manganese zinc ferrite which have use in power supply transformer cores.

- Manganese oxides form a complex oxide system as manganese can exist in different oxidation states (+2, +3, +4, +6).
- Hausmanite (Mn_3O_4) is one of the most stable phases of manganese oxides.
- Mn_3O_4 possess spinel structure in which Mn exist in two oxidation states +2 and +3 occupying the tetrahedral and octahedral voids respectively. Therefore it can be doped with other elements having the same oxidation state.
- Manganese oxides have wide range of applications because of their use as catalysts, magnetism, electrochemistry and air decontamination properties besides negative temperature co-efficient (NTC) behaviour.

Amongst many transition metal oxides being investigated for various applications, manganese oxides emerge as potential candidates for many niche applications (high power batteries, chemical sensing devices, catalysts electronics, etc.) in terms of cost and environmentally benign qualities.

As far as manganese oxide phases are concerned, the most common phases of manganese oxide in air at different temperatures are shown below. That is, the following thermal oxidation reactions are possible in manganese oxides. It is well known that MnO_2 exhibits thermochemical changes as shown below,



Amongst different phases of manganese oxide, Mn_2O_3 possesses poor electronic conductivity. Nevertheless, it pronounces electro-chemical redox activity via Mn^{3+} to Mn^{4+} transition giving rise to one electron transfer.

Manganese oxides nanoparticles have particular physical and chemical properties and are expected to apply in catalysis, energy storage, magnetic data storage and sensors.

1.9.1.1.1 Applications of Manganese Oxide (Mn_3O_4) Nanoparticles

Mn_3O_4 use in many applications, such as batteries, high-density magnetic storage media, electrochromic materials, corrosion-inhibiting pigment, and catalysts. It is also starting materials for synthesizing soft magnetic materials, which have extensive applications in electronic and information technologies. Nanometer-sized Mn_3O_4 with remarkably increased surface area and greatly reduced size will have enhanced properties. Magnetism of materials in the nanosize regime is of extreme importance due to their potential applications in diverse fields such as high-density recording media, ferrofluid technology, spin valves, magnetic resonance imaging, magneto caloric refrigeration, etc. When the crystallite sizes are of the order of a few nanometers, energy considerations favor the formation of single domain particles, which could exhibit unique properties such as superparamagnetism. It is an important catalyst for removing carbon monoxide and nitrogen oxide from waste gas.

1.9.1.2 Lanthanum hydroxide and Lanthanum Oxide

Lanthanum hydroxide, $\text{La}(\text{OH})_3$, is a white amorphous powder that can be formed by precipitating lanthanum salts by potassium hydroxide. It decomposes ammonium salts. Lanthanum Hydroxide, also called Lanthanum Hydrate, is mainly applied in specialty glass, water treatment and catalyst.

- Formula: $\text{La}(\text{OH})_3 \cdot x\text{H}_2\text{O}$
- Molecular Weight: 189.93
- Appearance: White
- Solubility: Soluble in strong mineral acids
- Stability: Easily hygroscopic

The thermal transformation from lanthanum hydroxide $\text{La}(\text{OH})_3$ to lanthanum oxide (La_2O_3) results in two successive endothermic effects, caused by a loss of water. Thermal analysis (DTA/TGA, DSC), and high-temperature powder X-ray diffraction (HT -XRD) were used to characterize this process. Lanthanum hydroxide oxide (LaOOH) was obtained as temporary product at $\sim 330^\circ\text{C}$. The structure of lanthanum hydroxide oxide was characterized by X-ray powder diffraction methods. It has a hexagonal structure.

Lanthanum oxide is an odorless, white solid that is insoluble in water, but soluble in dilute acid. Depending on the pH of the compound, different crystal structures can be obtained. La_2O_3 is widely used in industry as well as in the research laboratory.

- Lanthanum, a rare earth element with stable +3 oxidation state.
- La_2O_3 has largest band gap of the rare earth oxides at 4.3 eV, while also having the lowest lattice energy, with very high dielectric constant, $\epsilon = 27$.
- Lanthanum oxide has p-type semi-conducting properties because its resistivity decreases with an increase in temperature, average room temperature resistivity is $10^3 \Omega \text{ cm}$.

Lanthanum and its compounds have unique electronic structure and exhibit number of transition modes involving the 4f shell of these atoms/ions. These compounds have shown outstanding catalytic, optical, electrical and magnetic properties.

1.10 NTC THERMISTERS

A thermistor is an electronic component that exhibits a large change in resistance with a change in its body temperature. The word “thermistor” is actually a contraction of the words “thermal resistor”. The NTC thermistors which are composed of metal oxides. The most commonly used oxides are those of manganese, nickel, cobalt, iron, copper and titanium. The fabrication of commercial NTC thermistors uses basic ceramics technology and continues today much as it has for decades. In the basic process, a

mixture of two or more metal oxide powders are combined with suitable binders, are formed to a desired geometry, dried, and sintered at an elevated temperature.

By varying the types of oxides used, their relative proportions, the sintering atmosphere, and the sintering temperature, a wide range of resistivities and temperature coefficient characteristics can be obtained. The interest for temperature sensors is due to their high rate of change of resistivity with temperature. Negative temperature coefficient (NTC) thermistors are semiconducting ceramics. Resistance R measured at room temperature provides the resistivity $\rho = RA/L$ with A the metallized surface and L the thickness when components have a cylindrical disc shape. Their resistivity varies exponentially with temperature, as shown in the following Arrhenius equation:

$$\rho = \rho_0 \exp(B/T)$$

where

ρ is the resistivity of the material

T is the absolute temperature

B is the temperature coefficient.

Temperature sensors used for measurement and control include thermo-couples, thermistors, and semiconductor band gap sensors. Among these, thermistor is widely used due to high sensitivity, accuracy, low cost and unique thermo electric properties [21]. Thermistors have a wide array of applications in air-conditioners, refrigerators, freezers, water heaters, washing machines, computers, power supply facilities and communication equipment [22-23].

Various new materials and modifications of existing materials have been proposed to achieve better sensing devices [21, 24-25]. Oxides of manganese have attracted much interest during the last decade for many industrial applications involving Catalysis [26-28], magnetism [29], electrochemistry [30-31], air decontamination and temperature sensing [32-33]. NTC behaviour of bulk Mn_3O_4 and its composite with La_2O_3 has also been reported [31]. Komoba et al. [34] have investigated the use of Mn_3O_4 as a precursor in the synthesis of Li-Mn-O electrode material for rechargeable Lithium batteries. Studies have been reported by several groups describing the synthesis of Mn_3O_4 nanoparticles with varying properties through various techniques [34-37]. Negative temperature coefficient (NTC) thermistors are capable of measuring temperatures within a specific range with high accuracy and sensitivity thereby making them good candidates for applications in a number of electrical and electronic devices [38-39]. Thermistor materials typically exhibit Arrhenius behaviour over a wide

temperature range and are characterized by a thermister constant $\beta = \Delta E/K$, where ΔE is the activation energy and K is the Boltzmann constant. Typically, materials with $\beta > 3,000$ K find applications in temperature sensors [40]. Oxides of Manganese, Cobalt and Nickel which typically exist as spinel crystal structures have been studied for applications in NTC thermisters due to their interesting electrical properties [41]. Specifically, Mn_3O_4 is an important transition-metal oxide and is well known as a promising technological material for usage in NTC thermisters [33, 42]. However NTC characteristics of nano Mn_3O_4 powder have been discussed in this chapter. The oxide exists as $Mn^{+2}(Mn^{+3})_2O_4$ with Mn^{+2} and Mn^{+3} ions occupying the tetrahedral and octahedral sites respectively [43]. However, in the present study Mn_3O_4 , $La(OH)_3$ and $Mn_3O_4-La_2O_3$ ($LaMnO_3$) nanopowders show a totally different behaviour from their bulk counterparts and hence significantly change the performance of many functional materials, as discussed in Chapter 5.

1.10.1 Types of NTC Thermisters

Commercial NTC thermisters can be classified into two major groups depending upon the method by which electrodes are attached to the ceramic body. Each group may be further subdivided into various types of thermisters where each type is characterized by differences in geometry, packaging and/or processing techniques.

The first group consists of bead type thermisters. All of the bead type thermisters have platinum alloy leadwires which are directly sintered into the ceramic body. Bead type thermisters include the following:

- Bare Beads
- Glass Coated Beads
- Ruggedized Beads
- Miniature Glass Probes
- Glass Probes
- Glass Rods
- Bead-in-Glass Enclosures

The second group of thermisters has metalized surface contacts. All of these types are available with radial or axial leads as well as without leads for surface mounting or mounting by means of spring contacts. Metallized surface contact thermisters include the following:

- Disks
- Chips (Wafers)
- Surface Mounts
- Flakes
- Rods
- Washers

NTC thermistors are available in a wide variety of configurations and protective coatings can be useful for large no. of applications. The most stable and accurate thermistors available are those which are hermetically sealed in glass. Hermetically sealed thermistors are also used, which works at 300°C temperature, however requirement for lower working temperature is in the range of 100-300°C.

1.10.2 Properties of NTC Thermistors

NTC thermistors have electrical properties which are important considerations in each application. These properties are a function of the geometry of the thermistor, of the particular “material system” of metal oxides that is being used and of the additional materials (electrodes, inks, solders, leadwires, etc.) that are applied to the basic device. There are three basic electrical characteristics that account for virtually all of the applications in which NTC thermistors may be used.

- i. Current-Time Characteristic
- ii. Voltage-Current Characteristic
- iii. Resistance-Temperature Characteristic

There are also several applications where the NTC thermistor is indirectly heated by resistive devices or even other thermistors. These applications are merely special cases of one of the three basic electrical characteristics

1.10.3 Applications of NTC Thermistors

The NTC thermistor is a versatile component that can be used in a wide variety of applications where the measured is temperature dependent. Table 1 gives a partial listing of thermistor applications that are grouped according to one of the three fundamental electrical characteristics; the current-time characteristics, the voltage-current characteristic, and the resistance-temperature characteristic. Applications based

on the voltage-current characteristic generally involve changes in the environmental conditions or the electrical circuit parameters of a self-heated thermister. In turn, these changes will result in a shift of the operating point on any given voltage-current curve or family of such curves. These applications are further subdivided into four major categories depending on the type of excitation that causes the operating point to change. NTC thermisters are generally manufactured from pressed die chip of semi-conducting material-often a sintered ceramic oxide. One of the main reasons that semi-conductors are so useful for thermisters is that their electrical properties can be controlled and enhanced by 'doping' or alloying with impurities -either elements or compounds. NTC material should have high thermister constant (B) minimum of 3000K. Manganese based spinel semi-conducting ceramics have been studied as NTC thermisters since they possess interesting electrical properties. A common commercially available NTC thermister material is Mn_3O_4 which can be doped with varying amount of NiO . It is also possible to dope the Mn_3O_4 with other combination of impurities such as CoO , CuO and La_2O_3 . The bulk Mn_3O_4 possesses NTC behaviour with cut off temperature around 400°C .

The current study investigates the NTC behaviour of a Manganese oxide and lanthanum oxide nanocomposite. Majority of the studies related to Mn_3O_4 have been made with bulk materials but here we are synthesizing it in nano form. Synthesis, characterisation and applications of nanoparticles with diameter of few nanometers are subjects of intense research owing to the deviation of fundamental properties of materials from those of its bulk form.

CHAPTER – 2

LITERATURE REVIEW

AND

SCOPE OF WORK

LITERATURE REVIEW & SCOPE OF WORK

2.1 LITERATURE REVIEW

A number of methods have been employed for the preparation of manganese oxides and lanthanum manganese oxide composite. Chen et al. have synthesized α - Mn_2O_3 nanorods via a hydrothermal assisted cleavage decomposition mechanism. A hydrothermal cleavage-decomposition mechanism was used to synthesize single-crystal α - Mn_2O_3 nanorods at 160 °C for 16 h using KMnO_4 as manganese source and CTAB as reducing reagent. The as-synthesized products were characterized by powder X-ray diffraction, transmission electron microscopy, high-resolution transmission electron microscopy and infrared spectrum. The results indicate that the reaction temperature is a crucial factor for the formation of α - Mn_2O_3 nanorods. These nanorods exhibit single-crystal nature, and have an average diameter of 36 nm and lengths of up to 1 μm . Based on experimental results, a hydrothermal cleavage-decomposition mechanism has been proposed on the formation of α - Mn_2O_3 nanorods. [44]. Gibot et al. have reported hydrophilic and hydrophobic methods for synthesis of Mn_3O_4 nanoparticles. Mn_3O_4 Hausmanite nanoparticles were prepared in aqueous solution by using metallic salt and hydrazine as precursor and reducing agent, respectively. The crystallite sizes ranged from 10 to 20 nm and the particle diameter distribution was very narrow and estimated between 20 and 30 nm. Influence of some parameters such as temperature, time of reaction, surfactant nature was studied for a synthesis in an aqueous medium. These nanoparticles were characterized by X-ray diffraction, infrared spectroscopy, scanning and transmission electron microscopies and nitrogen absorption measurements. [45]. Ozkaya et al. synthesized Manganese oxide (Mn_3O_4) nanoparticles by a novel oxidation-precipitation method based on oxidation of manganese sulfate to manganese salts. Manganeseoxide (Mn_3O_4) nanoparticles were successfully prepared by a novel oxidation-precipitation method based on oxidation of manganese sulfate to manganese salts and hydrolyzing with NaOH and concentrated ammonium solution. X-ray diffraction (XRD) analysis confirmed the tetragonal hausmanite structure with average crystallite size of ~ 14 and ~ 11 nm; transmission electron microscopy (TEM) analysis showed crystallite size of 14 ± 5 and 12 ± 3 nm for NaOH- and NH_3 -hydrolyzed samples,

respectively. The ferromagnetic transition temperatures are 38 and 40 K for NaOH- and NH₃-hydrolyzed samples, respectively. These values are lower than that of bulk Mn₃O₄. [46]. Yuna et al. characterized nano-size whiskers of manganese oxide prepared by the soft chemistry templating synthesis method. Manganese oxide is used for a catalyst in organic chemistry, as electrodes for lithium ion batteries, and as a magnetic material. When manganese oxide is in a form of nano-size whiskers, it shows higher activity and efficiency. It was found that nanowhiskers grew three dimensionally from nanoparticles of Mn₃O₄. The structure and chemistry of whiskers were analyzed using transmission electron microscopy, electron energy loss spectroscopy, and energy dispersive x-ray spectrometry[47]. Fritsch et al reported Manganese oxides form a complex oxide system as manganese can exist in different oxidation states (+2, +3, +4). Hausmannite, Mn₃O₄, with a specific surface area of 10 m²/g has been oxidized at low temperatures (300°C < T < 425°C). In this temperature range both Mn²⁺ and Mn³⁺ cations are oxidized. The oxidation of Mn²⁺ to Mn³⁺ is governed by a diffusion process and the spinel structure is stable up to 425°C. Oxidation of Mn³⁺ to Mn⁴⁺ leads to the crystallization of the Mn₅O₈ phase. Careful oxidation studies show the formation of two metastable manganese oxides, Mn₅O₈ and a defect spinel of the formula Mn₂O_{2.78}. The coordination numbers and the cation–anion distances in Mn₃O₄, γ-Mn₂O_{2.78}, and α-Mn₂O₃ obtained by EXAFS (extended X-ray absorption fine structure) are compared [48]. Singla et al. explained in detail the NTC behaviour and other properties on Mn₃O₄ bulk material with cut off temperature of 400°C and other variants with cutoff temperature 330°C. Hausmannite (Mn₃O₄) is one of its most stable phases. Manganese oxides have wide range of applications because its use as catalysis, magnetism, electrochemistry and air decontamination. Singla et al. reported negative temperature co-efficient (NTC) behaviour Mn₂O₃ and Mn₃O₄ have also been used to produce soft magnetic materials such as manganese zinc ferrite which have use in power supply transformer cores. Majority of the Studies related to Mn₃O₄ were made with bulk materials. On the other hand, synthesis and applications of nanoparticles with diameter of few nanometers is a subject of intense research owing to the deviation of fundamental properties of a material from those of its bulk form. Negative temperature coefficient (NTC) thermistors have use in number of electronic and electrical devices. Study offers many desirable features for Temperature measurement and control within their operating temperature range. NTC behaviour occurs when the thermal conductivity of a material rises with increase in temperature, typically in a defined

temperature range. The NTC behaviour is governed by Arrhenius equation over a wide range of temperature $B_{T_1-T_2} = (\ln R_2 - \ln R_1) / (1/T_2 - 1/T_1)$. Where R_1 and R_2 are measured electrical resistance at temperature T_1 and T_2 respectively. The constant B is related to energy required for electrical conduction, hence as the value of B decreases, the material becomes insulating. Therefore, the NTC material should have high thermister constant (B) at minimum of 3000 K. NTC thermisters are generally manufactured from pressed die chip of semi-conducting material-often a sintered ceramic oxide. A common commercially available NTC thermister material is Mn_3O_4 which can be doped with varying amount of NiO . The bulk Mn_3O_4 Possesses NTC behaviour with out off temperature at about $400^\circ C$. It is also possible to dope Mn_3O_4 with other combination of impurities such as CoO , CuO and La_2O_3 . Among these Lanthanum, is a rare earth element which can also be used to form a composite of lanthanum and manganese oxide. La_2O_3 has largest band gap of the rare earth oxides at 4.3 eV. La_2O_3 is widely used in industry as well as in the research laboratories. Lanthanum oxide has p-type semi-conducting properties because its resistivity decreases with an increase in temperature, average room temperature resistivity is $10^3 \Omega \text{ cm}$. Various methods have been employed for the preparation of different manganese oxides. [49]. Mu et al. reported Manganese oxide (Mn_3O_4) nanoparticles were prepared by a facile solution method using starch as capping agent. The nanoparticles were characterized by means of X-ray diffraction (XRD) and AFM. The results showed that the Mn_3O_4 nanoparticles were single phase, spherical, and uniformly dispersive. The average particle size was evaluated to be approximately 35 nm [50]. Singh et al. reported Room temperature Mossbauer spectra of different nano metal oxides multiferroic systems prepared by solution combustion technique reveal the long range ferromagnetic ordering, supported by M-H loop measurements. Magnetic hyperfine interaction field and isomer shift for these nanocrystallite was also studied using X-ray photoelectron spectroscopy. A small residual magnetic moment is observed for these nanoparticles, which may be attributed to size confinement at nanoscale and to spin canting. These nanomaterials are of great importance in basic as well as applied research [51]. Baykal et al. have proposed low temperature synthesis of Mn_3O_4 nanoparticles from hydrous manganese (II) hydroxide gel [52]. Chen et al. have investigated that dripping speed of NaOH solution plays an important role in the nanostructure evolution of Mn_3O_4 nano-crystals [53]. Wu et al. has fabricated manganses oxide directly on stainless steel substrate and has also investigated the electrochemical performance of the synthesized manganese oxide in

aqueous electrolyte [54]. Thomas et al. have studied the nucleation and growth mechanism for the formation of MnO nanoparticles synthesized by decomposition of a manganese oleate complex in high boiling nonpolar solvents using TEM, FT-IR, and AAS analysis. The exceptionally narrow size distribution indicates that nucleation and growth are clearly separated. This leads to a uniform growth with a very narrow size distribution on the existing nuclei. The particle size can be controlled by adjusting the reaction time, reaction temperature, solvent, and heating rate. The particle size increases with temperature, reaction time, and the chain length (boiling point) of the solvent. FT-IR and NMR spectra revealed that the oleate capping agent binds to the surface in a bidentate manner. In addition, XPS measurements indicate that MnO nanocrystals are air-stable. No significant oxidation of Mn^{2+} to Mn^{3+} occurred even after several days [55]. Hassan et al. reported Mn_2O_3 nanowires with diameter ~ 70 nm were synthesized by a simple hydrothermal method using Mn(II) nitrate as precursor. X-ray diffraction, field emission scanning electron microscopy, transmission electron microscopy (TEM), and energy dispersive X-ray spectroscopy techniques were employed to study structural features and chemical composition of the synthesized nanowires. These results suggest that the pH is critical factor affecting the morphology and production of the Mn_2O_3 nanowires [56]. Liang et al. reported a solvothermal route has been developed to synthesize nanocrystalline Mn_2O_3 via the reduction of MnO_2 using ethanol as the reducing agent as well as the solvent at 130°C . X-ray diffraction and X-ray photoelectron spectroscopy analysis revealed that the as-synthesized products are of tetragonal structure Mn_2O_3 (g- Mn_2O_3). Transmission electron spectroscopy image showed that the obtained g- Mn_2O_3 comprises square-shaped nanocrystallites with the sizes of about 50 nm. The formation mechanism of Mn_2O_3 was studied [57]. Xiangying et al. reported an acidification-hydrothermal method was developed to synthesize α - MnO_2 nanowires, which was subsequently treated with ethanol, resulting in γ - Mn_2O_3 nanowire bundles on a large scale. The electrochemical characterisation was carried out by cyclic voltammetry, which indicated that the α - MnO_2 nanowires in $0.5 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ aqueous electrolyte was of an excellent electrode material for supercapacitor at the scan rate of 10 mV S^{-1} in the range of 0.0–0.85 V [58]. Yi-Fan et al. reported that a method is established in the synthesis of Mn_2O_3 nanocrystals by the thermolysis of manganese (III) acetyl acetonate and Mn_3O_4 nanocrystals by the thermolysis of manganese(II) acetyl acetonate on a mesoporous silica, SBA-15. In particular, Mn_2O_3 nanocrystals are the first to be reported to be

synthesized on SBA-15 [59]. Moon et al. reported Nanocrystalline manganese oxide powders have been prepared at 25°C by precipitation from $\text{Mn}(\text{NO}_3)_2$ aqueous solution. The presence and addition sequence of H_2O_2 significantly influence particle characteristics of the resulting manganese oxides, including crystal structure, particle size and morphology, and surface area, depending upon molar ratio of H_2O_2 with respect to Mn [60]. Li et al. reported uniform and well shaped Mn_3O_4 nano-octahedra are synthesized using a simple hydrothermal method under the help of polyethylene glycol (PEG200) as a reductant and shape-directing agent. The shape and crystal orientation of the nanoparticles is reconstructed by scanning electron microscopy and electron tomography. The magnetic testing demonstrates that the Mn_3O_4 nano-octahedra exhibit anomalous magnetic properties: the Mn_3O_4 nano-octahedra around 150 nm show a similar Curie temperature and blocking temperature to Mn_3O_4 nanoparticles with 10 nm size. Photodecomposition activity of Mn_3O_4 nano-octahedra is much superior to that of commercial Mn_3O_4 powders. The anomalous magnetic properties and high superior photo decomposition activity of well shaped Mn_3O_4 nano-octahedra should be related to the special shape of the nanoparticles. Therefore, the shape preference can largely broaden the application of the Mn_3O_4 nano-octahedra [61]. Tandon et al. reported Single phase nanocrystalline lead zirconate titanate (PZT) powder of composition $\text{Pb}(\text{Zr}(0.52)\text{Ti}(0.48))\text{O}_3$ has been prepared by sol-gel process by using lead acetate trihydrate, zirconium propoxide and titanium propoxide as lead, zirconium and titanium precursor materials respectively. XRD, FTIR and TGA/DTA techniques are used to characterize structural, vibrational and thermal changes involved during the formation of PZT nanocrystalline powder with tetragonal phase. XRD pattern exhibits the polycrystalline nature of the powder heat treated at 800 °C with preferential orientation of (110) plane. Simultaneous TGA/DTA studies of the gel powder show endothermic and exothermic peaks corresponding to weight loss at different temperatures and increase in weight between 750 °C and 800°C which confirms the improvement in crystallization. IR transmittance spectra of the powders heat treated at 650°C and 750 °C show the coexistence of rhombohedral and teragonal phases and above this temperature only teragonal phase exists [62]. Yang et al. reported Manganese oxide (hausmannite) polyhedralnanocrystals were prepared by a microwave-assisted solution-based method at 80°C. The as-prepared Mn_3O_4 nanocrystals were characterized by means of X-ray diffraction, field-emission transmission electron microscopy, field-emission scanning electron microscopy and

Raman spectrum. Mn_3O_4 polyhedral nanocrystals prepared by microwave heating at 80 °C for 60 min were of cubic and rhombohedral shapes with the edge lengths in the range of 15–40 nm. Mn_3O_4 nanocrystals grew following the Ostwald ripening mechanism with increasing reaction time. High-resolution transmission electron microscopy and selected area electron diffraction confirm that the as-obtained polyhedral nanocrystals were single-crystalline. The magnetic behaviour of Mn_3O_4 nanocrystals was studied. Mn_3O_4 nanocrystals show an obvious ferromagnetic behaviour at low temperatures. The magnetic behaviour of Mn_3O_4 nanocrystals was sensitive to crystal size. Ferromagnetic onset temperatures of samples 1 and 3 are 40.6 and 41.1 K, respectively, lower than that observed for bulk Mn_3O_4 (42 K) [63]. Taekyung et al. reported a novel and facile method for the synthesis of manganese oxide (Mn_3O_4) nanocrystals with various sizes and shapes. Mn_3O_4 nanocrystals were synthesized via a reaction of manganese (II) acetate with water in xylene in the presence of surfactants at the temperature of as low as 90 °C in air atmosphere. Structural characterisations revealed that the synthesized nanocrystals were tetragonal Mn_3O_4 structure and that they were highly crystalline in spite of the low reaction temperature. The size and shape of the nanocrystals were readily controlled by varying the experimental conditions such as precursors, surfactants, and injection temperature of water. Nanoplates with a thickness of 5 nm and side dimensions of 9, 15, and 22 nm were synthesized using oleylamine as the surfactant. When carboxylic acid was used as the cosurfactant along with oleylamine, spherical nanocrystals were obtained with sizes of 5.5, 6.2, 7.2, 8.5, and 15 nm.. The current procedure can be readily applicable to large-scale synthesis because of their facile and mild reaction conditions including low reaction temperature and air environment and the use of nontoxic and inexpensive reagents [64]. Yamashita et al. reported Mn_2O_3 is better than Mn_3O_4 for catalytic NO decomposition; regardless, appreciable activities were not observed below 773 K [65]. Wang et al. reported structural-controlled synthesis of manganese oxide nanostructures from single Mn_3O_4 precursor via hydrothermal method. The obtained products include and MnO_2 nanorods, MnO_2 urchin-like microspheres, birnessite nanowires and nanosheets. The morphology evolution process and the effect of varying reaction parameter to the phase and morphology are systematically investigated. The formation mechanisms have been rationalized [66]. Xing et al. reported Mn_3O_4 nanoparticles were prepared by a novel oxidation–precipitation method at a low temperature. The crystal phase, microstructure, surface area and electrochemical properties of the products were

characterized by X-ray diffraction (XRD), high-resolution transmission electron microscopy (HRTEM), N₂ adsorption–desorption isotherms and cyclic voltammetry (CV). The results indicate that the addition of citric acid and tartaric acid remarkably reduced the particle size and increased the specific surface area of Mn₃O₄ nanoparticles. The samples prepared by the addition of citric acid and tartaric acid have a narrow particle size distribution of 5–10 nm, a surface area of 119 and 122 m²/g, and a capacitance of 171 and 172 F g⁻¹, respectively [67]. Gui et al. reported nanocrystalline γ -Mn₂O₃ has been prepared directly by the reduction of aqueous KMnO₄ with hydrazine solution at ambient temperature, without post-treatment of heating. X-ray powder diffraction (XRD) pattern demonstrates its good phase purity. Transmission electron microscopy (TEM) images show homogeneous nanoparticles with a narrow size distribution. The average grain size is about 9 nm [68]. Chang et al. reported nanosized manganese oxide particles have been synthesized via vapor phase growth. The diameter of the nanoparticles can be controlled by the growth temperature: the higher the temperature, the larger the diameter of the particle. Magnetization measurements show that the manganese oxide nanoparticles have an obvious ferromagnetic behaviour with the Curie temperature around 40K. The latter is size-dependent, namely: the smaller is the diameter of the particles, the lower is the Curie [69]. Morsali et al. reported a new Mn(II) compound was synthesized by the reaction of pyterpy and mixtures of manganese(II) nitrate and sodium azide using heat gradient method. The compound characterized by IR spectroscopy, elemental analyses and X-ray crystallography. The crystal structure of compound was determined by single-crystal X-ray diffraction. Mn₃O₄ nanoparticles were obtained by thermolyses of compound in oleic acid at 320 °C under air atmosphere. The Mn₃O₄ nanoparticles were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared (FT-IR) spectroscopy and thermogravimetric analysis (TGA) [70]. Thackeray et al. reported Lithium has been inserted chemically and electrochemically into Mn₃O₄, at room temperature. X-ray diffraction confirms the coexistence of a cubic and a tetragonal phase in the compositional range $0.1 \leq x \leq 0.8$. [71]. Chowdari et al. synthesized metal oxides using molten salt method at low temperature 280°C for 30 min or 3h in air, at a heating and cooling rate of 3°C/min and quenching. Effects of different precursor concentration and then various salt combinations, and heating, cooling rate on morphology and crystal structure of the these oxides are also studied by X-Ray Diffraction (XRD), Scanning Electron

Microscopy (SEM), Density and Brunauer-Emmett-Teller (BET) surface area methods[72]. Yamashita et al investigated the Temperature-programmed desorption of NO adsorbed on Mn_2O_3 and Mn_3O_4 . When heated to 873 K, large amounts of H_2O along with lesser amounts of CO_2 and O_2 desorbed from single-phase samples of Mn_2O_3 and Mn_3O_4 to form O vacancies and create coordinatively unsaturated (CUS) cations. Exposure of these surfaces to NO at 300 K produced a certain amount of N_2O , but no other detectable gas-phase products, with more formation over Mn_2O_3 (0.72×10^{18} molecule $\text{N}_2\text{O}/\text{m}^2$) than that over Mn_3O_4 (0.10×10^{18} molecule $\text{N}_2\text{O}/\text{m}^2$). [73]. Komoba et al. investigated the use of Mn_3O_4 as a precursor in the synthesis of Li-Mn-O electrode material for rechargeable Lithium batteries [74]. Yadav et al. reported Mn doped BiFeO_3 nanoparticles were synthesized using sol-gel technique. The influence of Mn doping on structural, dielectric, magnetic, magnetoelectric and optical properties of BiFeO_3 was studied. Magnetic measurements revealed the enhancement of ferromagnetic property with increasing Mn doping in BiFeO_3 . On increasing Mn concentration from 5 to 15 mol% in BiFeO_3 , a change in magnetocapacitance from 1.46% to 2.6% showed the improvement of multiferroic properties [75]. Menaka et al. describes the control of the assembly of NiMn_2O_4 nanospheres and hexagonal particles by tuning the precursor (nickel manganese oxalate) morphology. The aspect ratio (2 to 24) of the nickel manganese oxalate precursors has been achieved by the variation of the surfactant, co-surfactant and non-polar phase by the reverse micellar route [76]. Bedi et al. reported thermal evaporation technique has been employed to grow silver phthalocyanine nanostructures on glass substrates kept at different substrate temperature in vacuum of 10^{-5} Torr. These samples have been studied for their structural and optical properties. TEM investigations show the formation of long nanowires in AgPc thin films prepared at substrate temperature of 298 and 303 K, whereas films prepared at 308 K show the formation of nanobelts. XRD observations reveal that silver phthalocyanine nanowires are crystalline in nature [77]. Nathan et al. reported an efficient single step combined sonochemical and solvothermal synthesis process to obtain bulk quantities of nanospherical particles of cubic Mn_2O_3 and characterized its pseudocapacitive characteristics in relevance to electrochemical capacitors for the first time [78]. Schmidt et al. reported NiMn_2O_4 ceramics exhibit a logarithmic increase of resistance with decreasing temperature (NTCR), which makes the compound well suited for use as a thermister material in temperature sensing applications. In bulk material there are often problems with poor stability and

reproducibility due to incomplete intergranular contact. The surface topology was examined by scanning-electron microscopy (SEM) and atomic force microscopy (AFM). The phase purity of the source powder and the films was assessed by X-ray diffractometry (XRD). The electrical properties were analysed by measuring the resistance - temperature characteristics [79]. Billik et al. have synthesized nanocrystalline, spherical α -Mn₂O₃ particles by mechano-chemical reduction [80]. Dierstein et al. suggested the novel method for electrochemical deposition of nanocrystalline metal oxides under oxidizing conditions. EDOC (Electrochemical Deposition under Oxidizing Conditions) is a new method for the electrochemical preparation of metaloxide nanoparticles. It is based on the reduction of metal ions; Coming from a sacrificial anode; In a non-aqueous medium. The formed metal clusters are immediately coated with stabilizers; Which prevent the particles from agglomeration and realize the nanocrystalline state [81]. Cushing et al. discussed the recent advances in the liquid phase synthesis of inorganic nanoparticles [82]. Tartaj et al. described state-of-the-art synthetic routes for the preparation of magnetic nanoparticles useful for biomedical applications. In addition to this topic, described detail of the possible applications of magnetic nanoparticles in the field of biomedicine with special emphasis on showing the benefits of using nanoparticles. Finally, addressed some relevant findings on the importance of having well-defined synthetic routes to produce materials not only with similar physical features but also with similar crystallochemical characteristics [83]. Katiyar et al. reported highly (100) textured graded manganese (Mn) doped Ba_{0.5}Sr_{0.5}TiO₃ [BST (50/50)] thin films were deposited on lanthanum aluminate substrates using sol-gel technique and demonstrated that graded acceptor doping is a promising technique to reduce the temperature coefficient of capacitance (TCC), loss tangent, and leakage current of BST thin films. In the temperature range between 175 and 260 K the reported TCC of Mn graded BST (50/50) films is less than $5.55 \times 10^{-4}/\text{K}$, which is comparable to the best capacitors known so far [84]. Buzea et al. reported nanomaterials' toxicity among scientists and manufacturers handling them. Significantly, technological advancement has also changed the character of particulate pollution, increasing the proportion of nanometer-sized particles-“nanoparticles”-and expanding the variety of chemical compositions. Adverse effects of nanoparticles on human health depend on individual factors such as genetics and existing disease, as well as exposure, and nanoparticle chemistry, size, shape, agglomeration state, and electromagnetic properties. The key to understanding the

toxicity of nanoparticles is that their minute size, smaller than cells and cellular organelles, allows them to penetrate these basic biological structures, disrupting their normal function. Nanostructured materials often exhibit beneficial properties, from UV absorbance in sunscreen to oil-less lubrication of motors[85]. Lu et al. reported the remarkable mechanical properties of nanocomposite coatings, such as superhardness, high elastic modulus and recovery, excellent resistance against cracking, low wear rate, and high thermal stability, are due to their unique structures and deformation mechanisms at the nanometer scale. Recent advances are reviewed mainly with respect to the understanding of the origin of superhardness in nanocomposite coatings. A few controversial issues relevant to the identification of superhard coatings are mentioned. Also discussed are several models, based on analyses and simulations at different levels from continuum to atomistic scales, to elucidate likely superhardening mechanisms. Finally, some open problems and continuing challenges are highlighted [86]. Satyanarayana et al. reported the quest for materials with molecular scale properties that can satisfy the demands of the 21st century has led to the development of onedimensional nanostructures, ODNS. Nearly, every class of traditional material has an ODNS counterpart. ODNS has a profound impact in nanoelectronics, nanodevices and systems, nanocomposite materials, alternative energy resources and national security. The interface of nanoscience and technology with biological and therapeutic sciences is expected to radically improve the ability to provide efficient treatments in otherwise impossible situations [87]. Packirisamy et al. reported Gold-poly(methyl methacrylate) nanocomposites are prepared by an in situ method, by irradiating spin-coated films containing the polymer and the gold precursor dissolved in acetone. The reduction of gold ions results in the formation of Au that nucleates and grows within the polymer film. It is shown that, depending on the energy source, gold nanoparticles with different shapes can be formed. Nanocomposites preparedthrough UV, thermal and MW-irradiation, respectively, show a low sensitivity toward the environment. However, by annealing the samples at temperatures well above the glass transition temperature of the polymer, the response to dielectric environment appears to be enhanced significantly. The results show that, by using adequate post-synthesis heat treatments, gold-polymer nanocomposites can be used as plasmonic sensing platforms [88]. Gunay et al. reported Mn_3O_4 nanoparticles were synthesized via an ionic liquid (IL) assisted process at room temperature, which is rather difficult to achieve by other techniques. The synthesized product was characterized by powder X-ray diffraction

(XRD), transmission electron microscopy (TEM), Fourier transform infrared (FT-IR) spectroscopy, thermal gravimetry (TG), and vibrating sample magnetometry (VSM). The prepared material showed a high purity, while crystallite size and particle size agree well with each other, 17 ± 2 and 19 ± 3 nm, respectively, revealing nearly single crystalline character of nanoparticles. [89]. Murphy et al. reported Wet chemical methods have been used for large scale production of nanomaterials. Solutions phase synthesis of nanorods / wires of controlled diamensions is still a challenging task as surface energy favours the sphearical particle formation [90]. Wang et al. reported single-crystal cubic NiO nanorods with diameters of 30–80 nm and lengths, of up to tens of micrometers were synthesized by using a simple precursor thermal decomposition in NaCl flux with NiCO_3 as the precursor, which was prepared by one-step, solid-state reaction of $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$ and Na_2CO_3 at ambient temperature. The crystallinity, purity, morphology, and structure features of the as prepared NiO nanorods were investigated by powder X-ray diffraction (XRD), transmission electron microscopy (TEM), selected area electron diffraction (SAED), high-resolution transmission electron microscopy (HRTEM), and Raman spectrum [91]. Zhang et al. reported without the use of any extra surfactant, template or other additive, shape-controlled synthesis of sphere, urchin and tube-like nanocrystallites has been realized just via hydrothermal treatment of different amounts. The possible mechanism for the formation of the various nanostructures of CuS in this system was discussed [92]. Kruis et al. reported Nanoparticles, smaller than 100 nm, have many properties which differ from the corresponding bulk material thereby making them attractive for many new electronic, optical or magnetic applications. They can be used for these functional applications in the form of granular films, nanocomposites or nanophase materials. These applications include quantum dots, luminescent materials, gas sensors, resistors and varistors, conducting and capacitive films, high-temperature superconductors, and thermoelectrical, optical and magnetic materials [93]. Kityk et al. studied UV -induced nonlinear absorption in lanthanum calcium borate single crystals in the spectral range of 475-1130 nm. UV-induced TPA measurements were performed in the spectral range of 475-1130 nm using as fundamental beam the third harmonics of the 28 ps Nd-YAG pulsed laser as a pumping beam for LiB_3O_5 optical parametrized generator using Z-scan method. Pumping laser beam created a thin surface layer (about 80-90 nm) that was the source of the observed photoinduced TPA [94]. Behera et al. conducted low temperature synthesis of spherical lanthanum aluminate nanoparticles by a novel

ultrasonic assisted combined gel synthesis from metal chloride solutions with ammonia destabilization. The decomposition and crystallization behaviour of the gel was studied by DTA/TGA. Phase pure lanthanumaluminate was obtained for powders calcined at a temperature as low as 600 °C for 4 h. SEM study revealed that the powders were uniformly distributed with occasional primary agglomerates. TEM micrographs show that the powders were spherical nanoparticles with sizes in the range of 25–40 nm. [95]. Lin et al. fabricated lanthanum borate nanowires by reacting lanthanum oxide and boron with carbon nanotubes at 1100°C. Lanthanum borate nano wires had been fabricated by reacting lanthanum oxide and boron with carbon nanotubes at 1100 °C. Electron microscopy studies show that the nanowires have a single-crystal structure with uniform diameters of ~ 15 nm and lengths up to several micrometers. The morphology of lanthanum borate nanowires depends on the shape of the carbon nanotubes at high reaction temperatures [96]. Mazloumi et al. studied the properties of lanthanum hydroxide ($\text{La}(\text{OH})_3$) nano-structures, including elliptical nanoparticles, octahedral rods and irregular nanoparticles prepared chemically in sodium hydroxide (NaOH) and potassium hydroxide (KOH) solutions. Lanthanum hydroxide ($\text{La}(\text{OH})_3$) and oxide (La_2O_3) are rare novel earth compounds which have so far been fabricated with various morphologies such as nanopowders, nanotubes, nanowires, nanorods and nanobelts [97]. Xiangyang et al. reported Lanthanum hydroxide ($\text{La}(\text{OH})_3$) nanorods with 6–15 nm in width and 200–400 nm in length have been prepared by a simple hydrothermal process. X-ray diffraction (XRD) shows that the nanorods are of hexagonal structure, and further more, high-resolution transmission electron microscopy (HRTEM) identifies that the lanthanum hydroxide nanorods are highly crystalline. Moreover, the mechanism for the hydrothermal synthesis of lanthanum hydroxide nanorods has been preliminarily presented [98]. Neumann et al. reported the thermal transformation from lanthanum hydroxide ($\text{La}(\text{OH})_3$) to lanthanum oxide (La_2O_3) results in two successive endothermic effects, caused by a loss of water. Thermal analysis (DTA/TG, DSC), and high-temperature powder X-ray diffraction (HT-XRD) were used to characterize this process. Lanthanum hydroxide oxide (LaOOH) was obtained as temporary product at ~330 °C. The structure of lanthanum hydroxide oxide was characterized by X-ray powder diffraction methods. The reaction enthalpies of the dehydration process were calculated by DSC. Further, the activation energy of the transformation lanthanum hydroxide to lanthanum hydroxide oxide was estimated by isothermal TG studies [99]. Murugan et al. used a simple gel to crystal

conversion route has been used for the preparation of nanocrystalline La_2O_3 at 80–100 °C under refluxing conditions. Freshly prepared lanthanum hydroxide gel is allowed to crystallize under refluxing and stirring conditions for 4–6 h. Formation of nanocrystallites of La_2O_3 is confirmed by X-ray diffraction (XRD) study. Transmission electron microscope (TEM) investigations revealed that the average particle size is 30 nm for these powders [100]. Imanaka et al. prepared Cubic lanthanum oxide by the oxidation of lanthanum iodide at 700°C in air atmosphere [101]. Wang et al. reported Lanthanum and its compounds have unique electronic structure and exhibit number of transition modes involving 4f shell of these atoms / ions. These compounds have shown outstanding catalytic, optical, electrical and magnetic properties [102]. Pawar et al. reported the temperature dependence of dc electrical conductivity was measured by two-probe technique in the vicinity of phase transition point for ferroelectrics sodium vanadate and rubidium vanadate doped with different concentrations of La_2O_3 . These materials show a sharp change in conductivity at their phase transition temperatures. The activation energy increases slowly with increase in doping concentration of La_2O_3 up to 0.1 mol%, however, it decreases with further increase in doping concentration, in both ferro and para states. The dc electrical conductivity below the Curie temperature is of mixed type (ionic-electronic) while it is electronic type above the Curie temperature [103]. Berger et al. prepared pure and strontium-doped lanthanum manganite nanopowders by solution combustion method using fuel nitrates as oxidants and different organic compounds as fuel (alanine, glycine, urea and semi-oxamazine). The complex precursors isolated before ignition of the system, were characterized by FT-IR spectroscopy and thermal analysis. Lanthanum manganite powders were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), specific surface area and magnetic measurements [104]. Djerdj et al. presented the preparation of lanthanum hydroxide and manganese oxide nanoparticles, based on an aqueous sol-gel process involving the reaction of $\text{La}(\text{O}i\text{Pr})_3$ and KMnO_4 with organic solvents such as benzyl alcohol, 2-butanone and a 1:1 vol. mixture thereof. The preparation of lanthanum hydroxide and manganese oxide nano particles is presented, based on a nonaqueous sol-gel process involving the reaction of $\text{La}(\text{O}i\text{Pr})_3$ and KMnO_4 with organic solvents such as benzyl alcohol, 2-butanone and a 1:1 vol. mixture thereof. The lanthanum manganese oxide system is highly complex and surprising results with respect to product composition and morphology were obtained. Independence of the reaction parameters, the $\text{La}(\text{OH})_3$

nanoparticles undergo a shape transformation from short nanorods with an average aspect ratio of 2.1 to micron-sized nanofibers (average aspect ratio is more than 59.5). Although not directly involved, KMnO_4 plays a crucial role in determining the particle morphology of $\text{La}(\text{OH})_3$. Postsynthetic thermal treatment of the sample containing $\text{La}(\text{OH})_3$ nanofibers and $\beta\text{-MnOOH}$ nanoparticles at the temperature of 800 °C for 8 h yielded polyhedral LaMnO_3 and worm-like La_2O_3 nanoparticles as final products [105].

Cortés Escobedo et al. reported on the synthesis of lanthanum manganese oxide (LaMnO_3) by solid state reaction using high energy reactive ball milling from manganese oxides (MnO , Mn_2O_3 , MnO_2) mixed with lanthanum oxide in stoichiometric ratios. Morphology and particle size of powders were investigated by SEM and laser diffraction at different milling times. Structural characterisation as a function of milling time was carried out by XRD as well as by TEM for specific samples.

synthesis of lanthanum manganese oxide (LaMnO_3) by solid state reaction using high energy reactive ball milling from manganese oxides (MnO , Mn_2O_3 , MnO_2) mixed with lanthanum oxide in stoichiometric ratios. Morphology and particle size of powders were investigated by SEM and laser diffraction at different milling times. Structural characterisation as a function of milling time was carried out by XRD as well as by TEM for specific samples. Lanthanum manganites were successfully obtained by the simplest possible process, a single step milling at room temperature showing however different transformation kinetics respective to the manganese oxide precursors. Complete reaction of LaMnO_3 using Mn_2O_3 and MnO_2 was achieved only after 210 and 270 min of milling, respectively obtaining a mixture of rhombohedral, cubic and orthorhombic phases. The crystalline structure of the manganites prepared using zirconia/nylamid milling system was mainly cubic [106].

Katiyar et al. studied the optical properties of undoped and Lanthanum doped lead titanate thin films, and also demonstrated that the optical characterisation of thin films can be used as an effective diagnostic tool to assess film quality. Absorption coefficient (α) and the band-gap energy (E_g) were obtained for undoped and La doped films with varying La concentration. It was found that the refractive index and packing fraction values decrease with La doping. La doping was found to decrease the grain size of the films and increase the density of individual grains. Increased La content led to clustering of smaller grains. The observed variation of band-gap energy with La doping has been correlated to the observed microstructure of these films [107].

Arulraj et al. reported electron transport and magnetic properties of the cation-deficient compositions of

LaMnO₃ were investigated after their defect structures were examined [108]. Jayakumar et al. reported surfactant assisted synthesis of Mn doped ZnO polycrystalline samples showing robust room temperature ferromagnetism as characterized by X-ray diffraction analysis, Transmission Electron Microscopy, Electron Paramagnetic Resonance and DC magnetization measurements. This surfactant assisted synthesis method, developed, is found to be highly reproducible. Further, it can also be extended to the synthesis of other transition metal doped ZnO. Significant enhancement of room temperature ferromagnetism is observed in surfactant coated polycrystalline Mn doped ZnO particles [109]. Dakhel et al. prepared (La-Mn) oxide thin films on glass and p-Si substrates have been characterised by UV-VIS absorption spectroscopy, energy dispersion X-ray fluorescence (EDXRF) and X-ray diffraction (XRD). The XRF spectrum was used to determine the weight fraction ratio of Mn to La in the prepared samples. XRD shows that La oxide and Mn oxide do not prevent each other to crystallise alone and do not form a solid solution. However, grains of LaMnO₃ compound were observed to be formed through a solid-state reaction for $T > 800^{\circ}\text{C}$. The ac-conductance and capacitance were studied, as a function of frequency and gate voltage [110]. Brinkman et al. analysed the resistance versus temperature characteristics of NiMn₂O₄ thermistors. In this study differentiated $R-T$ data were analyzed, allowing a clear distinction between different modes of hopping. In pressed pellets and thick screen printed films conduction was well described by a VRH model for a parabolic density of states, which was confirmed by scanning tunneling spectroscopy [111]. Savic et al. studied DC resistivity of sintered Nickel manganite (NTC thermister) as a function of activation time and reported resistivity falls with the increase of sintering temperature [112]. Number of other NTC materials consisting of metal oxides and organic polymers have also been recently reported. Hydrazine, a widely used reducing agent in the organic synthetic chemistry, has also been used successfully for preparing reduced inorganic materials, II-VI group semiconductor nano-rods and other transition metal chalcogenides. Zhang et al. prepared LaMnO₃ by milling Mn₂O₃ and La₂O₃ in a planetary ball mill for 180 min. Perovskite-type lanthanum manganite (LaMnO₃) powder was synthesized by room temperature milling of La₂O₃ and Mn₂O₃ powders using a planetary ball mill [113]. Scarr et al. reported thermistors are components of comparatively recent development and describes the theory of their operation, explains why they, in common with other semiconductor devices, possess a negative temperature coefficient of resistance and developed the

expressions which govern their parameters. Methods of manufacture of the various forms of thermister are outlined in general terms, and numerous applications of the device are described and discussed. The point is made that the thermister can now be used in many fields as an adequate alternative to components of more specialized application [114]. Umadevi et al. reported Vanadium pentoxide thick-film thermisters have been successfully prepared by screen-printing vanadium trioxide and firing in the temperature range 673–873 K. It has been observed by means of X-ray diffraction (XRD) and differential thermal analysis (DTA) that the V_2O_3 material undergoes transformation to V_2O_5 during the firing process [115]. Murugaraj et al. reported Carbon nanoparticle-polyimide (BTDA-ODA) composite thin films were shown to have semiconducting behaviour with a pronounced negative temperature coefficient of resistance (NTC) over a temperature range 300–425 K, unlike conventional polymer-based composite films that show predominantly positive temperature coefficients of resistance. Electrical resistivity of the nanocomposite thin films decreased progressively by six orders of magnitude as the carbon volume fraction was increased from 1% to 10%. The NTC parameters, characteristic of thermister performance of these thin films, indicated that polymer based nanocomposites can potentially be considered for NTC thermister applications. The materials presently studied, when compared with commercially available ceramic thermisters, were shown to exhibit smaller thermal sensitivity parameters [116]. Dmitry et al. described Negative temperature coefficient thermister oxide thin films with improved aging characteristics are described. Better thermal stability has been achieved by incorporating sol–gel techniques with metallo-organic decomposition methods. A compositional range was identified whereby borosilicate may incorporate into the thermister oxides, forming nanocomposites showing thermister electrical characteristics. Electrical resistance measurements verified characteristic thermister behaviour. Nanocomposite thin films exhibited a factor of four improvements as compared with pure oxides after aging at 150°C for 500 h [117]. Schmidt et al. reported the study of the paradigm of functional NTC thermister ceramics based on thick film spinel manganates by temperature dependent alternating current impedance spectroscopy. Three typical relaxation phenomena were detected, which all showed a separated temperature dependence of resistivity consistent with thermally activated charge transport [118]. Leea et al. reported Characteristics of thin-film negative temperature coefficient of resistance (NTC) thermal sensors fabricated by micromachining technology. By the results of microstructure, X-ray and NTC analysis,

NTC films, post-annealed at 700°C for 1 h, showed the best characteristics as NTC thermal sensing film [119]. Hosseini et al. reported $\text{NiCo}_x\text{Mn}_{2-x}\text{O}_4$ ($x = 0.4, 0.8, 1.2, 1.6$) thermister with nanopowders have been synthesized by the auto-combustion method at low temperatures. The grain size of NTC ceramics sintered at 1200°C is verified with scanning electron microscopy (SEM) images. Upon increasing the cobalt concentration, the grain size of NTC samples increases from about 2 μm to a few μm in size [120].

2.2 Scope of Work

However till date no study has been reported on NTC behaviour of nano materials of Mn_3O_4 and $\text{Mn}_3\text{O}_4\text{-La}_2\text{O}_3$ nanocomposite. In the present study, Synthesis of nano material of Mn_3O_4 , $\text{La}(\text{OH})_3$ and $\text{Mn}_3\text{O}_4 - \text{La}(\text{OH})_3$ nanocomposite have been carried out following bottom up approach (reduction Process) by selecting several combinations of precursors, reducing agent and stabilization agents. Reaction conditions have worked out for synthesis to have monodisperse nanomaterials of nearly uniform dimensions. $\text{Mn}_3\text{O}_4 - \text{La}(\text{OH})_3$ nanocomposite was transformed into $\text{Mn}_3\text{O}_4\text{-La}_2\text{O}_3$ following the sintering method. These materials have been characterized for their morphology, crystalline structure, composition and optical properties using TEM, XRD, FTIR, UV-Visible. Thermister in the form of thin wire compacted in a stainless steel tube of 2.0 mm diameter having two sensing wires of 0.3 mm in diameter were encapsulated parallel to each other within the sensing tube filled with the developed nano-ceramics materials. To work out the negative temperature coefficient (NTC) along with cut off temperature from these thermisters, resistivity measurements with the change in temperature was recorded with an interval of 10°C. Each study was conducted several times to study the reproducibility. From the resistivity values and temperature data parameter like thermister constant, activation energy and temperature coefficient have been derived. These thermisters will find applications to monitor and control critical systems like aero engine, armor tank and other strategic devices from overheating and fire.

CHAPTER-3

EXPERIMENTAL STUDIES

EXPERIMENTAL STUDIES

3.1 EXPERIMENTAL DETAILS

This chapter deals with the method used for the synthesis of manganese oxide (Mn_3O_4) and lanthanum hydroxide ($\text{La}(\text{OH})_3$) nanoparticles and $\text{Mn}_3\text{O}_4 - \text{La}(\text{OH})_3$ nanocomposite. It also covers various techniques used for the characterisation of the products. These nanoparticles and nanocomposites have been synthesized under similar conditions following chemical route (Bottom-up approach). The crystal structure and particle size was determined using XRD Analysis. FTIR has also been done to study the presence of surfactant and structural characteristics. The morphological studies were carried-out using transmission electron microscope (TEM). Thermogravimetric analysis (TGA) and differential scanning behaviour (DSC) has also been done to study the effect of heat on mass loss with rise in temperature on the synthesized products. UV-Vis spectroscopy has been carried out to study absorption radiation and shift in absorption maximum with variation in size. Negative Temperature Coefficient behaviour of the material was studied by measuring the resistance change over a temperature range of ambient to cut off temperature. Electrical characterisation of these materials have been also been done by making frequency dependent conductance and capacitance studies.

3.2 APPARATUS USED

The following apparatus have been used during the synthesis of nano materials.

3.2.1 Electronic Weighing Machine

Chemicals were measured by using METTLER TOLEDO AX 205 Electronic weighing machine, shown in figure-3.1. (Maximum: 205 gm; resolution = 0.01mg)



Fig 3.1: Photograph of Electronic Weighing Machine

3.2.2 Centrifuge Equipment

Synthesized nanoparticles were separated from residue using centrifugal machine. The centrifugation was carried at variable speeds using 3K₃O SIGMA, shown in Figure 3.2.



Fig 3.2 : Photograph of Centrifuge equipment

3.2.3 Vacuum Rotavapor

The nanomaterials & composite were dried using BUCHI Rota Vapor R-205, Vacuum controller V-800 and BUCHI heating bath B-490 (Fig 3.3) . The temperature was kept 60°C of heating bath which was filled by water. This equipment is based on the principle that the evaporation occur at fast speed at low pressure at a given temperature. During drying process the pressure is kept at minimum value by varying it from the pressure panel. This leads to fast drying of the solution which contains nanoparticles.



Fig 3.3 : Photograph of Vacuum Rotavapor

3.3 CHEMICALS FOR SYNTHESIS OF NANOMATERIALS

Following chemicals were used for synthesis :

- i. Potassium permanganate (KMnO_4 , 99%), Qualigens, M.W.=158.04 gm
- ii. Lanthanum nitrate ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), Loba Chemie, M.W.=433.02 gm
- iii. Monohydrate hydrazine ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$, 98%), Loba Chemie, M.W.=50.06 gm
- iv. N-Cetyl-N,N,N, Trimethylammonium bromide (CTAB), – Loba Chemie M.W.=364.46 gm
- v. Tetrabutylammonium bromide (TBAB) Spectrochem M.W.=322.38 gm
- vi. Absolute ethanol ($\text{C}_2\text{H}_5\text{OH}$), Brampton
- vii. Deionised Water from M/S Millipore systems

3.4 SYNTHESIS PROCEDURE ADOPTED

Nano range manganese oxide (Mn_3O_4), lanthanum hydroxide ($\text{La}(\text{OH})_3$) and their nanocomposite ($\text{Mn}_3\text{O}_4 - \text{La}(\text{OH})_3$) were synthesized by reduction of precursors with respective hydrazine hydrate in aqueous medium. Potassium permanganate (KMnO_4) and Lanthanum nitrate ($\text{La}(\text{NO}_3)_3$) were taken as precursors. The unlimited growth of the nano particles have been controlled with the use of N-Cetyl-N,N,N, Trimethylammonium bromide (CTAB) and Tetrabutylammonium bromide (TBAB) as surfactant and co-surfactant respectively which prevents the agglomeration of the nano-particles by surface capping. The resulting precipitates were separated out via centrifugation. Each precipitate was washed with, DI water and ethanol before vacuum drying at about 60°C .

3.4.1 Synthesis of Mn_3O_4 Nanoparticles

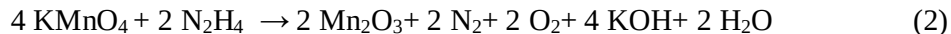
Mn_3O_4 nanoparticles were synthesized chemically by the following procedure. In a typical procedure, 5 mmol CTAB (1.82 g), 5 mmol TBAB (1.61 g) and 5 mmol KMnO_4 (0.79 g) were dissolved together in to 100 ml of DI water. The mixture was allowed to get homogenized under slowly stirring for about 10 minutes in order to avoid foam formation. 50 mmol of monohydrate hydrazine (2.42 ml) was added rapidly to the salt / surfactant solution under vigorous magnetic stirring. The color of the solution immediately turned from dark purple to black / brown then to orange / brown. The

reactive system kept was heated at 70°C for 1 h and cooled down to room temperature by removing the heat source. An orange / brown material was precipitated and separated out via centrifugation. The solid residue was washed several times with DI water and in the last with ethanol. The residue was dried in a vacuum using rota-vapour for about 3h at 60°C. On similar pattern the precursor/ reducing agent molar ratio was also altered to study their effect on synthesis conditions. However, chemical, physical and electrical characterisation were presented on the material, which was reported above, as the same resulted in the maximym yields. In a separate study under similar condition, synthesis was carried out in CTAB alone.

3.4.1.1 Reaction Mechanism

Both Mn₃O₄ (major constituent) and Mn₂O₃ (minor) nanomaterials were produced during above synthesis which was confirmed through thermal and chemical analysis discussed in the later parts of results and discussion in chapter 4.

It can be attributed to the reduction of KMnO₄ by hydrazine monohydrate through two step mechanisms:



Thus the presence of both Mn₃O₄ and Mn₂O₃ has been possible as per equation (1) and (2) which was also seen from TGA plots. Hydrazine hydrate being a powerful reducing agent releases nitrogen gas and hydrogen ions during its oxidation, while reducing KMnO₄. Oxygen is one of the byproducts in potassium permanganate hydrolysis reaction. The nano powder was found to have a major proportion of Mn₃O₄ with certain amount of Mn₂O₃.

3.4.2 Synthesis of La(OH)₃ Nanomaterial

La(OH)₃ nanomaterial was synthesized using wet chemistry path following the similar procedure used for the synthesis of manganese oxide nanoparticles. In a typical procedure, 5 mmol CTAB (1.82 g), 5 mmol TBAB (1.61 g) & 5 mmol La(NO₃)₃.6H₂O (2.2 g) were dissolved together in 100 ml of DI water. The reaction mixture was allowed to get homogenized under slowly stirring for few minutes in order to avoid foam formation. Then, 50 mmol of monohydrate hydrazine (2.42ml) was added rapidly to this reaction mixture solution under vigorous magnetic stirring. The system was heated at 70°C for 1 h in order for complete precipitation of the hydroxide. It was

further cooled to room temperature by removing the heat source. A white residue was separated from the resulting solution using centrifugation machine. This solid residue was washed several times with DI water and ethanol to remove any unreacted species. This left out residue was dried under vacuum using rota vapour at 60°C.

3.4.2.1 Mechanism of formation

Surfactant assisted synthesis is considered an effective methodology for shape controlled synthesis of nanomaterials in aqueous phase [121-122]. Hydrazine hydrate is freely soluble in water, but since N_2H_4 is basic in character, chemically free active ions are normally N_2H_5^+ and OH^- as per in equation (3). Lanthanum ions in aqueous solution quickly react with hydroxyl ions to form lanthanum hydroxide due to electrostatic interactions. However, the presence of excess amounts of water in warm conditions resulted in the formation of complex co-ordinate compound of $\text{La}(\text{OH})_4^{-1}$ which immediately stabilized with the cationic part of the surfactant present in the reaction mixture. This reaction product acts as seeding crystal for the transformation into short anisotropic rods of $\text{La}(\text{OH})_3$



Growth mechanism for $\text{La}(\text{OH})_3$ rods /crystal in the presence of CTAB / TBAB is different than the reaction system free from surfactant. A highly surface active surfactant blocks some of the crystal planes of the crystal because of their preferential adsorption, thereby directing the overall growth in specific directions. The presence of surfactant molecules in the reaction mixture also reduces the surface tension of the solution, which lowers the energy needed to form a new phase, resulting in the formation of $\text{La}(\text{OH})_3$ crystals in a lower super saturation [123]. Both CTAB and TBAB are ionic compounds and completely soluble in aqueous medium. The cations ions are positively charged tetrahedron with a long hydrophobic chain in case of CTAB and short butyl chains with TBAB. Growth unit for $\text{La}(\text{OH})_3$ crystal is considered as $\text{La}(\text{OH})_3$ which have tetrahedron geometry, but negatively charged [124]. Thus $\text{La}(\text{OH})_4^{-1}$ and cation CTA^+ form ion pair due to electrostatic interactions. The complementary between these ion pairs is to provide the surfactant the capability to act as ionic carrier [125]. The Lanthanum particles are negatively charged and CTA^+ cations adsorbed on the surface to form a film. This film is floatable and act as seeding source for assembly/growth of regular crystal structure in the form of anisotropic nanorods. In the growth process the surfactant molecule serves as growth controller as

well as agglomeration inhibitor by the forming a covering film on the $\text{La}(\text{OH})_3$ rods. These seed crystals are the nucleating centers and the surfactant molecules carrying the growing unit are adsorbed on the seed surface. This seeding process occurs on the surface of $\text{La}(\text{OH})_3$ (0001). As the surfactant starts forming the film and the molecules get perpendicularly adsorbed on the surface. It has been earlier studied that the presence of CTAB alone in the reaction mixture has resulted in the formation of long fibers with unsymmetrical growth. However, the addition of TBAB restricts the fast longitudinal growth to some extent, because of short butyl groups having large hydrophobic volume. TBA^+ ions get mingled in between CTA^+ and both (TBA^+ and CTA^+) have been adsorbed on the top of growing crystal surface. Presence TBAB, alone, in the reaction mixture may not be stabilized nano-crystals because of short molecular structure. It may not have stable adherence with another surface and can easily be removed in several washings. Therefore it has become possible in the present study to synthesize short anisotropic rods of nearly uniform dimensions using CTAB and TBAB together.

3.4.3 Synthesis of Mn_3O_4 – $\text{La}(\text{OH})_3$ Nanocomposite

For the synthesis of nanocomposite of Mn_3O_4 – $\text{La}(\text{OH})_3$, Varying concentrations of KMnO_4 , $\text{La}(\text{NO}_3)_3$, CTAB and TBAB were dissolved together in separate flasks (marked 1 to 5) in 100 ml DI water as per table 3.1. All final results discussed are as per sample 5, 6, 7. Each reaction mixture was allowed to get homogenized under slowly stirring for a few minutes so that it becomes free from foam. Monohydrate hydrazine reducing agent was rapidly added in these salt/surfactant solutions under vigorous magnetic stirring. The color of each solution turned from dark purple to black/brown then to orange/brown. These were further heated at 70 °C for about 1 h for complete precipitation. Room temperature cooling was done after removing the heat source. The Brown colored compound was separated using centrifugation. Each solid residue has been washed several times with DI water and ethanol before vacuum drying. Sintering of the Mn_3O_4 – $\text{La}(\text{OH})_3$ nanocomposite synthesized with an equal molar ratio (1:1) of KMnO_4 and $\text{La}(\text{NO}_3)_3$ precursors were done at 1000 °C resulting in its transformation into Mn_3O_4 – La_2O_3 composite. Further in a series of experiments concentration of precursors, capping agent and reducing agent was also altered design several such compounds.

Table 3.1 : Composition of precursors, surfactants and reducing agent used for nanocomposite synthesis

Sample name	Concentration of KMnO_4 (mmole)	Concentration of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (mmole)	Concentration of CTAB (mmole)	Concentration of TBAB (mmole)	Concentration of $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ (ml)
Sample 1	0.5	0.05	0.55	0.55	0.96
Sample 2	0.2	0.05	2.0	2.0	0.96
Sample 3	5.0	1.0	6.0	6.0	2.42
Sample 4	5.0	3.0	8.0	8.0	2.42
Sample 5	5.0	5.0	10.0	10.0	2.42
Sample 6	-	5.0	5.0	5.0	2.42
Sample 7	5.0	-	5.0	5.0	2.42

3.4.3.1 Mechanism of formation

A mechanism for the formation of Mn_3O_4 and $\text{La}(\text{OH})_3$ has been discussed at para no.3.4.1.1 and 3.4.2.1. Since each synthesis involves the use of respective precursor, hydrazine hydrate as reducing agent and CTAB/TBAB surfactant, in a similar way $\text{Mn}_3\text{O}_4 - \text{La}(\text{OH})_3$ nanocomposite has been prepared using a mixture of precursors, surfactant/ co-surfactant, reducing agent under similar reaction conditions, individually discussed at para no.3.4.1.1 and 3.4.2.1. Thus the reaction mechanism in this study involves the reduction of both precursors together results in formation of Mn_3O_4 nanoparticles coated / adsorbed on the surface of $\text{La}(\text{OH})_3$ nanorods due to surfactant interactions. Sintering has resulted in the formation of $\text{Mn}_3\text{O}_4 - \text{La}_2\text{O}_3$ due to removal of water as well as any amount of Mn_2O_3 present reduces to Mn_3O_4 . sintering of residue from sample 3, 4 & 5 converts it into $\text{Mn}_3\text{O}_4 - \text{La}_2\text{O}_3$ (LaMnO_3) residue as water has been lost from $\text{La}(\text{OH})_3$ and any amount of Mn_2O_3 also get reduced into Mn_3O_4 .

3.5 CHARACTERISATION TECHNIQUES

All these nanomaterials were characterized by XRD. In material characterisation basically characterisation of the synthesized material was carried out by variety of techniques to assure that the appropriate materials with suitable properties are synthesized. Some of the characterisation techniques used for the characterisation of materials is described below. Some brief details of the XRD techniques are presented.

3.5.1 X-Ray Diffraction (XRD)

X-Ray diffraction is a versatile, non destructive analytical technique for identification and quantitative determination various crystalline forms. Figure 3.4 shows the basic features of an X-ray diffractometer, in which the diffraction angle 2θ is the angle between the incident and diffracted X-rays. A typical diffraction spectrum consists of a plot of reflected intensities versus the detected angle 2θ . The 2θ values of the peak depend on the wavelength of the anode material of the X-ray tube. By choosing the right anode and energy of accelerated electrons, a known wavelength and therefore a known energy of X-rays will be generated. Copper X-ray tubes are most commonly used for X-ray diffraction of inorganic materials. For practical applications of X-ray diffraction, we typically want to use x-rays of a single wavelength, i.e. monochromatic radiation to improve experimental results

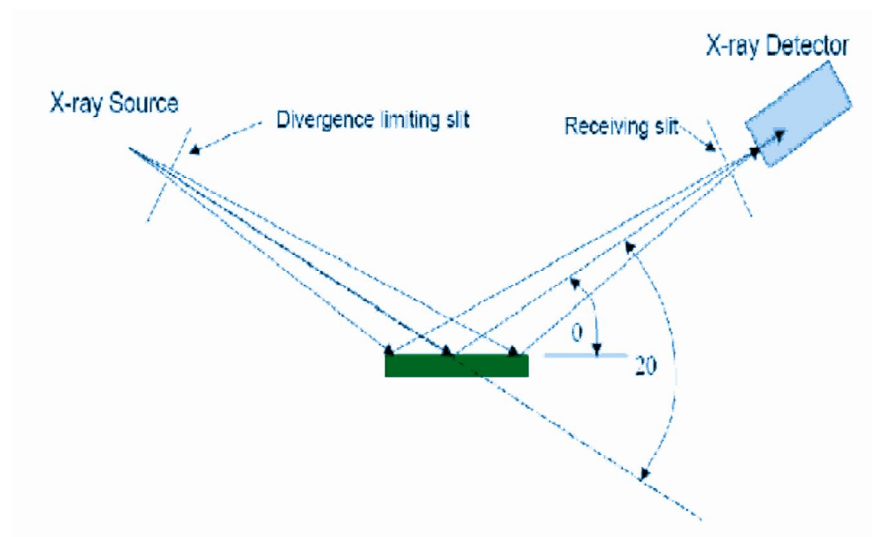


Fig 3.4 : Basic features of an X-ray diffractometer

W.L.Bragg formulated the condition that specifies the direction along which the diffraction should occur, when X-Rays interact with a crystal. The incoming beam (coming from upper left) causes each scatterer to re-radiate a small portion of its energy as a spherical wave. If scatterers are arranged symmetrically with a separation d , these spherical waves will be in synch (add constructively) only in directions where their path-length difference $2 d \sin \theta$ equals an integer multiple of the wavelength λ . In that case, part of the incoming beam is deflected by an angle 2θ , producing a reflection spot in the diffraction pattern.

The Bragg's law may be written as

$$2d\sin\Theta = n\lambda$$

Where,

- n is an integer,
- Θ is the angle between the planes in the atomic lattice,
- λ is the wavelength of X-rays, moving electrons, protons and neutrons and
- d is the spacing between the planes in the atomic lattices.

Particle sizes (D) can be estimated from X-ray diffraction data using the Scherrer formula for Mn_3O_4 , $La(OH)_3$ and composites.

$$D = \frac{K\lambda}{FWHM \cos \theta} \quad \text{or} \quad \frac{0.9\lambda}{\beta \cos \theta}$$

where K = Scherrer constant,

FWHM = full width at half maximum of the reflection peak that has the same maximum intensity in the diffraction pattern, (β)

The Scherrer constant (K) in the formula accounts for the shape of the particle and is generally taken to have the value 0.9. The size obtained from the Scherrer formula yields the apparent or average particle-size for a material. Powders of materials are generally aggregates of smaller particles, and thus consist of a distribution of particle sizes. XRD analysis of Mn_3O_4 powder, $La(OH)_3$ nanorods, $Mn_3O_4 - La(OH)_3$ composite and $Mn_3O_4 - La_2O_3$ ($LaMnO_3$) have been discussed in the proceeding section.

In the present study X-ray Diffraction (XRD) patterns were determined with a Panalytical's X'Pert Pro powder X-ray diffractometer using Cu K α radiation ($\lambda = 1.5406$ Å) from a sealed tube operated at 30kV and 40mA.



Fig 3.5 : X'PERT PRO X-Ray Diffractometer

3.5.2 Fourier Transform Infrared (FTIR) Spectroscopy

FTIR has been deployed to study the presence of surfactant (CTAB & TBAB) on the surface of nanoparticles. The presence of absorption peak at mid IR a specific wavelength provides the information. Metal oxygen intraction has also been interpreted from FTIR spectra. Infrared spectroscopy has been a workhorse technique for materials analysis in the laboratory for over seventy years. An infrared spectrum represents a fingerprint of a sample with absorption peaks which correspond to the frequencies of vibrations between the bonds of the atoms making up the material. Because each different material is a unique combination of atoms, no two compounds produce the exact same infrared spectrum. Therefore, infrared spectroscopy can result in a positive identification (qualitative analysis) of every different kind of material. In addition, the size of the peaks in the spectrum is a direct indication of the amount of material present. With modern software algorithms, infrared is an excellent tool for quantitative analysis. In the present study Fourier transformation infrared (FT-IR) spectrum was recorded on Perkin Elmer RX-1FTIR spectrophotometer in frequency ranging from 500 to 4000 cm^{-1} . The spectra were taken in KBr powder in the form of pellets.



Fig 3.6 : Spectrophotometer, FTIR, Perkin Elmer

3.5.3 Transmission Electron Microscope (TEM)

Transmission Electron microscopy (TEM) studies were carried out using a Hitachi H-7500 operated at an accelerating voltage of 120KV. The samples of TEM image were prepared by drop casting the dispersed particles solutions on a carbon coated copper grid. The Hitachi H-7500 tungsten/LaB6 TEM is an instrument also suitable for high magnification examination of biological tissues and soft materials. It is fitted with Bruker thin-window energy dispersive X-ray (EDS) detector which is capable of detecting elements ranging from boron upwards. A slow scan AMT CCD camera with pixel resolution 1024 x1024 is fitted side mount to the column. The status of the electron microscope is displayed graphically on TEM computer, which allows the user to call out window for setting parameters to suit their needs. The TEM image of Mn_3O_4 , $\text{La}(\text{OH})_3$, composite material and LaMnO_3 are presented in results and discussion section.

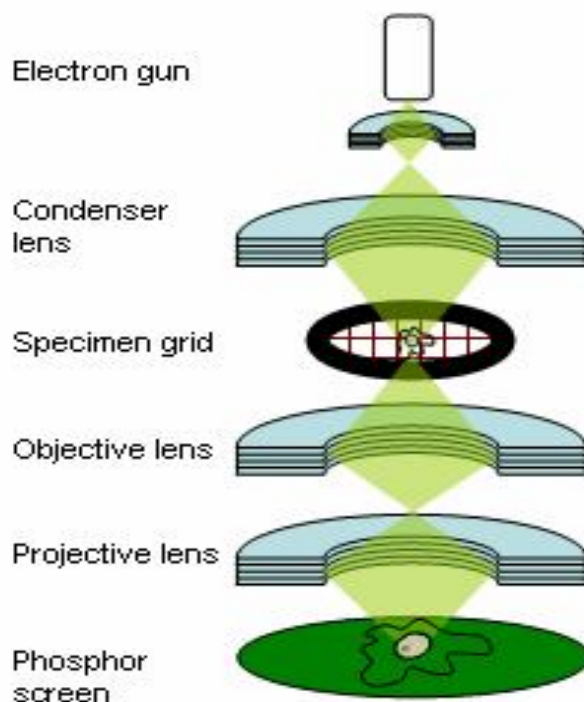


Fig 3.7 : Components in a basic TEM Single Crystal



Fig 3.8 : Photograph of Transmission Electron Micrograph

3.5.4 Thermal Analysis

3.5.4.1 Thermo-Gravimetric Analysis (TGA) / Differential Scanning Calorimetry (DSC)

Thermogravimetric Analysis or TGA is a type of testing that is performed samples to determine changes in weight in relation to change in temperature. Such analysis relies on a high degree of precision in three measurements: weight, temperature, and temperature change. As many weight loss curves look similar, the weight loss curve may require transformation before results may be weight loss is most apparent. Again, interpretation is limited without further modifications and deconvolution of the overlapping peaks may be required. TGA is commonly employed in research and testing to determine characteristics of materials, to determine degradation temperatures, absorbed moisture content of materials, the level of inorganic and organic components in materials, decomposition points of explosives, and solvent residues. It is also often used to estimate the corrosion kinetics in high temperature oxidation.

Differential Scanning Calorimetry (DSC) is widely used to characterize the thermo physical properties of materials. DSC is a thermo analytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference are measured as a function of temperature. Both the sample and reference are maintained at nearly the same temperature throughout the experiment. Generally, the temperature program for a DSC analysis is designed such that the sample holder temperature increases linearly as a function of time. The reference sample should have a well-defined heat capacity over the range of temperatures to be scanned.

For thermogravimetric analysis (TGA/DSC), Universal V4.1D TA Instrument (SDT Q 600) was used. Mass change variation of powdered samples were recorded in the temperature range of ambient to 1000°C in nitrogen atmosphere, at the heating rate of 5°C min⁻¹. It uses a horizontal balance system to place the sample, the heating rate can also be varied. TGA-DSC analysis of the as prepared samples was done in nitrogen atmosphere from room temperature to 1000° C, using TA instruments model: SDT Q600. Figure 3.9 shows a commercial TGA-DSC, TA instruments model SDT Q600. The thermal stability and other characterisation of the other material were carried out using the above system and results have been discussed in next section.



Fig 3.9 : TGA-DSC TA Instruments Model : SDT Q600

3.5.5 Ultra Violet-Visible (UV-Vis) Spectroscopy

3.5.5.1 Introduction

Ultraviolet-visible spectrophotometers (UV-Vis) involve the spectroscopy of photons interaction with sample in the UV-visible region. The absorption in the visible ranges directly affects the color of the chemicals involved. In this region of the electromagnetic spectrum, molecules undergo electronic transitions. An absorption spectrum will show a number of absorption bands corresponding to structural groups within the molecule. Instruments for measuring the absorption of UV / visible radiation consist of radiation source, optics, sample holder, detector and display. Both deuterium and hydrogen lamps emit radiation in the range 160 – 375 nm. Quartz windows must be used in these lamps, and quartz cuvettes must be used, because glass absorbs radiation of wavelengths less than 350 nm. The tungsten filament lamp is commonly employed as a source of visible light. This type of lamp is used in the wavelength range of 350 – 2500 nm. The energy emitted by a tungsten filament lamp is proportional to the fourth power of the operating voltage. Tungsten/halogen lamps contain a small amount of iodine in a quartz “envelope” which also contains the tungsten filament. Tungsten/halogen lamps are very efficient, and their output extends well into the ultra-violet. They are used in many modern spectrophotometers. Polychromatic radiation (radiation of more than one wavelength) enters the monochromator through the entrance slit. The beam is collimated, and then strikes the dispersing element at an angle. The beam is split into its component wavelengths by the grating. By moving the dispersing element or the exit slit, radiation of only a particular wavelength leaves the monochromator through the exit slit. Cuvettes contains the sample and reference solution must be transparent to the radiation which will pass through them. Quartz or fused silica cuvette are required for spectroscopy in UV region. These cells are also transparent in the visible region.

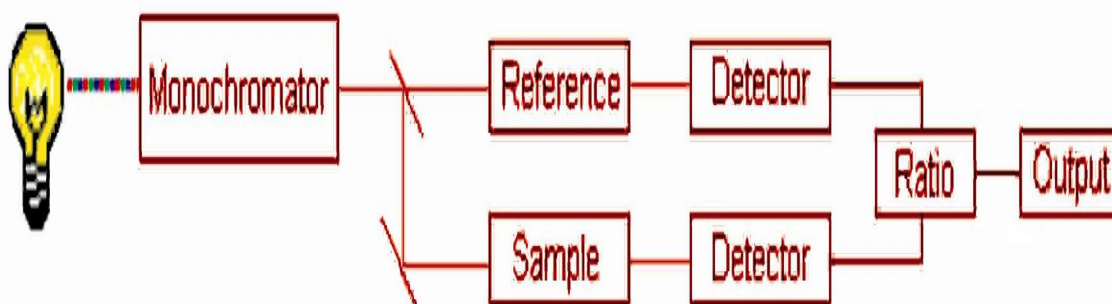


Fig 3.10 : Schematic diagram of a double-beam UV-Vis. Spectrophotometer

In the present study, UV-Vis Spectrophotometer Perkin Elmer Lambda 35 as shown below was used.



**Fig 3.11 : UV-Vis Spectrophotometer
Perkin Elmer Lambda 35**

CHAPTER 4
RESULTS
AND
DISCUSSIONS
OF
SYNTHESIZED NANOMATERIALS

RESULTS & DISCUSSIONS

4.1 X-RAY DIFFRACTION ANALYSIS

4.1.1 XRD Studies of Mn₃O₄ nanoparticles

The XRD pattern of Mn₃O₄ nanoparticles synthesized in presence of CTAB alone is given in figure 4.1. The XRD pattern confirmed the nano-crystalline nature of the product. The crystalline phase of the sample studied is preferentially indexed according to tetragonal structure. The XRD pattern for nano-Mn₃O₄ is in agreement with JCPDS- international center for diffraction data for sample code 24-0734 – Hausmmanite. The crystallite size of Mn₃O₄ for the most intense peak ($2\theta \sim 36^\circ$, 211 plane) was determined from the X-ray diffraction data using Debye – Scherrer formalism.

$$D = 0.9\lambda / \beta \cos \theta$$

where,

- “D” is the crystallite size;
- “ β ” is the full width of the diffraction line at half the maximum intensity measured in radian.
- “ λ ” is the X-ray wavelength of Cu = 1.54 Å and
- “ θ ” is the Bragg angle.

The crystallite size calculated from XRD data prepared was found ~15 nm. It can be seen that the other phase of manganese oxide co-exist with tetragonal Mn₃O₄. 1. It is well known that XRD cannot easily discriminate between Hausmannite Mn₃O₄ and γ Mn₂O₃ because both materials assume tetragonally-distorted cubic lattices of nearly identical dimensions.

The details of the standard pattern 24-0734 and synthesized Mn₃O₄ nanoparticles are given in Table 4.1. in this study only CTAB was used as capping agent without the addition of co-surfactant TBAB, however formation of somewhat large size nanoparticles occurred.

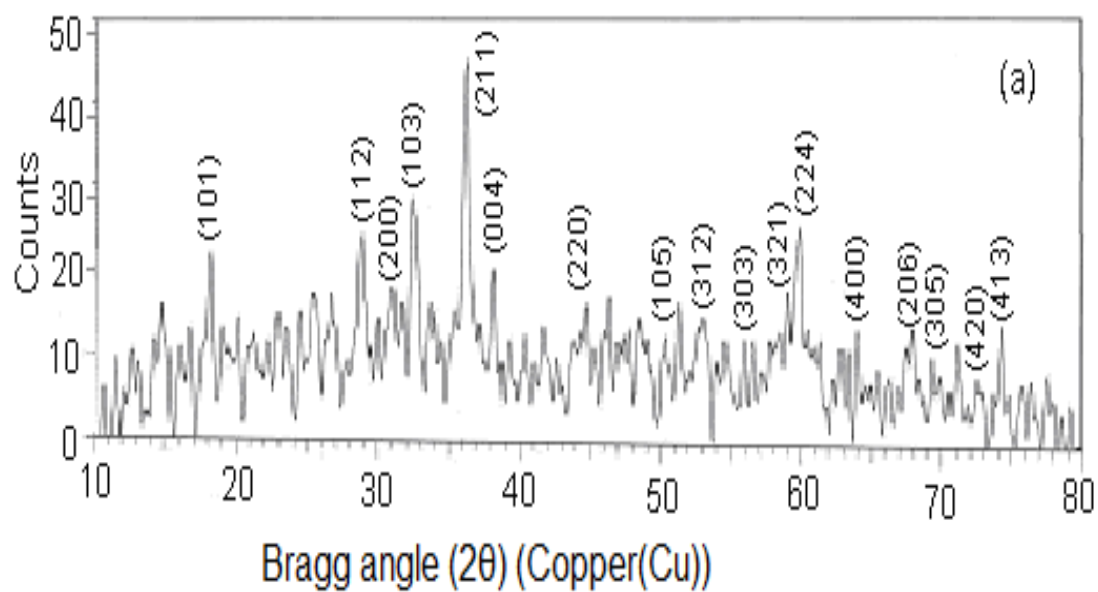


Fig.4.1 XRD pattern of Mn_3O_4 using CTAB only

Table 4.1: Data Analysis from the Diffraction pattern of Mn_3O_4 Synthesized using CTAB only

JCPDS card no. 24-0734		Nano- Mn_3O_4			Diffraction Planes <i>Hkl</i>
2θ ($^\circ$ A)	I (%)	2θ	FWHM (2θ)	I (%)	
28.88	40	28.83	3.09	53	112
32.32	85	32.34	2.77	63	103
36.08	100	36.19	2.48	100	211
37.98	20	38.18	2.35	44	004
44.44	25	44.67	2.07	35	220
50.71	50	51.28	1.78	36	105
59.84	20	59.92	1.54	57	224

XRD pattern of Mn_3O_4 nanoparticles synthesised using both CTAB and TBAB as surfactant and co-surfactant is given in Figure 4.2. The analysis of diffraction peaks is given in Table 4.2. The XRD pattern confirms nanocrystalline nature of the product. The formation of smaller size nanoparticles than in synthesise with CTAB alone as per Table 4.1 shows that the use of co-surfactant helped to reduce the size which is given in Table 4.2.

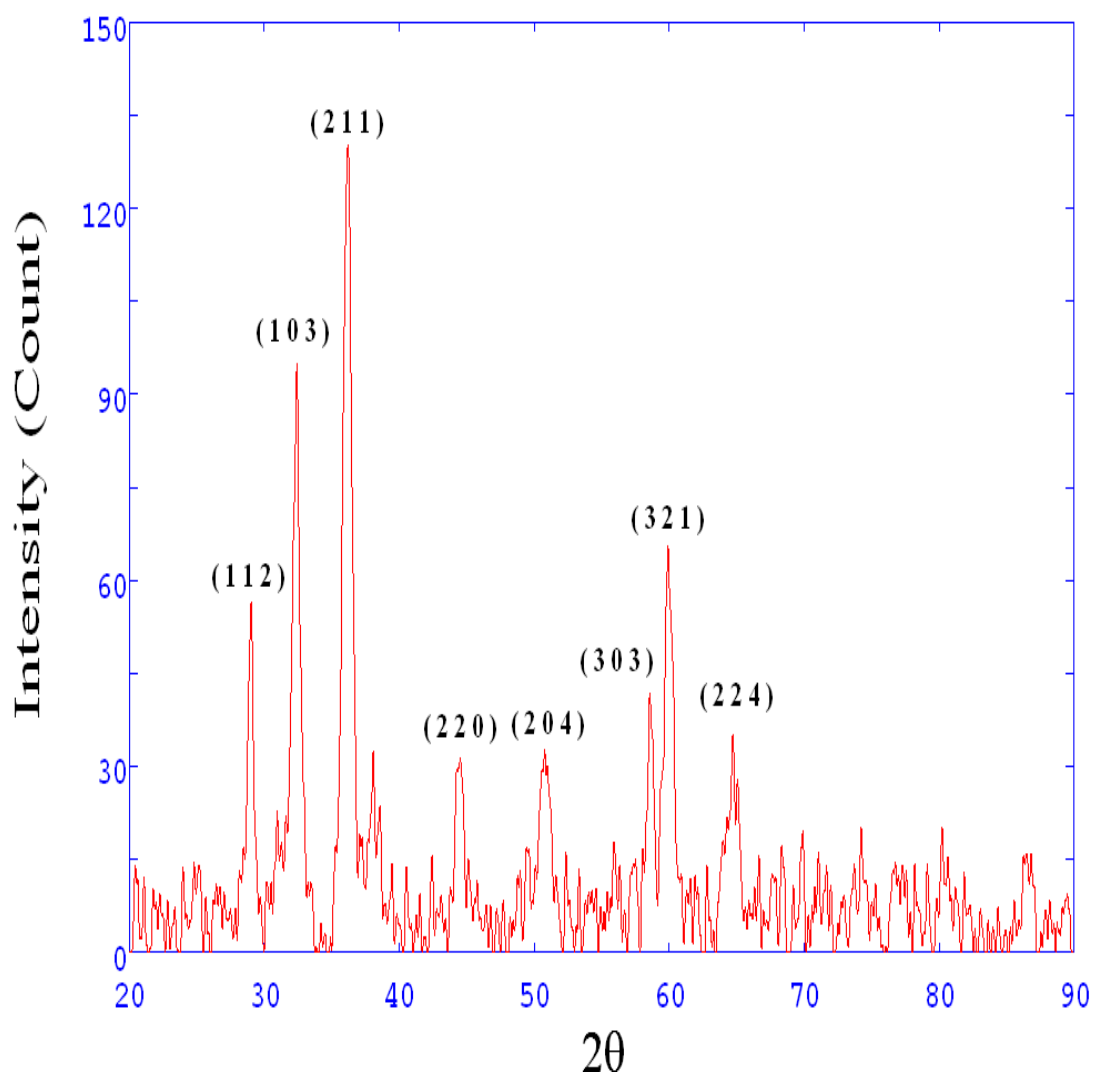


Fig 4.2 : XRD pattern of Mn_3O_4 nanoparticles using both CTAB & TBAB

Table 4.2: Data Analysis from the Diffraction pattern of Mn₃O₄ Synthesized using both CTAB and TBAB

2θ	Diffraction Peaks hkl	d (Å)	Height	Area	FWHM	Crystallite Size (nm)	Average Crystallite Size (nm)
29.024	112	3.07400	53.0	3228.8	1.0370	7.9125	7.5
32.413	103	2.75994	92.1	5521.9	1.0540	7.8484	
36.193	211	2.47988	127.5	7970.3	1.0710	7.8029	
44.660	220	2.02742	30.8	1685.1	0.9860	8.0794	
50.767	204	1.79692	30.7	1886.8	1.0540	8.3149	
58.565	303	1.57488	40.0	1461.1	0.6970	13.0664	
59.913	321	1.54263	62.9	3501.1	0.9520	9.6306	
64.708	224	1.43942	32.2	2456.1	1.3090	7.1836	

The XRD pattern of as synthesized Mn₃O₄ NPs showed the tetragonal Hausmmanite nano-crystalline nature. These patterns of Mn₃O₄ powder are in agreement with (JCPDS- international center for diffraction data for sample Card File No. 24-0734) – Hausmmanite. However the detailed study shows that crystalline phase of the synthesized particles seems to be better indexed as a tetragonal structure (JCPDS – Sample Code 24-0734- Hausmmanite) but some peaks corresponding to γ- Mn₂O₃ (JCPDS Card No.06-0540) were also observed, since it is difficult to distinguish Mn₃O₄ Hausmmanite (JCPDS Card No. 24-0734) from γ-Mn₂O₃ (JCPDS Card No. 06-0540) as a consequence of their highly similar XRD patterns [126]. It is observed that the XRD pattern of the sample prepared using surfactant and co-surfactant at 70°C have broader and less intensive diffraction peaks due to its smaller grain size. It was also observed that crystallinity increases by giving the heat treatment. The crystallite size of Mn₃O₄ was determined from the X-ray diffraction data using Debye-Scherrer formula and for the most intense peak (2θ ~36°, 211 plane) comes out to be approximately 7.8 nm and average crystallite size found to be 7.5nm. The presence of both Mn₃O₄ and Mn₂O₃ in as synthesized material may be attributed to the reduction of

KMnO_4 with hydrazine monohydrate through two competing mechanism as discussed in equation 1 & 2. Presence of Mn_2O_3 nano material in Mn_3O_4 has been observed from thermal analysis. Hydrazine being a powerful reducing agent releases nitrogen gas and hydrogen ions during its oxidation [127] while reducing KMnO_4 . Oxygen is one of the by product in potassium permanganate hydrolysis reaction [128]. It can be seen that the other phase of manganese oxide co-exist with tetragonal Mn_3O_4 . It is well known that XRD cannot easily discriminate between Hausmannite Mn_3O_4 and $\gamma\text{-Mn}_2\text{O}_3$ because both materials assume tetragonally-distorted cubic lattices of nearly identical dimensions. The study shows that mixture of surfactant and co-surfactant helped in the formation of stabilized mono disperse nanoparticles.

4.1.2 XRD Studies of $\text{La}(\text{OH})_3$ nanomaterials

The XRD pattern of $\text{La}(\text{OH})_3$ nanomaterials synthesized by using CTAB and TBAB are shown in figure 4.3 confirms the crystalline structure and phase purity of the as prepared product. The XRD pattern for nano- $\text{La}(\text{OH})_3$ is in agreement with hexagonal structure JCPDS- international center for diffraction data for sample code 36-1481].

The details of standard pattern 36-1481 and synthesized $\text{La}(\text{OH})_3$ are given in Table 4.3. The XRD pattern confirm crystallite structure and phase purity of the prepared product.

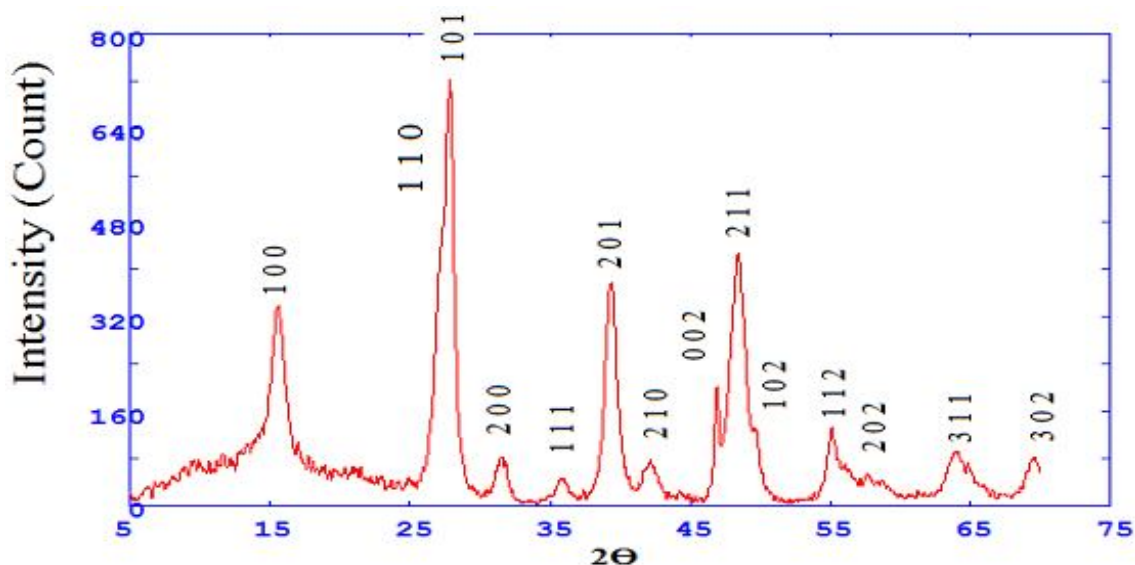


Fig.4.3 : XRD pattern of $\text{La}(\text{OH})_3$ nanomaterial using both CTAB & TBAB

Table 4.3 Data Analysis from the Diffraction pattern of La(OH)₃ Synthesized using both CTAB and TBAB

JCPDS card no. 36-1481		Nano-La(OH) ₃			Diffraction planes hkl
2 θ ($^{\circ}$ A)	I (%)	2 θ	FWHM (2 θ)	I (%)	
15.665	59	15.558	.4250	480.6	100
27.309	62	27.837	0.4590	745	110
27.973	100	27.862	0.5440	1046	101
31.624	16	31.593	0.3230	116,11.08	200
36.014	8	36.02	0.3003	88	111
39.478	75	39.467	0.8160	557	201
42.268	12	42.22	0.3225	114	210
47.063	13	46.939	0.3400	274.9	002
48.644	61	48.463	0.9180	647.2	211
49.891	9	49.693	0.4080	186.3	102
55.265	21	55.350	0.4590	159.3	112
57.822	6	57.78	0.2660	118	202
64.028	15	64.104	0.2040	124.6	311
69.708	14	69.544	0.4420	113.5	302

The details of standard pattern of La(OH)₃ powder (JCPD 36-1481) and nano synthesized La(OH)₃ matches as per Table 4.3 with each other showing the formation of pure La(OH)₃ nanomaterial. The study shows that mixture of surfactant and co surfactant helped to attain more uniform and small sized nanoparticles. From the X-RD Patterns, it is clear that the product obtained is a pure crystalline of La(OH)₃ phase with a hexagonal crystal structure. All diffraction peaks can be indexed as hexagonal La(OH)₃ with lattice constants $a = 6.5286 \text{ \AA}$, $c = 3.8588 \text{ \AA}$ which belongs to $P6_3/m$ space group. Typical reflections were found to match JCPDS-International Centre for diffraction data for sample cord 36-1481. No peak could be attributed to the existence of any other impurity or of La₂O₃. The average crystalline size of as the synthesized product was calculated using Debye-Sherrer formula. The crystallite size of nano La(OH)₃ calculated from the most intense peak ($2\theta \sim 27^{\circ}$, 101 plane) is $\sim 7 \text{ nm}$ in Figure 4.3. Mazloumi et al. [129] observed average crystalline size between 50 & 65 nm, when synthesis was carried out in various alkaline solutions whereas in another study [130] size was reported to be fine when synthesis was carried out by hydrothermal method in KOH without the use of any surfactant. The broadening of diffraction peaks in the present study clearly indicates the fine crystalline size, which is due to controlled growth of nanocrystal in presence of a mixture of surfactant.

Nanoparticles of $\text{La}(\text{OH})_3$ synthesised using CTAB surfactant alone.

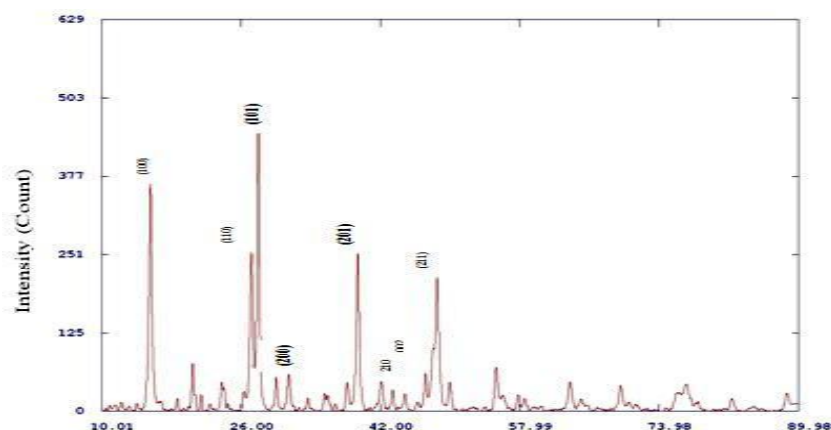


Fig 4.4 : XRD pattern of La(OH)₃ nanomaterial using CTAB alone

In another study, CTAB alone was used as surfactant and no co-surfactant was added. The diffraction pattern of the powder is shown in Figure 4.4. From the diffraction pattern it appears that peaks are not very sharp. The size was calculated from the most intense peak was around 12nm indicates that co-surfactant helped to attain the nano disperse & control in size.

4.1.3 XRD Studies of Mn_3O_4 - $\text{La}(\text{OH})_3$ Nanocomposite

Five different composite samples of Mn_3O_4 - $\text{La}(\text{OH})_3$ were synthesised by altering the precursor, reducing agent and capping agents concentration as per Table given below:

Composition of precursors, surfactants and reducing agent used for nanocomposite synthesis

Sample name	Concentration of KMnO ₄ (mmole)	Concentration of La(NO ₃). 6H ₂ O (mmole)	Concentration of CTAB (mmole)	Concentration of TBAB (mmole)	Conc. of N ₂ H ₄ . H ₂ O (ml)
Sample 1	0.5	0.05	0.55	0.55	0.96
Sample 2	0.2	0.05	2.0	2.0	0.96
Sample 3	5.0	1.0	6.0	6.0	2.42
Sample 4	5.0	3.0	8.0	8.0	2.42
Sample 5	5.0	5.0	10.0	10.0	2.42
Sample 6	-	5.0	5.0	5.0	2.42
Sample 7	5.0	-	5.0	5.0	2.42

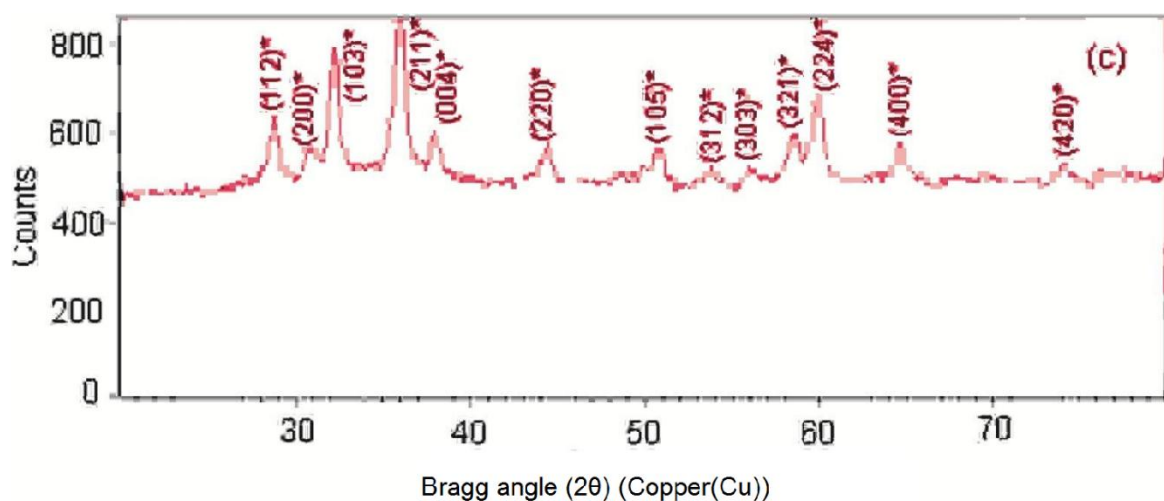


Fig 4.6 : XRD pattern of sample 2

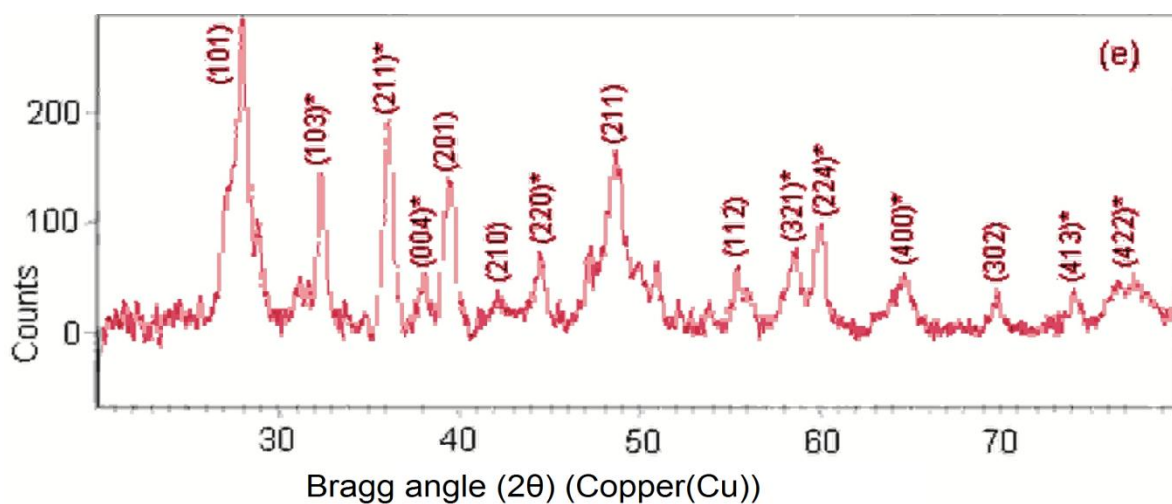


Fig 4.7 : XRD pattern of Sample 3

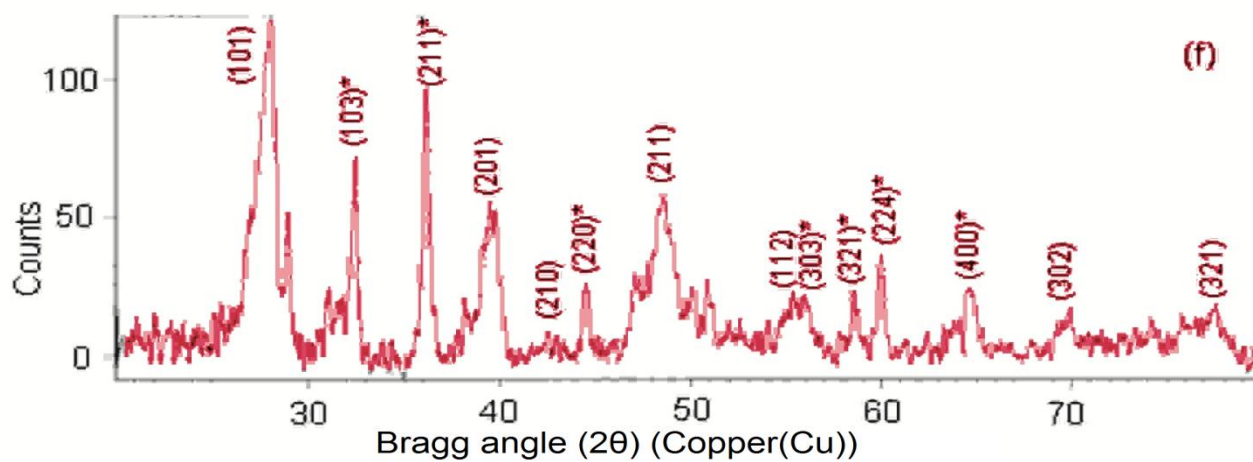


Fig 4.8 : XRD pattern of Sample 4 (Mn_3O_4 - $\text{La}(\text{OH})_3$ Nanocomposite)

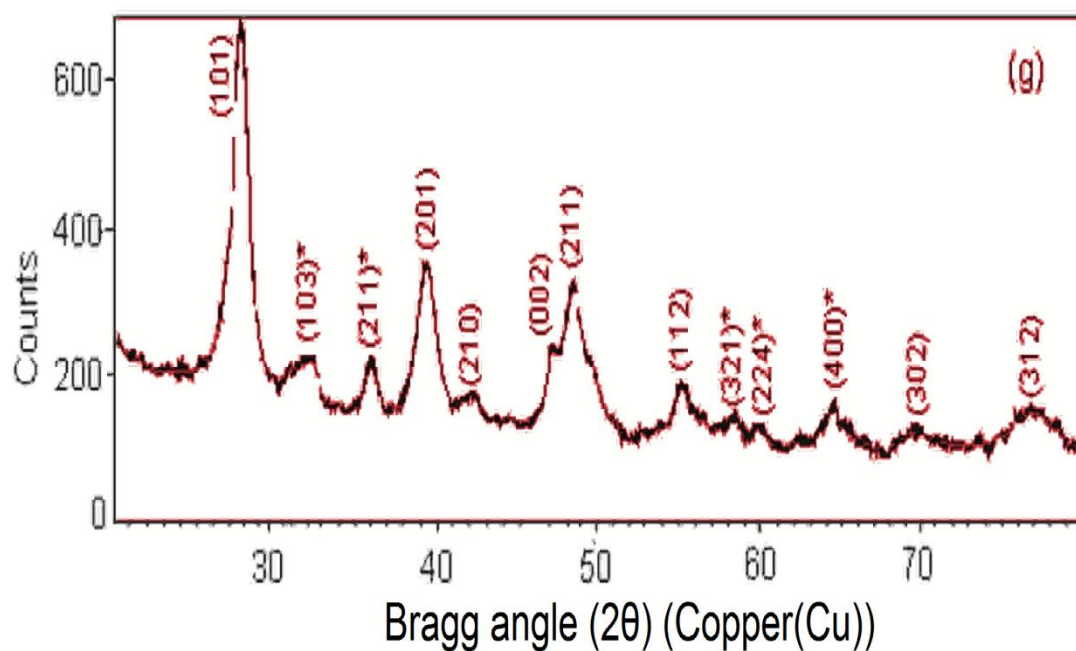


Fig 4.9 : XRD pattern of Sample 5 (Mn_3O_4 - $\text{La}(\text{OH})_3$ Nanocomposite)

Table 4.4 : XRD Data for composite samples

Sample 5 5 : 5			Sample 4 5 : 3			Sample 3 5 : 1			Sample 2 0.5 : 0.05			Sample 1 2 : 0.05		
2θ	FW HM (2 θ)	1 (%)	2θ	FW HM 2θ	1 (%)	2θ	FW HM (2θ)	1 (%)	2θ	FW HM (2θ)	1 (%)	2θ	FW HM (2θ)	1(%)
27	0.80	100	28	0.66	100	28	0.40	100	27	0.46	44	27	0.46	445
-	-	-	32	0.40	59	32	0.33	51	32	0.53	73	32	0.53	86
36	0.66	14	36	0.40	82	36	0.53	72	36	0.46	100	36	0.46	100
39	0.93	46	39	0.93	41	39	0.66	47	39	0.73	21	39	0.73	30
48	0.93	17	48	0.80	52	48	0.33	59	48	0.80	19	48	0.80	26
58	0.80	5	58	0.40	20	58	0.40	23	58	0.60	30	58	0.60	33
64	0.66	11	64	0.40	18	64	0.53	15	64	0.73	18	64	0.73	25

4.1.4 XRD Studies of Mn_3O_4 - La_2O_3 (LaMnO_3) Ceramic after Sintering

Figure 4.10, 4.11 and 4.12 represents the XRD patterns of oxides formed after annealing Mn_3O_4 - La_2O_3 at 1000°C for 1hr. The XRD pattern of Sample 3 nanocomposite after sintering exhibits (112), (200), (211), (004), (220), (321), (224), (400), (413) diffraction line of tetragonal phase of Mn_3O_4 . The diffraction pattern analysis of Sample 3, 4 & 5 are given in Table 4.5. Figure 4.10 (a) in the XRD pattern of ceramic oxide formed after sintering Sample 3 (Mn_3O_4 – $\text{La}(\text{OH})_3$) powder at 1000°C for 1 hr. Also for comparison Figure 4.10(b) represent the XRD pattern of the Sample 3 before sintering. Similarly, XRD pattern of Sample 4 and Sample 5 are given in Figure 4.11 and 4.12 respectively. In the figures 4.10 to 4.12, the diffraction lines of Mn_3O_4 planes are marked by asterik (*) sign. Unmarked belongs to $\text{La}(\text{OH})_3$.

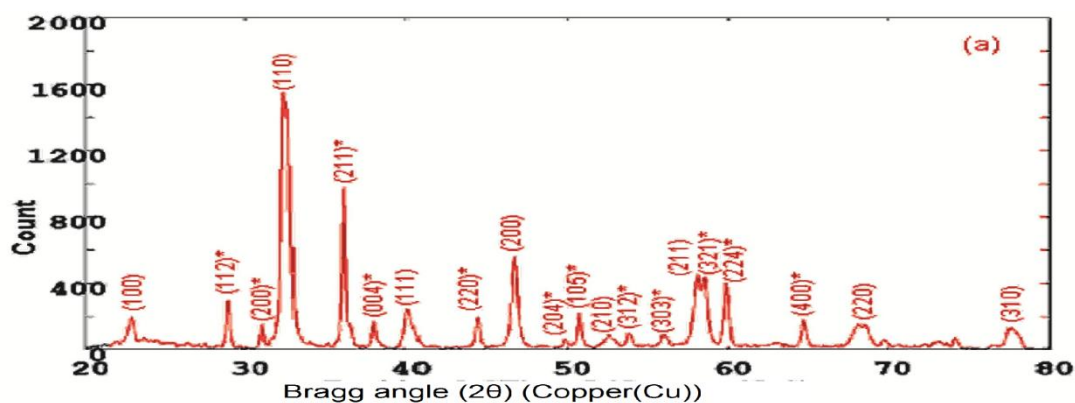


Fig 4.10 (a) : XRD pattern of Sample 3 after annealing

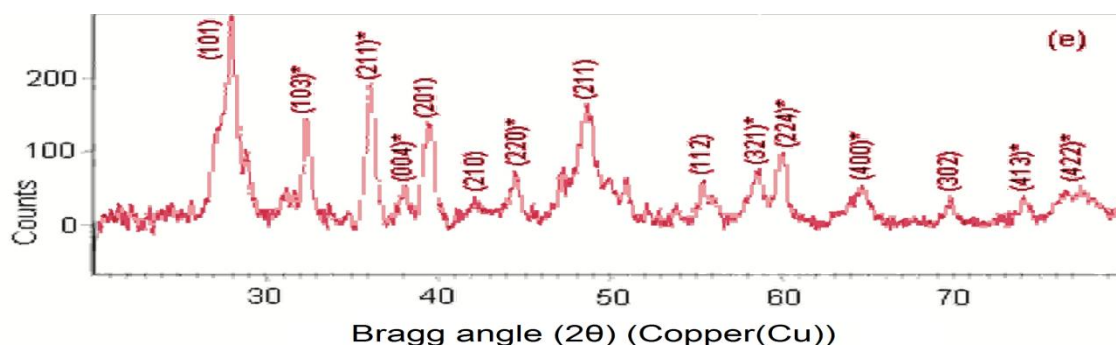


Fig 4.10 (b) : XRD pattern of Sample 3 before annealing

The XRD pattern of sample 3 represents nanocomposite (prepared from KMnO_4 and $\text{La}(\text{NO}_3)_3$ precursor in 5:1 ratio) after sintering exhibits diffraction plains of cubic LaMnO_3 JCPDS Code 75-0440 as well as tetragonal JCPDS Code 24-0734

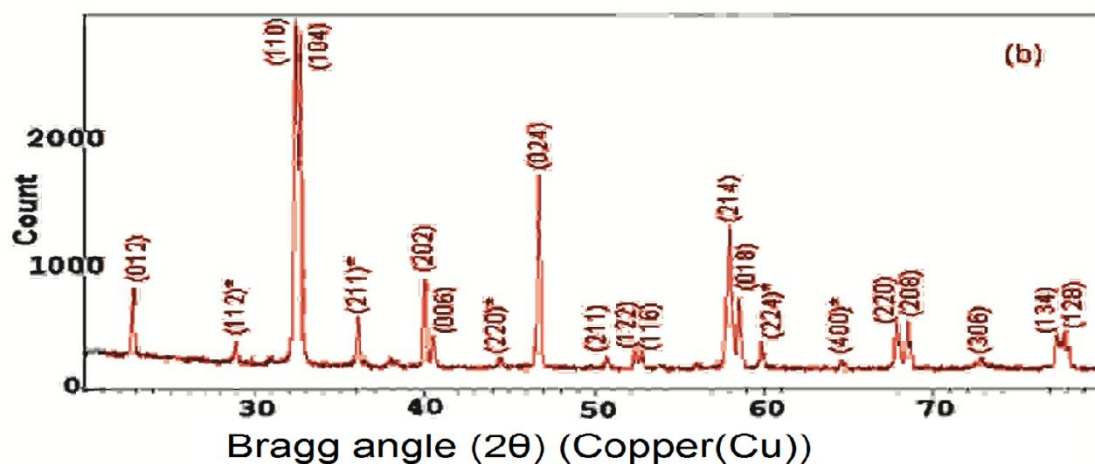


Fig 4.11 (a) : XRD pattern of Sample 4 after annealing

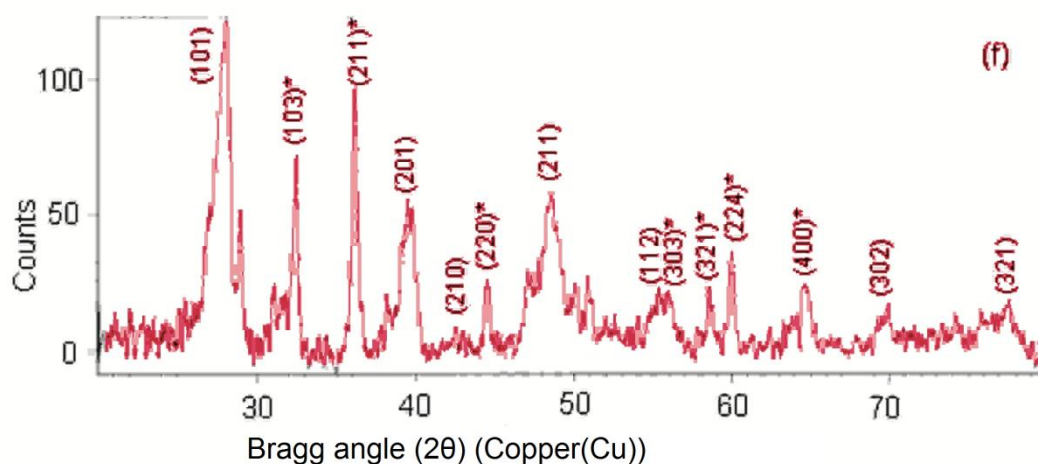


Fig 4.11 (b) : XRD pattern of Sample 4 before annealing

The XRD pattern of sample 4 represents nanocomposite (prepared from KMnO_4 and $\text{La}(\text{NO}_3)_3$ precursor in 5:3 ratio) after sintering exhibits diffraction plains of rhombohedral $\text{La}_{0.93}\text{MnO}_3$ JCPDS Code 82-1152 as well as tetragonal Mn_3O_4 plains JCPDS Code 24-0734

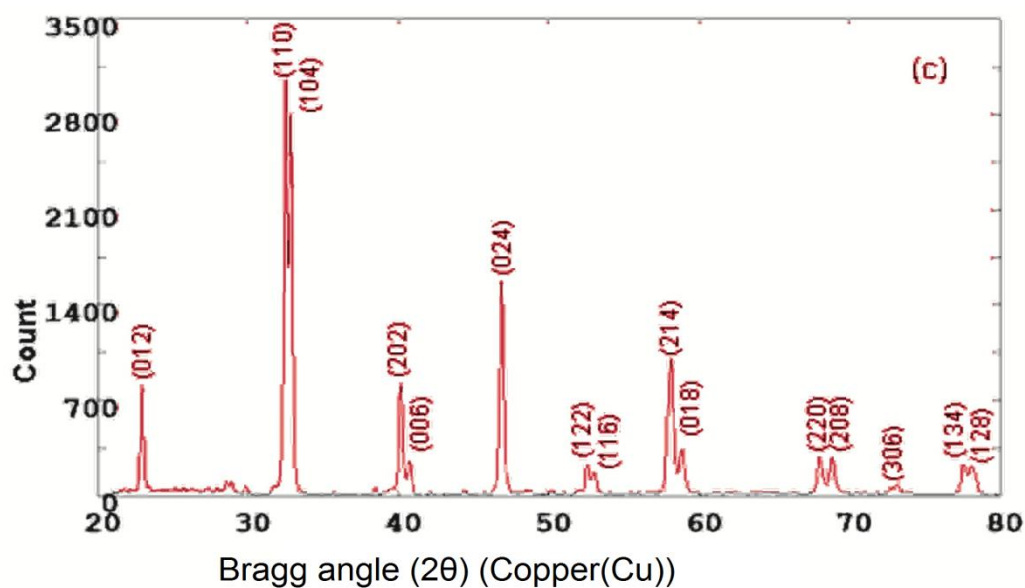


Fig 4.12 (a) : XRD pattern of Sample 5 after annealing

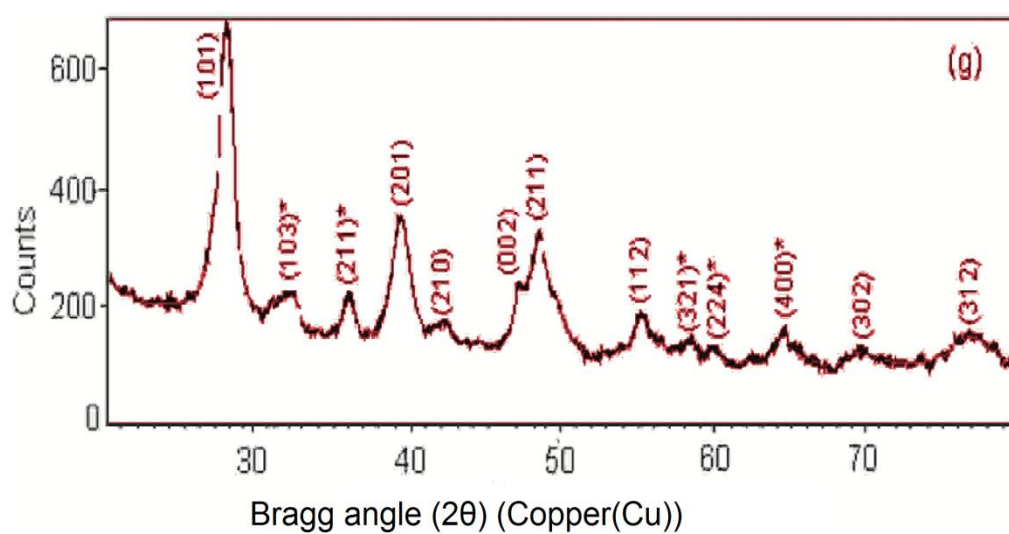


Fig 4.12 (b) : XRD pattern of Sample 5 before annealing

The XRD pattern of sample 5 represents nanocomposite (prepared from KMnO_4 and $\text{La}(\text{NO}_3)_3$ precursor in equal ratio) after sintering was indexed as rhombohedral $\text{La}_{0.993}\text{MnO}_3$ JCPDS Code 82-1152 with phase purity

Table 4.5 : XRD Data for composite samples annealed at 1000°C

SAMPLE 5 (5:5)			SAMPLE 4 (5:3)			SAMPLE 3 (5:1)		
2θ	FWHM(2θ)	I (%)	2θ	FWHM(2θ)	I(%)	2θ	FWHM(2θ)	I(%)
22.9	0.2210	784	2.8	0.2007	19.54	22.9	0.7650	154.6
			28.8	0.2007	5.85	28.9	0.8160	294.3
32.4	0.2040	3013.8	32.3	0.2007	100	31.02	0.6880	130.5
32.8	0.2040	2758.2	32.6	0.2007	94.78	32.593	0.7990	1407.9
			36.08	0.2007	15.01	36.1	0.8160	962.5
40.1	0.250	800.9	40.0	0.2007	27.04	40.1	0.8500	229.2
46.8	0.2720	1558.3	46.6	0.2007	64.21	46.7	0.7990	182.6
			57.9	0.3346	43.26			
58.1	0.3230	956.7	58.5	0.2007	17.81	58.4	1.0200	270.3
68.8	0.3570	255.7	68.4	0.2676	14.44	68.1	1.1730	128.8
77.5	0.3400	215.1	77.3	0.2007	10.3	77.6	0.9350	115.5

Fig 4.10 (a), 4.11 (a) & 4.12 (a) represent XRD pattern of $\text{Mn}_3\text{O}_4 - \text{La}_2\text{O}_3$ (LaMnO_3) ceramic mixture after sintering at 1000°C for 1hr. XRD pattern of Sample-3 nanocomposite after annealing exhibits (112), (200), (211), (004), (220), (321), (224), (400), (413) diffraction line of tetragonal phase of Mn_3O_4 [JCPDS- international center for diffraction data for sample code 24-0734] whereas (100), (110), (111), (200), (220) diffraction line because of cubic LaMnO_3 [JCPDS- international center for diffraction data for sample code 75-0440], which indicates the presence of $\text{Mn}_3\text{O}_4 - \text{La}_2\text{O}_3$ and Mn_3O_4 ceramic mixture after annealing. XRD pattern of Sample 4 nanocomposite after annealing consist of diffraction by (012), (110), (104), (202) (006), (024), (211), (122), (116), (214), (018), (220), (208), (306) planes of Rhombohedral $\text{La}_{0.93}\text{MnO}_3$ [JCPDS- international center for diffraction data for sample code 82-1152] alongwith diffraction by (112), (211), (220), (224) and (400) planes of tetragonal Mn_3O_4 [JCPDS- international center for diffraction data for sample code 24-0734]. XRD pattern of Sample-5 is in agreement with Rhombohedral $\text{La}_{0.93}\text{MnO}_3$ structure [JCPDS- international center for diffraction data for sample code 82-1152]. This XRD pattern confirms the complete conversion of $\text{Mn}_3\text{O}_4\text{-La}(\text{OH})_3$ nanocomposites to $\text{Mn}_3\text{O}_4 - \text{La}_2\text{O}_3$ ceramic with phase purity. XRD data reveal that $\text{Mn}_3\text{O}_4\text{-La}(\text{OH})_3$ nanocomposites prepared using equimolar of precursors completely undergoes complete conversion into $\text{Mn}_3\text{O}_4\text{-La}_2\text{O}_3$ ceramic on annealing whereas in other cases a part of Mn_3O_4 left unconverted. Crystallite size calculated from the most intense peak ($2\theta \sim 32^\circ$, 110 plane) is found to be nearly 50nm. It was found that after heating the nano-particles at 1000 °C the size increases due to the agglomeration of nano-particles because of loss of surfactant. With the loss of surfactant, growth of the particle become fast which results increase in size of the particle.

4.2 FTIR STUDIES

4.2.1 FTIR Spectra of Mn_3O_4 Nanoparticles

To study the presence of capping molecules as well as the chemical nature of the synthesized nanomaterials, infrared spectroscopy analysis was carried out. The detailed process of sample preparation has been discussed earlier in the instrumentation section where all samples have been prepared in preheated KBr powder in the form of pellets. Figure 4.13 and 4.14 shows the FT-IR spectra of as-prepared sample of Mn_3O_4 nanomaterial in two separate experiments, one in CTAB surfactant alone and the other where a mixture of surfactant of CTAB and TBAB has been used.

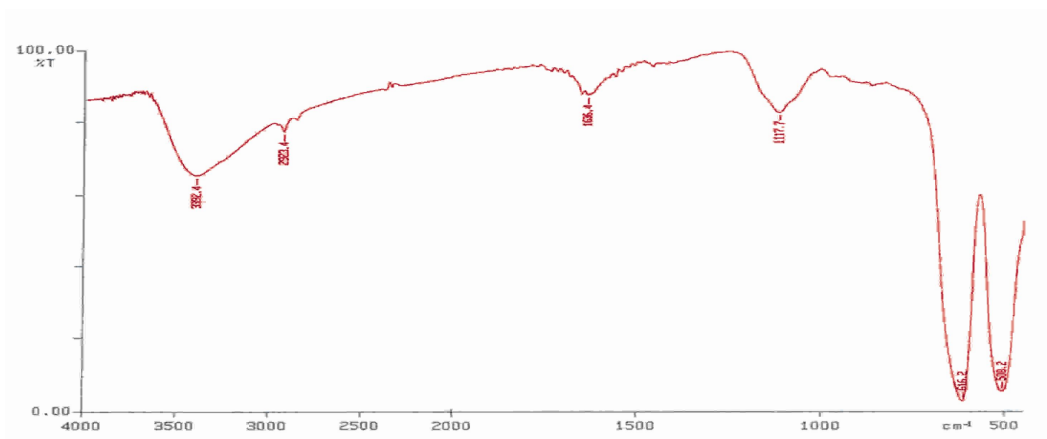


Fig 4.13 : FTIR spectra of Mn_3O_4 NPs synthesized in CTAB alone

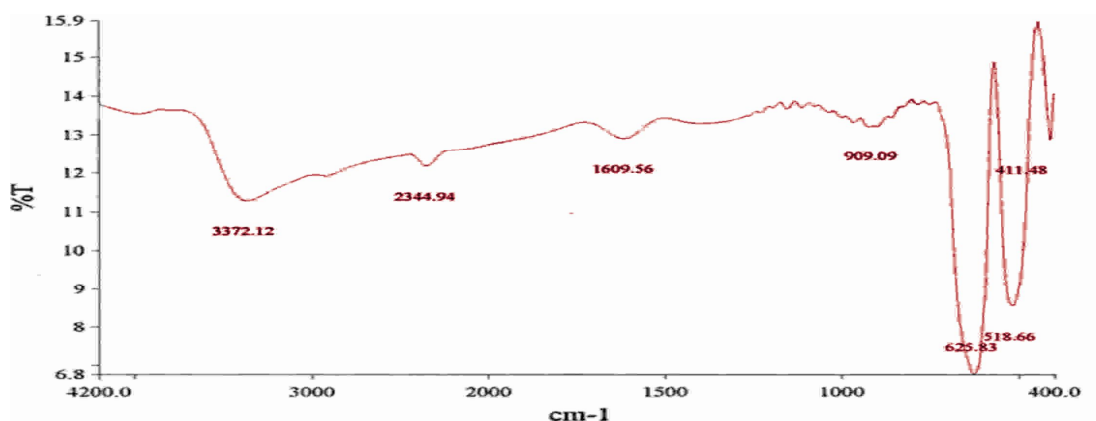


Fig 4.14 : FTIR spectra of Mn_3O_4 NPs using both CTAB & TBAB surfactants

A perusal of the FTIR spectra of Mn_3O_4 NPs, in Fig.4.13 & Fig 4.14 appears to be similar with minor peak shift in C-H or O-H stretchings, clearly indicated that a peak appeared at 508 cm^{-1} was attributed to the symmetrical stretching (V_{sym}) and peak at

616 cm^{-1} was attributed to the asymmetrical stretching (V_{asym}) of Mn-O-Mn unit in Mn_3O_4 . The broad band at 3372 or 3392 cm^{-1} was due to combined vibration of physisorbed water molecules and N-H stretching vibration of surfactant. The weak band at 2923 cm^{-1} was attributed to C-H stretching due to methyl and methylene groups. The moderate bands at 1609 or 1636 cm^{-1} was assigned to N-H bending vibrations of CTAB/TBAB. The presence of C-H, N-H and C-N stretching vibration confirm the surfactant capping of Mn_3O_4 NPs. And its minor shift may be due to presence of CTAB alone or mixture of both CTAB & TBAB.

Table 4.6 FT-IR Analysis of as-synthesized Mn_3O_4 NPs as per spectrum Fig 4.14

Band position (cm^{-1})	Description of vibration modes
411	$\text{Mn}_{\text{octahedral}} \longleftrightarrow \text{O}$ stretching
511 and 626	Due to coupling modes between $\text{Mn}_{\text{octahedral}} \longleftrightarrow \text{O}$ and $\text{Mn}_{\text{tetra}} \longleftrightarrow \text{O}$ [131]
1,000–1,250	Weak bands due to C–N stretching modes
1,609/1636	O–H stretching in adsorbed water molecules on the surface of Mn_3O_4 NPs
2,980–2,850	C–H stretching vibration
3,372, 3392	(a) N–H stretching vibration
	(b) O–H stretching of adsorbed water

4.2.2 FTIR Spectra of La(OH)₃ Nanomaterial

Fig. 4.15 shows the FT-IR spectra of as-prepared sample La(OH)₃. Nanopowder prepared in presence of CTAB surfactant and TBAB co surfactant. The spectra has been taken in KBr powder. Presence of the various absorption peaks of functional groups of CTAB / TBAB surfactant molecules on La(OH)₃ nanorods powder was confirmed from its spectra in 4000-500 cm⁻¹.

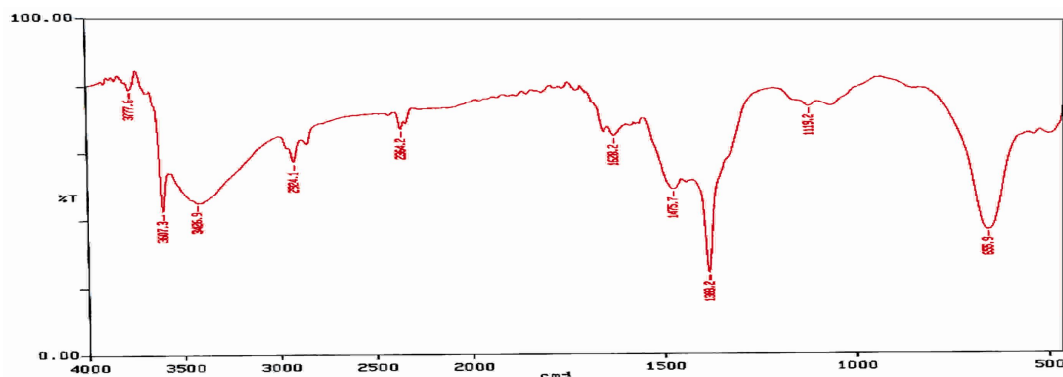


Fig 4.15 : FTIR Spectra of La(OH)₃

A peak appeared at 655.9 cm⁻¹ was attributed to La-OH deformation. The broad band at 3426 cm⁻¹ was due to stretching vibration physisorbed water molecules. Similar peak was also observed in Mn₃O₄ nanopowder. The peak at 2924.2 cm⁻¹ is due to C-H asymmetrical stretching. The peak at 1628.2 is also ascribed to physisorbed water molecules. The band appeared at 1475.7 cm⁻¹ is attributed to the C-H asymmetrical bending, indicates the presence of free surfactant CTAB molecule remained trapped inside the product [132]. In the present study CH₂ stretching vibration lies at 2924.0 cm⁻¹ and 2850.0 cm⁻¹ indicates almost no shift in the head group of the surfactant molecules. The N-C-H scissoring vibration of N-R has shown a peak at 1628.2 cm⁻¹ which is a significant shift in comparison to pure surfactant molecule. However a peak at 1475.7 cm⁻¹ indicates the presence of free surfactant CTAB molecule remained trapped inside the product. Also peak appeared at 1119.2 cm⁻¹ is due to -C-N stretching from CTAB molecules have significantly shifted than pure CTAB molecules because adsorption of surfactant molecule. The peak at 1383.2 cm⁻¹ can be attributed to -CH₃ bending vibration of tertiary butyl of surfactant TBAB [133]. For pure CTAB/TBAB symmetric and asymmetric peaks were reported at 2914.0 and 2864.0 cm⁻¹ and C-H scissoring vibration of N-R moiety were reported at 1550.0 and 1474.0 cm⁻¹. This study shows that presence of both CTAB and TBAB molecules on the surface of La(OH)₃.

4.2.3 FTIR Spectra of $\text{Mn}_3\text{O}_4 - \text{La}(\text{OH})_3$ Nanocomposite

To study the chemical nature and presence of the surfactant molecule of the as-made nano composite, infrared spectra were taken in KBr. Fig. 4.16 shows a typical FT-IR spectra of as-prepared $\text{Mn}_3\text{O}_4 - \text{La}(\text{OH})_3$ nanocomposite sample.

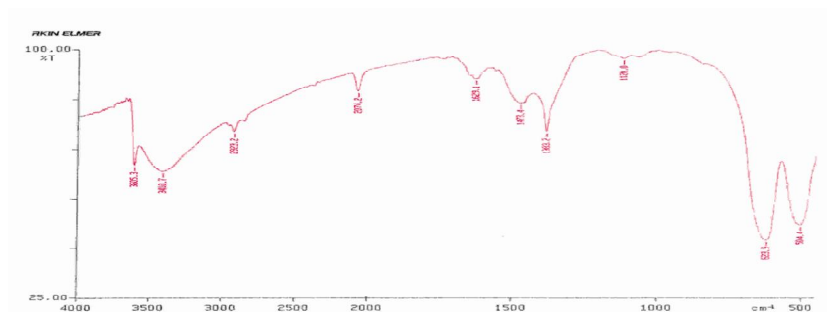


Fig 4.16 : FTIR Spectra of $\text{Mn}_3\text{O}_4 - \text{La}(\text{OH})_3$ nanocomposite

A perusal of the FTIR spectra (Fig. 4.16) clearly indicated that a peak appeared at 504.4 cm^{-1} was attributed to the distortion vibration of Mn-O in octahedral environment. The La-OH deformation and Mn-O stretching mode at tetrahedral sites appeared as a combine overtone at 623.9 cm^{-1} . This study shows that the formation of Mn-O in two stretching/ distortion modes. The combined tone also indicates the interaction in between La-O as well as Mn-O, thus making a composite. The broad absorption band at 3410.7 cm^{-1} were due to combined vibration of physisorbed water molecules remained with the composite even after vacuum drying.. The peak at 2923.2 cm^{-1} is due to C-H asymmetrical stretching from surfactant molecules. The peak at 1629.1 is ascribed to physisorbed water molecules. The bend appeared at 1473.4 cm^{-1} is attributed to the C-H asymmetrical bending. The peak at 1383.2 cm^{-1} can be attributed to $-\text{CH}_3$ stretching of tertiary butyl group of surfactant TBAB. The C-C skeletal vibration appeared at 1120 cm^{-1} . The presence of C-H stretching, C-H bending and C-C skeletal vibrations confirmed the capping of TBAB and CTAB surfactant at nano-particle surface. Similar mode of vibrations were also seen in Mn_3O_4 as well as $\text{La}(\text{OH})_3$ nano materials. From this study, it is clear that there has been a shift in its absorption peaks as compare to Mn_3O_4 or $\text{La}(\text{OH})_3$ alone given in spectra 4.14 & 4.15, however all peaks were in the same pattern. This shift in peak also indicates the formation. Interaction with in $\text{La}(\text{OH})_3$ & Mn_3O_4 resulting in a new material $\text{Mn}_3\text{O}_4 - \text{La}(\text{OH})_3$ nanocomposite.

4.3 TRANSMISSION ELECTRON MICROSCOPY (TEM)

4.3.1 TEM Images of Mn_3O_4 Nanoparticles

TEM imaging was carried out using Hitachi Model H-7500 120KV TEM. TEM images (Figure 4.17) of the manganese oxide nano material showed the formation of monodispersed particles. These nanoparticles are nearly spherical and appears some times pebbles like in shape with average size in the range of 5 to 8 nm. It can be observed that the Mn_3O_4 nanoparticles are uniformly distributed throughout the grid when image were taken in different portion of the grid. Size control and monodispersity was attributed due to the presence of combined CTAB – TBAB surfactants which have capped the particles and does not allow aggregations to occur due to steric hinderance. The transparent cloud around nanoparticles may be the presence of capped surfactants molecules. Short chain TBA^+ ions functions as filler ions (through hydrophobic interactions between alkyl chains of CTAB and butyl chains of TBAB) in gaps of adsorbed long chain CTAB micelles which further stabilize the naonparticles by preventing irregular growth into such gaps [133-134].

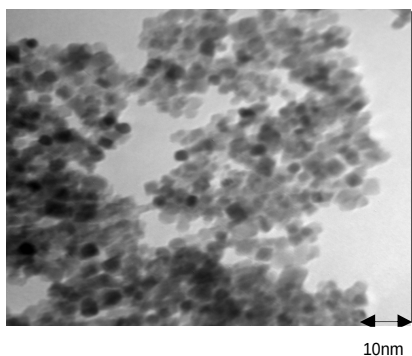


Fig 4.17 (a) : TEM Image of Mn_3O_4 in CTAB & TBAB

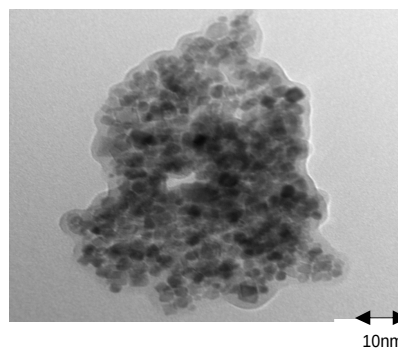


Fig 4.17(b) : TEM Image of Mn_3O_4 in CTAB alone

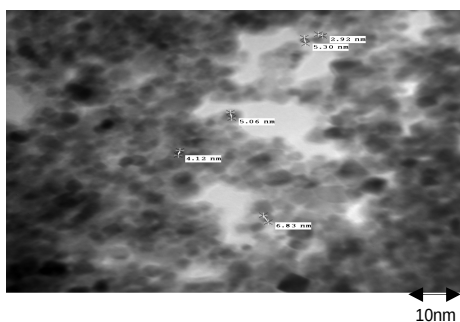


Fig 4.17(c) : Enlarged view of TEM Image of Mn_3O_4 synthesized in CTAB & TBAB

4.3.2 TEM Images of $\text{La}(\text{OH})_3$ Nanorods

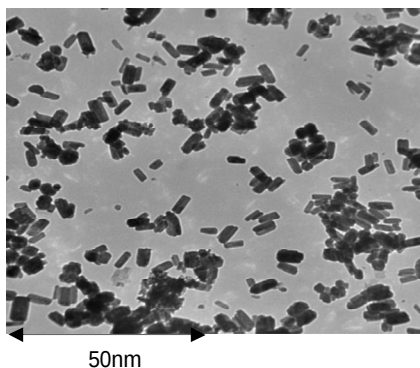


Fig 4.18(a) : TEM Image of $\text{La}(\text{OH})_3$ in CTAB & TBAB

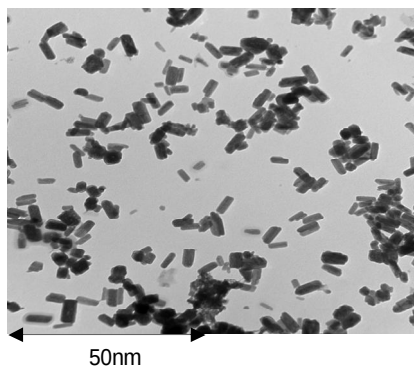


Fig 4.18(b) : TEM Image of $\text{La}(\text{OH})_3$ in CTAB alone

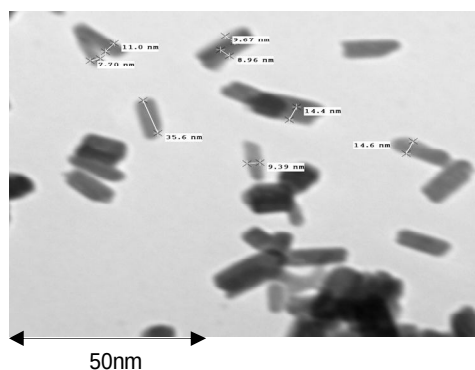


Fig 4.18 (c) : TEM Image of $\text{La}(\text{OH})_3$ nanorods synthesized in CTAB & TBAB, measurements from selected with its dimensions

Figure 4.18 (a) & (b) represents the TEM image of typical sample and 4.18 (c) shows the particle size marking of the selected area of the image. TEM image of $\text{La}(\text{OH})_3$ nanopowder clearly shows monodisperse of anisotropic nanorods with 7-12nm in width and 30-50 nm in length. The retention of monodispersed nanoparticles were resulted with the presence of surfactant molecules on their surface. However, nanorods are uniformly dispersed when viewed at different portions of grid for the same sample. Few rods are appearing as overlapping on each other and some are touching to each other whereas at some image represent only top surface of the rods. The nanoparticles formation is of rod shape and appeared to be anisotropic. The driving force for the anisotropic growth of $\text{La}(\text{OH})_3$ nanorod is derived from the inherent crystal structure of $\text{La}(\text{OH})_3$ materials and their chemical potential in solution. The transparent cloud surrounding the nanorods are also seen in these images reveals the use of surfactants for its stabilization

4.3.3 TEM Images of Mn_3O_4 – $\text{La}(\text{OH})_3$ Nanocomposite

Figure 4.19 shows the TEM image of Mn_3O_4 – $\text{La}(\text{OH})_3$ Nanocomposite sample synthesized from equal molar ratio in presence of CTAB/TBAB. TEM image shows that the formation of mono dispersed nano rods which irregularly present at different sites. The globular Mn_3O_4 nanoparticles appeared to be embedded on the surface or lying in the close vicinity of nanorods of $\text{La}(\text{OH})_3$. The size of these nano rods is around 20nm in width and 30 to 50 nm in length showing that thickness of the rods has increased which is due to presence of Mn_3O_4 nanoparticles on the surface of $\text{La}(\text{OH})_3$ resulted in the formation of their nanocomposite. The embedment has been possible due to negative charged of hydroxyl group towards Mn being metallic, it is positive in nature. Moreover the presence of same surfactant for capping may interact with both Mn_3O_4 as well as $\text{La}(\text{OH})_3$ thus brings both type of nano surfaces close to each other or may merge together. No free Mn_3O_4 or $\text{La}(\text{OH})_3$ was seen showing the formation of composite and the structure of the rods remains intact. At same places it appears that Mn_3O_4 nano particles has more concentration at the corners of the rods. It is due to more surface area available at the end of the cap.



Fig 4.19 : TEM image of Mn_3O_4 - $\text{La}(\text{OH})_3$ nanocomposite.

4.3.4 TEM Images of $\text{Mn}_3\text{O}_4\text{-La}_2\text{O}_3$ Nanocomposite

Figure 4.20 (a) and 4.20 (b) are the TEM image of two different samples of $\text{Mn}_3\text{O}_4 - \text{La}_2\text{O}_3$ nanocomposite, i.e. sample 4 & sample 5. The images show nearly spherical pebbles like in shape having a diameter of 40 to 60 nm. The regular rod type shape of $\text{La}(\text{OH})_3$ has disappeared due to the sintering process at high temperature with the formation of growing units. Though there is no surfactant present in the ceramic, however it appears that it may be trying to form a regular crystal structure, for which it is not possible to provide the explanation, where more study is needed. It also appears that at some places rods are lying as such especially at some corners. The reason may be that while on sintering some particles are quickly diffusing in each other and leaving others as such, may be due to poor contact among these. From the TEM image, it is concluded ceramic powder of $(\text{Mn}_3\text{O}_4 - \text{La}_2\text{O}_3)$ tries to generate a definite crystalline pattern with retained monodispersity.

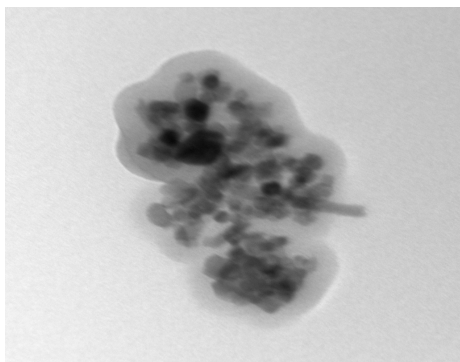


Fig 4.20 (a) TEM Image of Sample 4, $\text{Mn}_3\text{O}_4 - \text{La}_2\text{O}_3$ (LaMnO_3) nanocomposite

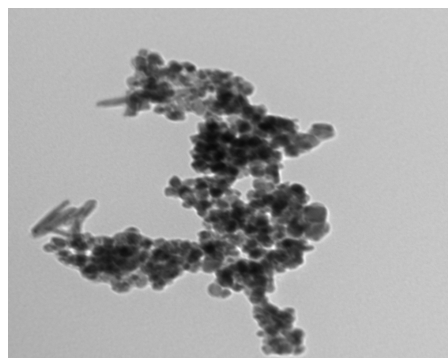


Fig 4.20 (b) TEM Image of Sample 5, $\text{Mn}_3\text{O}_4 - \text{La}_2\text{O}_3$ (LaMnO_3) nanocomposite

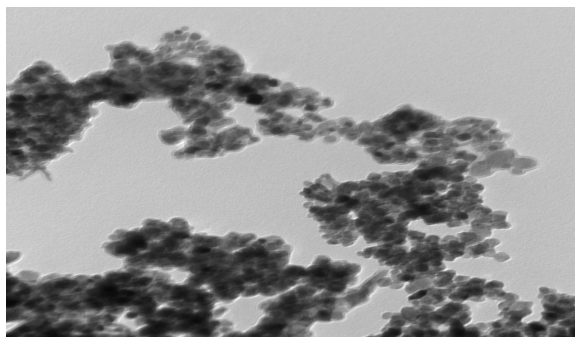


Fig 4.20 (c) Magnified TEM Image of Sample 5, $\text{Mn}_3\text{O}_4 - \text{La}_2\text{O}_3$ (LaMnO_3) nanocomposite

4.4 THERMAL STUDIES

TGA and DSC studies of Mn_3O_4 , $\text{La}(\text{OH})_3$ and $\text{Mn}_3\text{O}_4 - \text{La}(\text{OH})_3$ have been discussed in this chapter. Thermal stability of nano-particles has been investigated using thermogravimetric analysis (TGA). TGA was performed under N_2 atmosphere so that the mass increase due to oxidation of manganese should be eliminated.

4.4.1 Thermogravimetric Analysis (TGA) of Mn_3O_4

Fig 4.21 depicts the thermogram of nano- Mn_3O_4 .

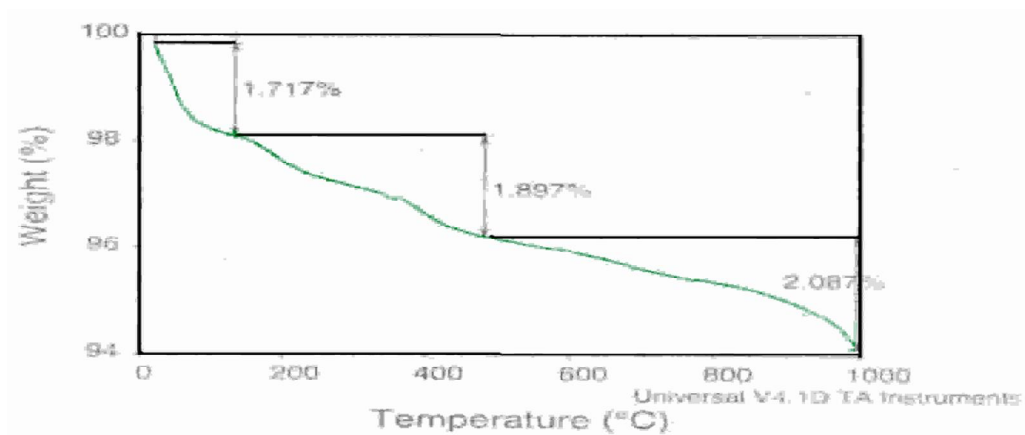


Fig 4.21 (a) : TGA Curve of Mn_3O_4

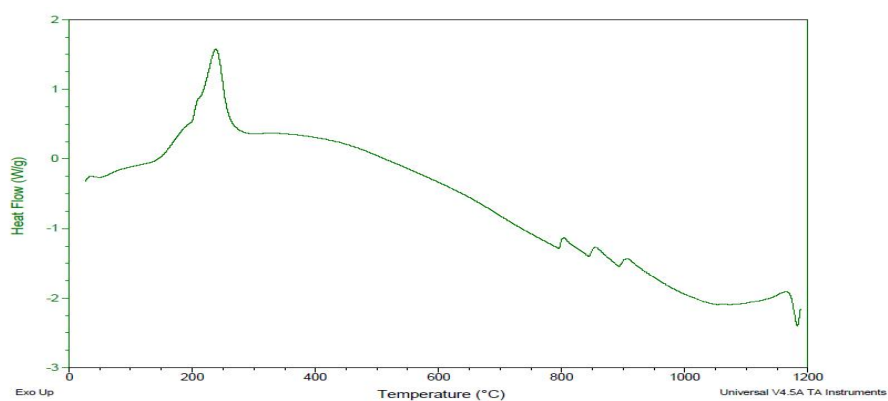
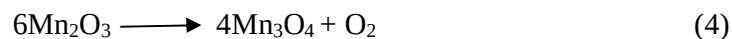


Fig 4.21 (b) : DSC Curve of Mn_3O_4

Thermal analysis of Mn_3O_4 nanoparticles in the temperature range of 30-1000°C in N_2 atmosphere as is shown in Figure 4.21 (a) have three gradual weight loss transitions. The first transition with a 1.72% weight loss in the temperature range 30-120°C is ascribed to the expulsion of adsorbed water molecules at the surface of nano- Mn_3O_4 .

The moisture has been retained during synthesis, since vacuum drying was done at 60°C only. The second transition with a weight loss of 1.89% in the temperature range 120-480°C is due to loss of surfactant CTAB & TBAB present on the surface of nanoparticles. The surfactant disintegrates into its C, H, N molecules.

The final transition with 2.08% weight loss is attributed to the loss of O₂ due to conversion of higher oxides into lower oxides at high temperatures [135].



This weight loss transition indicated that pristine nano-particles may consist of minor quantity of Mn₂O₃ which start converting to Mn₃O₄ on heating above 600°C and completely transformed into Mn₃O₄ upto 1000°C.

It can be concluded that the as-synthesized oxide mixture contained about 30% Mn₂O₃ that completely transformed into Mn₃O₄ at higher temperatures in agreement with XRD results. On further heating beyond 1000°C, no further mass loss was observed. DSC curve of Mn₃O₄ nano-particles is given in figure 4.21 (b), showed a sharp endothermic peak at around 250°C, which may be due to removal of surfactant. No clear cut absorption peak is visible for the conversion of Mn₂O₃ into Mn₃O₄.

4.4.2 Thermogravimetric Analysis – TGA/DSC of La(OH)₃ Nanorods

Figure 4.22 shows Thermogravimetric Study – TGA/DSC of La(OH)₃ nanorods. TGA/DSC plot of the product in the temperature range of ambient to 1000°C is given in Fig. 4.22. The profile indicates the corresponding weight loss in various temperature range which is divided in four steps, (1) in the temperature range of ambient 199.66 °C. The weight loss of 6.572 % is due to physisorbed water molecules as well as unbounded CTAB/TBAB molecules. In FT-IR spectra (Fig.4.15) the broad band at 3,426.9 and 1,628.2 cm⁻¹ due to stretching vibration ‘of physisorbed water molecules also confirms the presence of water moiety. A peak at 1,457.7 cm⁻¹ also confirms the presence of free CTAB. (2) further gradual weight loss of 9.673 % in the temperature range 263.23°C is due to the decomposition of the bounded surfactant molecules into C, H and N moiety. Both CTAB/TBAB were got adsorbed on the surface of the nanorods during synthesis (3) on further ramping in the temperature range from 263.23 to 649.16°C the weight loss of 10.66 % was observed due to dehydration of La(OH)₃ to

LaOOH (lanthanum hydroxide-oxide)[136], (4) another weight loss of 5.88% up to the temperature of 730.92 °C was due to complete dehydration of LaOOH into La₂O₃.

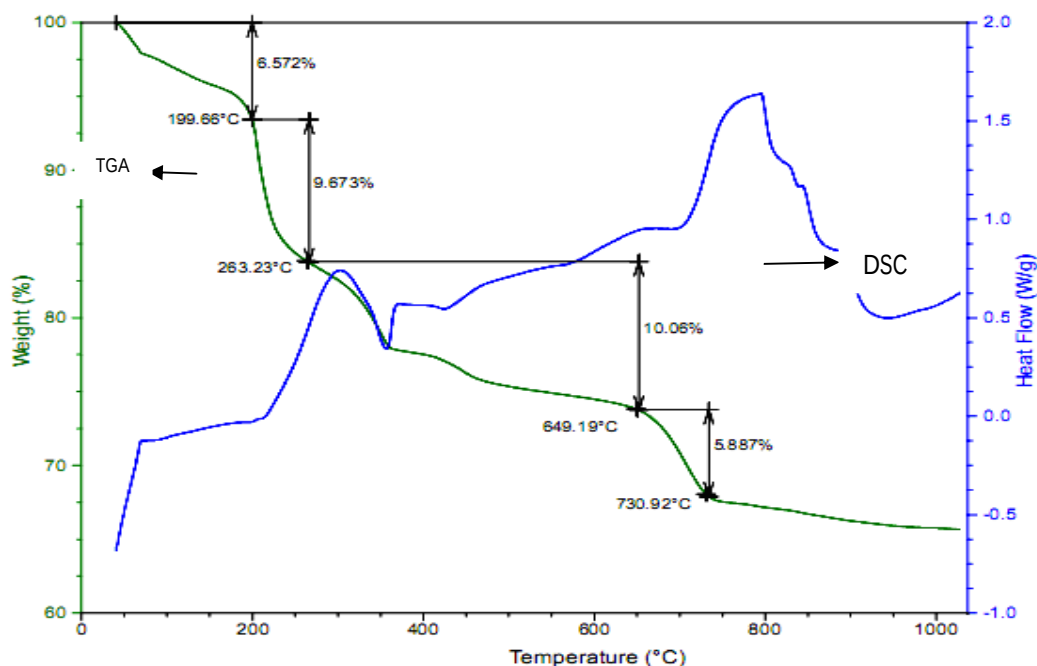
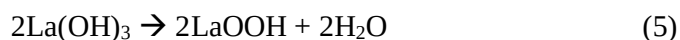


Fig 4.22 : Thermogravimetric Study – TGA & DSC of La(OH)₃ nanorods

It has already been reported that the La(OH)₃ phase first get transformed to the LaOOH phase in the temperature range of 330-400°C which is an intermediate phase with monoclinic crystal structure and P21/m (No.11) space group. It further gets dehydrate form La₂O₃ up to 600°C as per Eqs. (5) and (6) [136-137]. However, in the present study there is a possibility that both reaction (5) and (6) may be occurring simultaneously and clear cut distinction may not be possible.



According to eqs. (5) and (6), the total thermal transformation weigh loss for the conversion of La(OH)₃ to La₂O₃ theoretically should be should 13.4%, which is somewhat higher in the present stud and the decomposition temperature of La(OH)₃ to La₂O₃ ranges in the temperature range of 330-730°C. In the present study the shift in dehydration temperature may be the result of surface modification of particles due to CTAB/TBAB capping.

In DSC curve (Fig 4.22) two endothermic peaks were observed. First peak temperature is 295.99°C having area 449.2 Jg⁻¹ amounting ~85.3 kJ mol⁻¹. This reaction enthalpy change is due to first dehydration (transformation of La(OH)₃ to LaOOH) and is in agreement with the results reported by Neumann and Walter[136]. The second peak temperature at 782.92 °C having peak area 406.7 Jg⁻¹ corresponds to 77.0 kJ mol⁻¹ which is due to transformation of LaOOH to La₂O₃. The second reaction enthalpy is higher than already reported[136] may be due to rigid and an isotropic nature of the compound formation.

4.4.3 Thermogravimetric Analysis (TGA/DSC) of Mn₃O₄ - La(OH)₃ Nanocomposite

Figure 4.23(a) depicts the thermogram of nanocomposite of Mn₃O₄ - La(OH)₃. The thermogram exhibited a typical 3 step weight loss transitions. The first step weight loss transition (2.02%) in the temperature range 25 – 120⁰C was ascribed to expulsion of physically adsorbed water molecules at the surface of Mn₃O₄ - La(OH)₃ nanocomposite. This weight loss is close to weight loss in Mn₃O₄ nanoparticles but far away La(OH)₃ nanorods indicating that nanorods have been covered with Mn₃O₄ during synthesis which does not allow water molecules to directly interact with La(OH)₃ surface. The study indicates the formation of composite, different than Mn₃O₄ or La(OH)₃ nanomaterials.

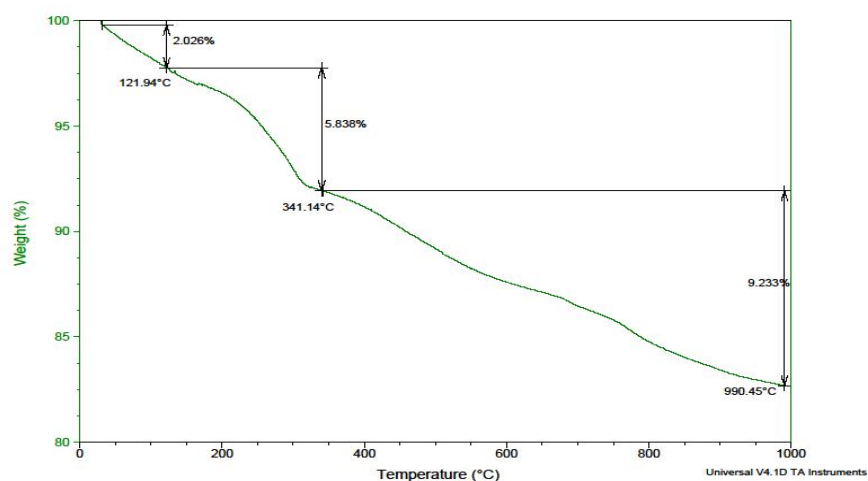


Fig 4.23 (a) : TGA of Mn₃O₄ - La(OH)₃ Nanocomposite

The second step weight loss transition (5.08%) in the temperature range 120-400⁰C was ascribed to loss of CTAB / TBAB surfactants molecules that has capped the

nanoparticles or got adsorbed during synthesis. The weight loss in the second step is found to be in between the weight loss of Mn_3O_4 and $\text{La}(\text{OH})_3$ nanoparticles respectively, it indicate that surfactant molecules have interaction at both the surfaces, however its presence will be more at Mn_3O_4 showing Mn_3O_4 presence on $\text{La}(\text{OH})_3$ nanorods. Thereafter, curve is stable upto 600°C and above 600°C third step weight loss transition (9.23%) was attributed to the loss of O_2 due to conversion of $\text{Mn}_3\text{O}_4/\text{La}(\text{OH})_3$ nanocomposites to manganese lanthanum oxide which is almost equal to theoretical weight loss value according to following reaction:



The decomposition of $\text{Mn}_3\text{O}_4/\text{La}(\text{OH})_3$ nanocomposites into $\text{La}_{0.93}\text{MnO}_3$ observed in XRD Sample 5 the results are in agreement.

During DSC study as shown in Figure 4.23(b) an endothermic peak at about 250°C is observed due to decomposition of surfactant. Another small peak at around 675°C is due to LaMnO_3 .

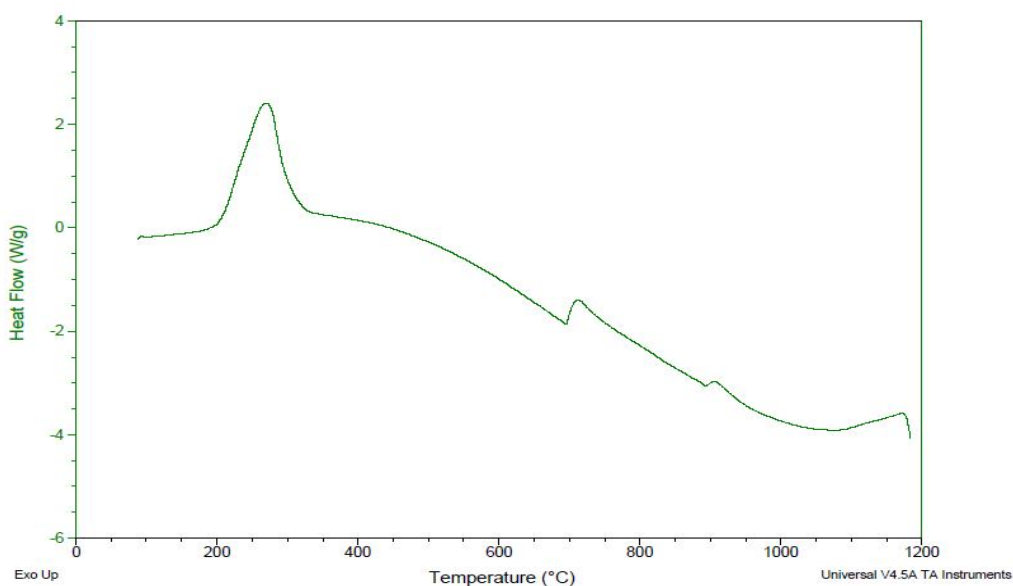


Fig 4.23 (b) : DSC of Mn_3O_4 - $\text{La}(\text{OH})_3$ nanocomposite

4.5 UV-Vis SPECTROSCOPY

To study the formation of Mn_3O_4 and $\text{La}(\text{OH})_3$ nanopowder, absorption studies were also conducted in UV Visible region. Being coloured solution of Mn_3O_4 nanoparticles, it has been scanned in visible region. The nanopowder was dispersed in ethanol and spectrum was also recorded using ethanol as reference solution. Maximum absorbance observed at 440°C which confirm the formation of Mn_3O_4 . This peak appears too broad indicating that the distribution of nanoparticles is somewhat random, which usually occurs in oxide nano particles of such small size. The absorption (extinction) depends upon size, shape, intensity and di-electric constant of the medium. The absorption peaks shown blue shift than bulk Mn_3O_4 confirm the formation of nanosized. It has been observed that with the increase of Mn_3O_4 concentration in the solution, the absorption intensity increases showing the interaction of nano particles with visible radiation, however, absorption maxima peak remain intact indicating that distribution of nano particles is nearly uniform.

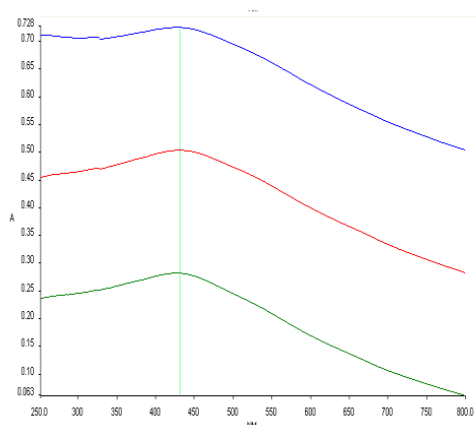


Fig 4.24(a) : UV-Vis Spectra – Mn_3O_4 Nanoparticles

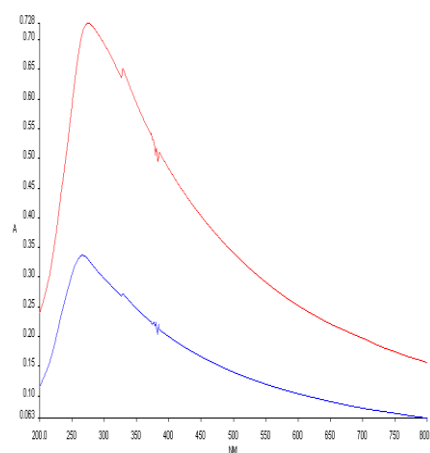


Fig 4.24(b) : UV-Vis Spectra – $\text{La}(\text{OH})_3$ Nanomaterial

The absorption maxima in case of $\text{La}(\text{OH})_3$ nano powder dispersed in ethanol was observed at 260°C. Being colorless, it does not absorb in visible region. This absorption may also be from the surfactant molecules, however, absorption intensity increases with increase of $\text{La}(\text{OH})_3$ concentration. The sharp absorption peaks indicates that the formation of nearly uniform disperse nano rods / nano particles. From this study, it can be concluded that the formation of nano materials / nano rods, their interaction with UV radiation, absorption pattern and its blue shift shows the formation of nano samples. The spectrum of Mn_3O_4 – $\text{La}(\text{OH})_3$ not so sharp so same has not been reported.

CHAPTER-5

RESULTS & DISCUSSIONS

FOR

ELECTRICAL

CHARACTERISATION

RESULTS & DISCUSSIONS FOR ELECTRICAL CHARACTERISATION

ELECTRICAL CHARACTERISATION AND NTC BEHAVIOUR STUDY OF Mn_3O_4 , $\text{La}(\text{OH})_3$ AND $\text{Mn}_3\text{O}_4 - \text{La}_2\text{O}_3$ (LaMnO_3)

5.1 ELECTRICAL CHARACTERISATION AND NTC BEHAVIOUR STUDY OF Mn_3O_4

5.1.1 NTC Behaviour of Mn_3O_4

The study was carried with surfactant and without surfactant (sintering at 500°C). Before presenting the results, brief outline of the importance of the work has been discussed. In the present study, nanoceramic Mn_3O_4 synthesized powder using both CTAB & TBAB surfactant; thermistors were fabricated by pressed die chip technique as well as continuous thermister by cold drawn technique. The thermistors were used to study its NTC characteristics. The conductance and impedance studies were carried out as a function of temperature from ambient to 300°C or cut-off temperature.

5.1.2 DC Conductivity Measurement of Mn_3O_4 nanoparticles

To investigate the NTC behaviour, dc conductivity studies of this material was done by in-house setups. NP powder was ramified in a Stainless Steel tube of length 10 mm with openings (2.0 mm diameter) at both ends. Metal contacts were provided through Chromel and alumel wires (0.1 mm diameter) inserted at opposite ends. Resistivity measurement was performed with Fluke 177 digital multimeter. The temperature was controlled through a muffle furnace with digital temperature controller ($\pm 1.0^\circ\text{C}$ accuracy). The temperature ramp was kept at 2°C min^{-1} . The similar observation was repeated several times on the same sensor and also on newly fabricated sensors to see repeatability.

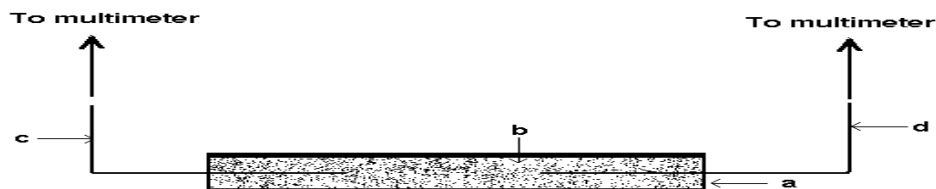


Fig 5.1 : Schematic diagram of sensor: (a) Stainless Steel Tube of 10 mm length 2mm diameter; (b), ceramic powder; (c) chromel; (d) alumel, sensing wires of diameter 0.3 mm.

Resistance variation were measured with respect to temperature and a plot was made between resistance versus T, where resistance is in ohm and T is absolute temperature in °C. As per Figure 5.2, it was observed on repeated studies that resistance value of the compacted nano powder in mega ohm at ambient temperature, showing it as insulated material, with the increase in temperature, resistance begins to drop and become lowest and nearly constant, which does not change with further increase in temperature and found to be $190 \pm 5^\circ\text{C}$ indicating its NTC cut-off temperature.

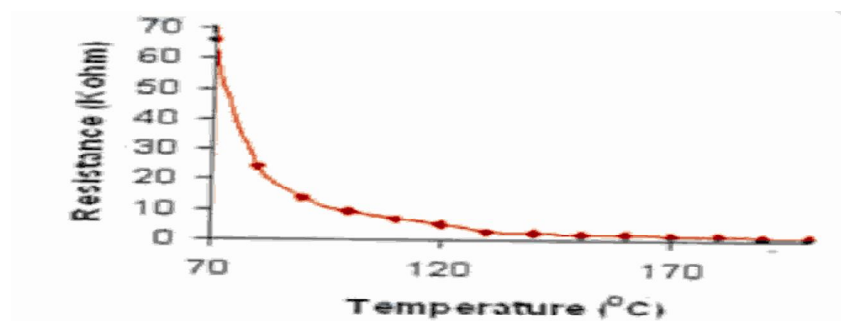


Fig 5.2 : NTC cut off temperature of Mn_3O_4

The explanation / mechanics of thermal behaviour of ceramic is as under :

The Arrhenius behaviour is described by $\rho = \rho_0 \exp(\beta/T)$, where ρ is the resistivity, β is the thermister constant and T is the temperature. The dc resistivity studies of the as synthesized nanoparticles indicate thermally activated multiple conduction mechanisms that show Arrhenius behaviour with two different activation energies. The values of the corresponding thermister constants β_1 ($25^\circ\text{C} < T < 107^\circ\text{C}$) & β_2 ($107^\circ\text{C} < T < 190^\circ\text{C}$) were calculated from the plot of $\ln \rho$ versus $1/T$ (Fig. 5.3(a)) and are found to be 10,897 K ($\Delta E_1 = 939.02 \text{ meV}$) and 1,529 K ($\Delta E_2 = 131.75 \text{ meV}$) respectively. The temperature coefficient of resistance ($\alpha = -\beta/T^2$) is found to be -0.111 K^{-1} at 313K.

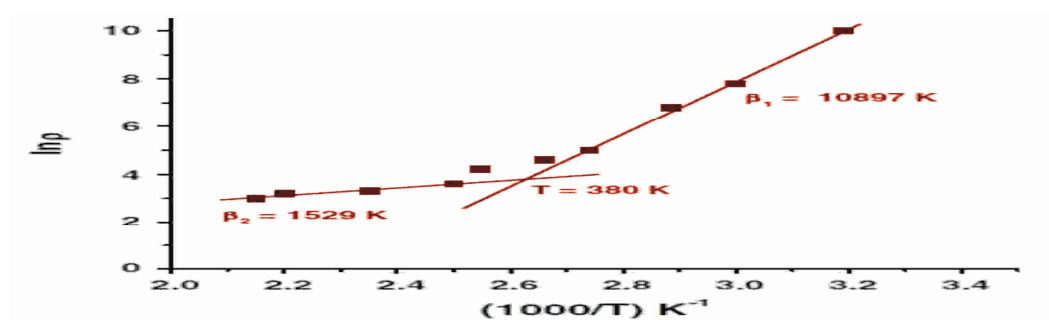


Fig 5.3(a) : DC Behaviour ($\ln \rho$ vs. $1/T$ plot) for a as-synthesized Mn_3O_4 nanoparticles in the temperature range of $40\text{--}200^\circ\text{C}$ having surfactant molecules

A similar study with the thermally treated NPs at 500°C which is free from surfactant also showed two slopes with activation energies ($\beta'_1 = 9,759 \text{ K} (\Delta E'_1 = 813 \text{ meV})$ and $\beta'_2 = 4,132 \text{ K} (\Delta E'_2 = 344 \text{ meV})$ but with significantly larger resistivity (Fig. 5.2(b)). The temperature coefficient of resistance (a) at 313 K was found to be -0.0996 K^{-1} . This difference in behaviour can be attributed to larger grain sizes in thermally treated NPs due to the removal of surfactant and co-surfactant that were stabilizing the NPs, leading to aggregation. Such studies were repeated several times. The DC conductivity studies showed two steps in order to find its mechanism, AC / Impedance studies were carried out.

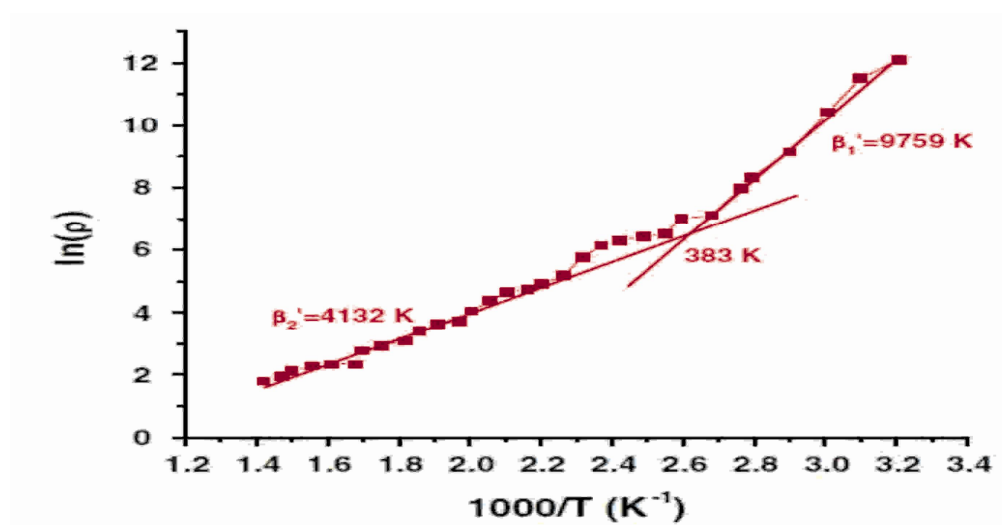


Fig 5.3(b) : DC Behaviour ($\ln \rho$ vs. $1/T$ plot) for thermally treated Mn_3O_4 nanoparticles in the temperature range of 40–200°C without surfactant molecules

5.1.3 Impedance Studies of Mn_3O_4 Nanoparticles

In order to determine the conduction mechanism, ac impedance of the as-synthesized nanopowder was measured over a wide range of frequencies at different temperatures.

For ac conductivity measurements, the powder sample was compressed into a pellet (diameter $\sim 10 \text{ mm}$) and coated with silver paste on both sides to provide the metallic contacts. Impedance measurements were done using HIOKI 3532-50 LCR Hit-ester LCR in a frequency range of 1 kHz–1 MHz inside an in-house designed digitally controlled temperature assembly over a range of 40–200°C.

Temperature and frequency dependent impedance behaviour of the as synthesized Mn_3O_4 samples were evaluated over a temperature range of 40–140°C and a frequency range of 1 kHz to 1 MHz delineates the role of electron hopping between Mn^{2+} and Mn^{3+} in the conduction process. The plots of real (Z') and imaginary (Z'') parts of the impedance data are shown in Fig 5.3(a) & 5.3(b).

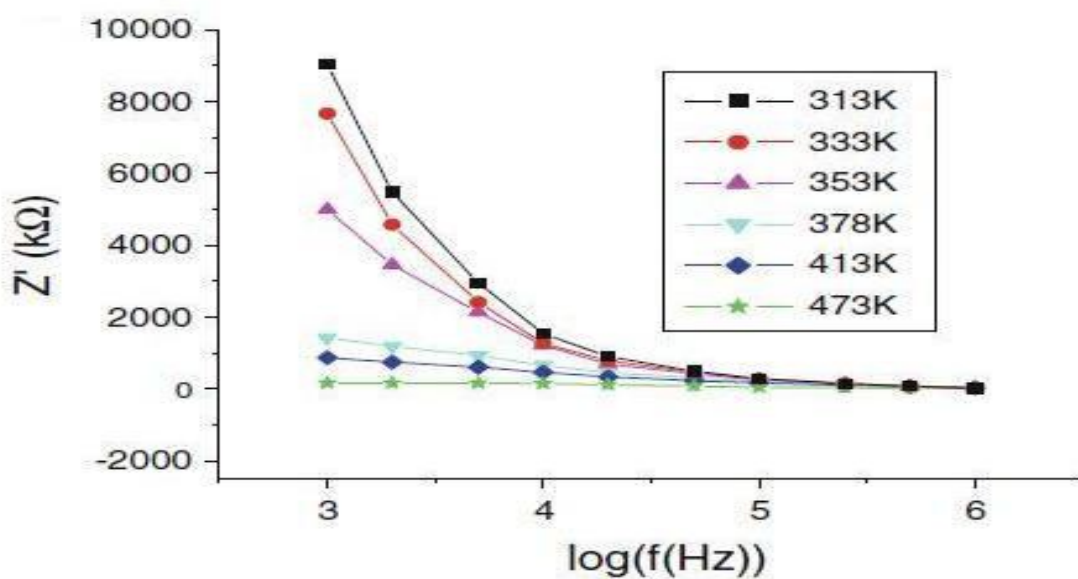


Fig 5.4(a) : Impedance studies: Real Part (Z' resistance versus frequency)

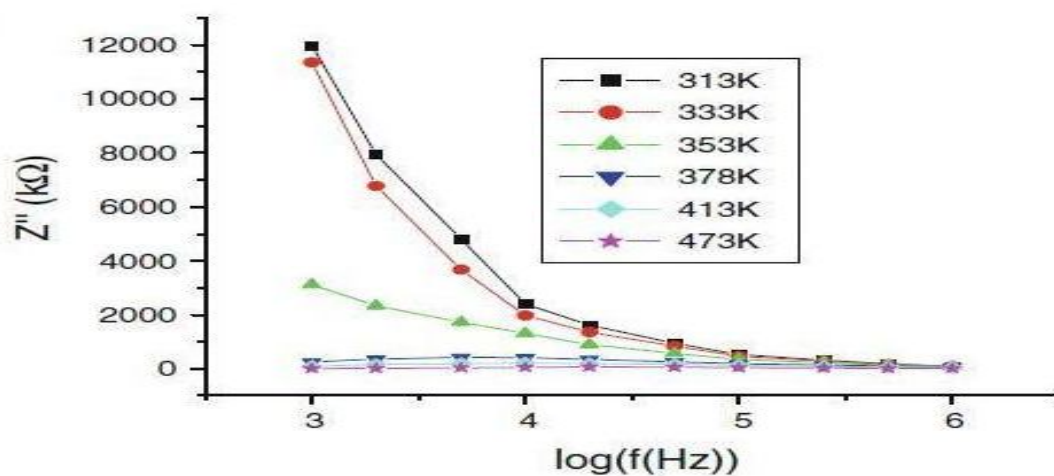


Fig 5.4(b) : Impedance studies : Imaginary Part (Z'' reactance versus frequency)

The impedance is found to decrease with increase in temperature as expected in a thermally activated process fig 5.3(b). Additionally, from the impedance plots at lower temperatures, a decrease in both resistance and reactance with increase in frequency was observed. Such a behaviour can be explained using the phenomenon of electron hopping between manganese cations (Mn^{2+} and Mn^{3+}) of differing valences. The increase in frequency of the applied voltage increases the probability of electron hopping [138-140]. However, at higher temperatures beyond 140°C, a deviation from this behaviour was observed in the reactance plot indicating additional contributions from other mechanisms. From these studies, it can also be concluded that these mechanisms are in series configuration as the mechanism with larger resistivity dominates. Hence, one may conclude that the additional resistivity is due to the grain boundaries. It is observed that this mechanism limits the conductivity at higher temperatures. The low limiting resistance observed in as-synthesized nanopowder can be attributed to higher grain boundary conductivity due to larger volume fraction of grain boundaries [141]. The apparent difference in the y-intercepts of the two slopes indicates different carrier densities. The larger carrier density for grain boundary conduction may be attributed to additional charge carriers or ions present in the grain boundaries in addition to those supplied by the grain. In addition, various other parameters like porosity, chemical composition, particle size and cation distribution have been reported to have significant effect on the conductivity and activation energies in spinel structures [142-143]. In order to study the reproducibility, the thermal behaviour of the samples was studied by subjecting them to heating cycles and the behaviour was found not to vary significantly hence implying applications in stable NTC thermistors. These studies present monodispersed Mn_3O_4 NPs as promising material for NTC thermistor in the low temperature range with cut off temperature 107°C and 190°C for continuous thermistor.

5.1.4 Possible Mechanism Proposed

Synthesized material has spinel structure Mn_3O_4 ($MnO \cdot Mn_2O_3$). On increase of temperature, lattice vibration increases. Some of Mn^{2+} present in Mn_3O_4 ($MnO \cdot Mn_2O_3$) surface enters into sites occupied by Mn^{3+} . Increased Mn^{3+} concentration, facilitate the NTC behaviour at lower cut-off temperature. Thus Concentration of Mn^{3+} increases due to presence of Mn_2O_3 also present in the ceramic. In order to maintain the neutrality and stabilize Mn^{2+} , some of Mn^{3+} exchange by hopping process into

Mn⁴⁺. NTC behaviour of the thermister material could be attributed to the electron hopping phenomenon between the two oxidation states of manganese i.e. Mn³⁺ and Mn⁴⁺ of Mn₃O₄. Thus Mn₃O₄ nanomaterial showed reproducible NTC characteristics. This material could be a potential candidate to fabricate thermister for detection and control of low temperatures around 200°C in comparison to the bulk size Mn₃O₄ powder, having cutoff NTC temperature about 400°C. It has already been investigated by several authors that the behaviour of Mn, Ni, CO oxide spinel ceramic bulk materials as NTC thermister with cut-off temp of 400°C and above. However Singla et al. reported NTC behaviour of Mn₃O₄ – La₂O₃ in a temperature range of 330-400°C using bulk ceramic [49]. In the present study, Mn₃O₄ nanomaterial the values are found to be 190°C indicating that nano structure material have low cut off temp leading a different mechanism which has been discussed above.

5.1.5 Comparative Data of Surfactant Capped Mn₃O₄ Nanoparticles & Thermally Sintered(500°C) Mn₃O₄ Nanoparticles

	Mn ₃ O ₄ Nanoparticle		Thermally Sintered Mn ₃ O ₄ (500°C)	
	Temp. Range		Temp. Range	
Characteristics	40-107 ⁰ C	107-200 ⁰ C	40-107 ⁰ C	107-200 ⁰ C
Thermister Constant (β)	β ₁ =10,897K	β ₂ =1,529K	β' ₁ =9,759K	β' ₂ =4,132K
Activation Energy (ΔE)	ΔE ₁ =939.02meV	Δ'E ₂ =131.75meV	ΔE' ₁ =813meV	ΔE ₂ =344meV
Temp. Coefficient (α) at 313K	α= -0.111K ⁻¹		α = -0.0996K ⁻¹	

Table 5.1 : Characteristics comparison Mn₃O₄ Nanoparticles & Thermally Sintered Mn₃O₄ at 500°C

Difference in behaviour of as synthesized (with surfactant) and sintered at 500°C (without surfactant) can be attributed to larger grain sizes in thermally treated nanoparticles due to removal of surfactant and co-surfactant that were stabilizing the nanoparticles, leading to aggregation. Thermister constant (β₁) and NTC values are found to be higher than that of bulk Mn₃O₄ in range of 40-107°C. Observed behaviour implies an enhanced sensitivity in nanopowder based thermister. These studies present monodisbursed Mn₃O₄ nanoparticles as promising materials for NTC thermister in the low temperature range 40-107°C. Grain boundary conduction is proposed as the

limiting mechanism at higher temperatures. The significantly high thermister constant and reproducible properties imply an enhanced sensitivity and stable nanopowder based NTC thermisters. Temperature dependent behaviour of the as-synthesized samples indicates the role of electron hopping between Mn^{2+} and Mn^{3+} as the conduction mechanism at lower temperatures. Temperature dependent behaviour DC resistivity showed reproducible NTC characteristics over the range of 40-200°C with two thermister constants $\beta_1=10,897K$ for 40-107°C and $\beta_2=1,529K$ for 107-200°C and negative temperature coefficient $\alpha=-0.111K^{-1}$ at 40°C.

5.2 ELECTRICAL BEHAVIOUR OF $La(OH)_3$ NANORODS

$La(OH)_3$ nano rods does not show NTC behaviour since hopping of electron/proton is not possible however, electrical properties like variation of conductance and capacitance with frequency has been studied as shown in Figure 5.4 (a) & 5.4(b) and in Table 5.2.

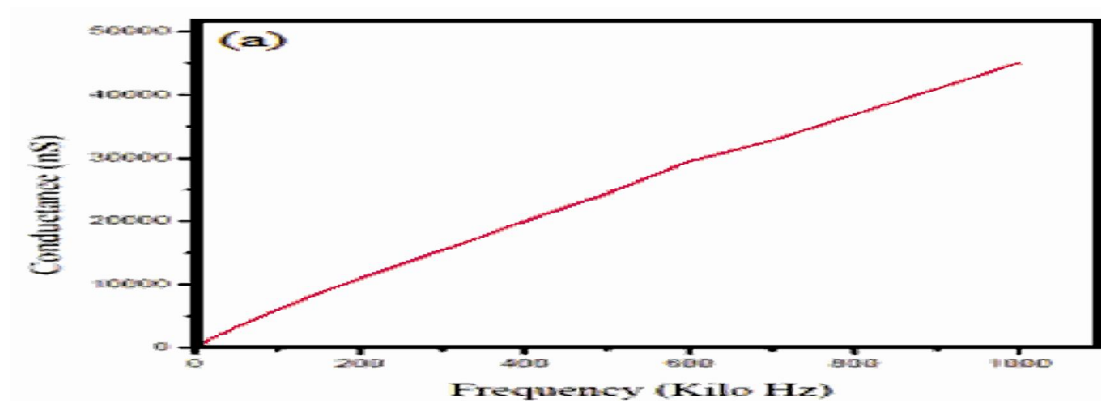


Fig 5.5(a) : Frequency Vs Conductance characteristics of $La(OH)_3$

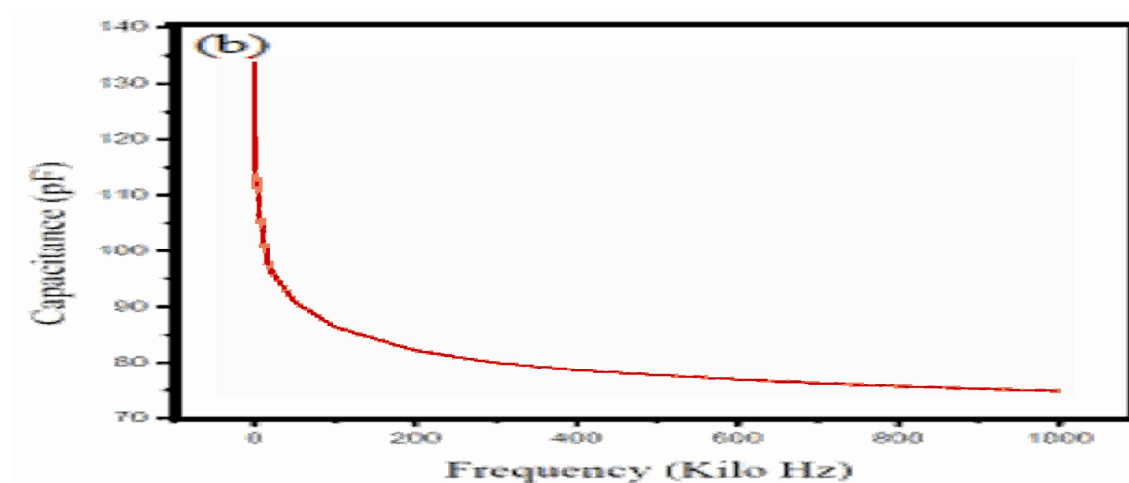


Fig 5.5(b) : Frequency Vs Capacitance characteristics of $La(OH)_3$

Frequency (Kilo Hz)	Capacitance (pF)	Conductance (nS)
0.1	142.432	1.2204
0.5	123.53	41
1	116.63	75.055
10	103.65	83.17
50	91.335	1437.7
100	86.995	3212.7
500	78.148	19990
1,000	75.558	38600

Table 5.2 : Capacitance and conductance data of La(OH)₃ nanomaterial in the selected frequency range of 0.1-1000 KHz.

Figure 5.4(a) and 5.4(b) shows the variation in electrical connectivity of the material in the frequency ranging from 10^2 to 10^6 Hz and Table 5.2 comprises of capacitance and conductance values with respect to variable frequency range selected for the study. The A.C. conductivity was measured in ns, which non-linearly increases with the increase in frequency. Total conductivity of the system is given by

$$\alpha = \alpha_o(T) + \alpha(\omega, T) \quad (8)$$

Here, the first term is dc conductivity which is independent of frequency. The second term is A.C. conductivity may be due to auto behaviour ion or polarization which occurred due to electro negativity difference between the Lanthanum and hydroxyl groups resulting in hopping between metal ions under the effect of electric field.

It may also be possible that some of free La⁺³ ions left entrapped inside the crystal structure during the synthesis process which may generate defects in the La(OH)₃ crystal. Electron transfer experiments in these materials involve the transfer of charge from one end to another end but no net flow of charge or associated current in between contacts or molecules. However more detailed study is needed to understand proper mechanism. It has observed that capacitance value first decrease sharply at lower frequency and then slowly and becomes nearly constant as shown in Fig. 5b. The capacitive behaviour may be due to space charge behaviour ion from inhomogeneous dielectric structure. Inhomogeneous structure may be due to nano- pore defects in the crystal but exact cause is not clear. This type of electrical behaviour may be useful for

designing low loss dielectric capacitors and sensors for monitoring and comparing the conductivity levels of bio-fluids.

Repeated A.C. conductance measurements showed conductivity in the level of nano-seimen (ns) which has application for various bio- fluids hence this material can be utilized to compare A.C. conductance behaviour of such compounds. Due to pF capacitance behaviour, it can be used to build capacitors with low loss.

The A.C. conductivity was found to be of the order of nano-seimen (ns), which non-linearly increases with the increase in frequency (10^2 - 10^6 Hz) The capacitance behaviour was observed in pF in mid frequency region, which can be useful as low loss dielectric material. Nano rods may work as standard materials to monitor conductivity levels in biofluid proteins.

5.3 ELECTRICAL CHARACTERISATION OF Mn_3O_4 - $\text{La}(\text{OH})_3$ NANOCOMPOSITE

Figure 5.5(a) and 5.5(b) shows the dependance of conductance and capacitance of Mn_3O_4 - $\text{La}(\text{OH})_3$ nanocomposite on frequency ranging from 10^2 to 10^6 Hz and Table 5.3 comprises of capacitance and conductance values with respect to variable frequency range selected for the study. Value of conductance increases non-linearly with the increase in frequency whereas value of capacitance decreases with the increase in frequency.

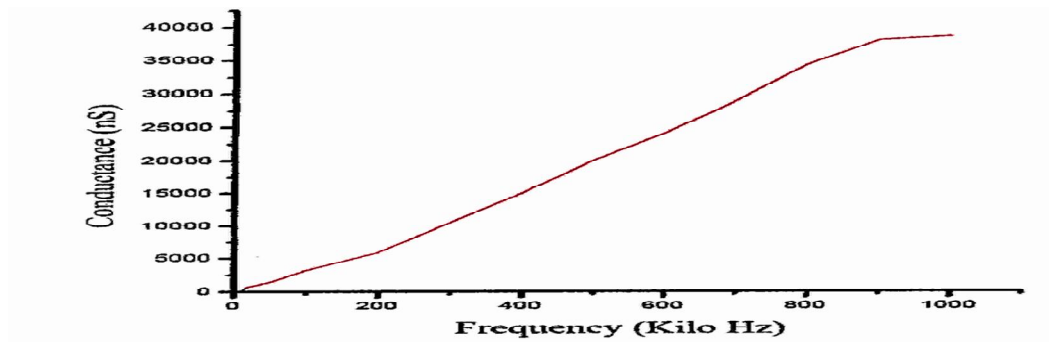


Fig 5.6(a) : Frequency dependent characteristics of Mn_3O_4 - $\text{La}(\text{OH})_3$

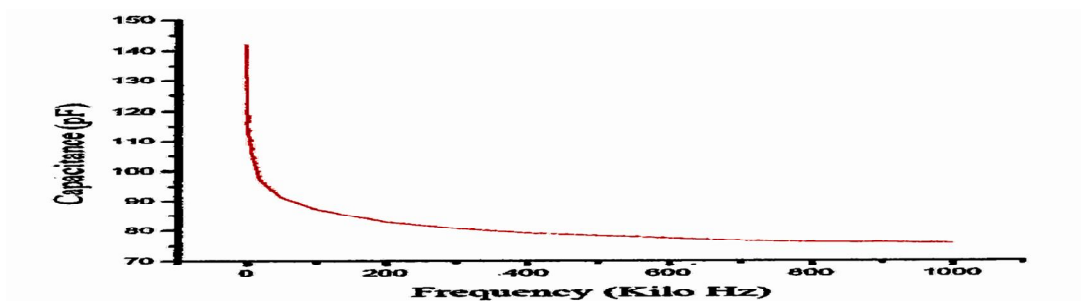


Fig 5.6(b) : Frequency dependent characteristics of $\text{Mn}_3\text{O}_4\text{-La(OH)}_3$

Frequency (Kilo Hz)	Capacitance (PF)	Conductance (nS)
0.1	134.03	8.0668
0.5	120.78	41.097
1	114.65	81.075
10	102.78	760.65
50	90.839	3280.6
100	86.406	6056.4
500	77.747	24394

Table 5.3 : Frequency Vs Capacitance, Conductance values obtained for $\text{Mn}_3\text{O}_4\text{-La(OH)}_3$ nanocomposites

From this data, it appears that capacitance values are similar to that of La(OH)_3 nanorods, showing that presence of Mn_3O_4 has not altered the behaviour. The capacitive behaviour may be due to space charge polarization from inhomogeneous dielectric structure. Inhomogeneous structure is due to nano pore defects in the crystal and presence of Mn_3O_4 , however exact cause is not clear. The conductance values have also found to lower than La(OH)_3 at different frequencies due to fact that composite has large grain boundary which restrict the flow of charge.

5.4 NTC behaviour of Sintered Mn_3O_4 alone at 1000°C for 2hrs

Mn_3O_4 nano powder was sintered at 1000°C where Mn_2O_3 completely decomposes into Mn_3O_4 , this ceramic is pure Mn_3O_4 and free from surfactant.

Electrical Properties

A point of interest is the electrical behaviour of the nano-particles. The resistance of nano-particles with smallest size was measured in air as a function of temperature range from ambient to 450°C and plots are shown in Figure. The plot of $\ln\rho$ vs. $1/T$ is almost linear where ρ is the resistivity and T is the temperature in Kelvin. It was found that the resistance value of the nano-particles measured at ambient temperature was of the order

of mega-ohm, decreased continuously with increase in temperature. In case of manganese oxide NTC behaviour was observed with lowest resistance value at 400°C. This decrease in resistance with temperature is attributed (i) electron hopping between two oxidation states of manganese i.e. Mn^{2+} and Mn^{3+} . As Mn_3O_4 has normal spinel structure with Mn^{3+} and Mn^{2+} ions occupying the octahedral and tetrahedral sites respectively [25], (ii) Increase in the mobility of surfactant molecules capping the nanoparticles as TGA study also supports the observation that the surfactant molecules remained on the surface upto 350°C. The results indicate that the nano- Mn_3O_4 particles can be used as NTC material with cut-off temperature in the range of 400°C. The β value for the sample derived by Arrhenius type equation was found 4685.5K^{-1} . Hence support the observation of nano- Mn_3O_4 to act as a NTC material. Activation energy (ΔE) has been calculated from the relation $\beta = \Delta E/K$, where K is the Boltzmann constant was found 403.4 meV.

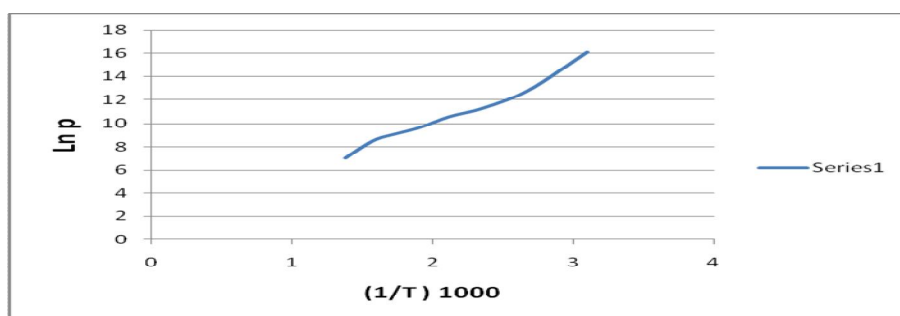


Fig 5.7 : Plot for Mn_3O_4

5.5 NTC behaviour of $\text{Mn}_3\text{O}_4 - \text{La}_2\text{O}_3$ (LaMnO_3) nanocomposite samples:

Three composite samples 3, 4 & 5 were sintered at 1000°C for 1 hour to convert the composite into $\text{Mn}_3\text{O}_4 - \text{La}_2\text{O}_3$ (LaMnO_3). Each ceramic powder was used to fabricate thermister as shown in figure 5.1. These thermisters were characterized for NTC behaviour, the NTC study of $\text{Mn}_3\text{O}_4 - \text{La}_2\text{O}_3$ (LaMnO_3) nanocomposite has been carried out from ambient to 500°C, where temperature verses resistance values were noted. Electric characterisation, i.e. temperature vs resistance was studied for each sample. Plots of $\ln p$ vs. $1/T$, where p is resistance and T is absolute temperature are shown in figure 5.8. It was observed that there is a decrease in resistance in each thermister with increase in temperature, however this change is not uniform because of the composition variation in the ceramic. Electrical conductivity increases with the Lanthanum oxide content while activation energy decreases. Low values of the

calculated activation energies are in agreement with the small polaron hopping mechanism [144]. As the concentration of lanthanum oxide is increased a remarkable change in β value is observed. The β value decreases as the concentration of lanthanum oxide increases and also the upper limit of temperature range decreases. The β value for $\text{Mn}_3\text{O}_4 - \text{La}_2\text{O}_3$ (LaMnO_3) nanocomposites is found between $7668\text{--}4928\text{K}^{-1}$ in the temperature range $40\text{--}500^\circ\text{C}$ for different concentrations. Thus, the study revealed that these nanocomposites can be used for fabrication of thermister and continuous thermocouples.

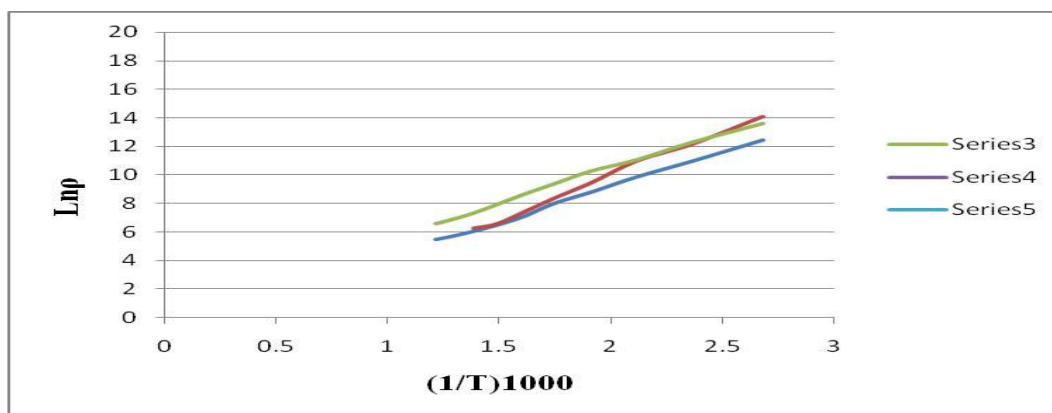


Fig 5.8 : Plot for nanocomposites

Red :- Sample 3 , Slope= 7668

Blue :- Sample 4 , Slope=5556

Green :- Sample 5 , Slope=4928

Name	Concentration of lanthanum nitrate	Temperature range	Slope (K^{-1})	Activation Energy (meV)
Sample 3	1mmole	40 to 300°C	7668	660.2
Sample 4	3mmole	40 to 350°C	5556	478.3
Sample 5	5mmole	40 to 460°C	4928	424.3

Table 5.4 : Values obtained for thermister constant and activation energy for $\text{Mn}_3\text{O}_4 - \text{La}_2\text{O}_3$

NTC studies of all the three ceramic samples reveals that for Sample 3 & 4, the resistance value continue to decrease and finally become constant providing the necessary cut off temperatures. However, in the Sample-5, which has been prepared equivimolar concentration of KMnO_4 & $\text{La}(\text{NO}_3)_3$, the minimum resistance value was seen at 460°C , however, with further increase in the temperature it began to rise, not

giving a sharp cut off temperature. Thus the concentration of upto 37% $\text{La}(\text{NO}_3)_3$ in the synthesis system was maximum limit for such thermister devices.

From this study, it is concluded that the Mn_3O_4 Nanoparticle capped with CTAB/TBAB works as thermister with cut-off temperature 190°C . Though, it has two transitions, one at 107°C , other at 190°C . The Mn_3O_4 nanoparticle sintered at 500°C without capping also shows similar behaviour, but with lower thermister constant. $\text{La}(\text{OH})_3$ does not show NTC behaviour, however it has variable conductance and capacitance with the variation in frequency. Mn_3O_4 and $\text{Mn}_3\text{O}_4 - \text{La}_2\text{O}_3$ (LaMnO_3) composite prepared on sintering at 1000°C provide cut-off temperature, 400°C for Mn_3O_4 and between 300 to 460°C for $\text{Mn}_3\text{O}_4\text{-La}_2\text{O}_3$ (LaMnO_3).

CHAPTER-6

CONCLUSION

6. CONCLUSIONS

On the basis of this study performed following conclusions have been drawn :

The chemical route (bottom up) for the synthesis of Mn_3O_4 nanoparticles, $\text{La}(\text{OH})_3$ nanorods and $\text{Mn}_3\text{O}_4\text{-La}_2\text{O}_3$ nanocomposite has been worked out. This involves the reduction of metallic ions from its salt with hydrazine hydrate (reducing agent) in aqueous medium. The stabilization of these nanomaterials has been done using a mixture of CTAB surfactant and TBAB co-surfactant. Moreover monodisperse nanosize dimensions have been possible with the use of mixture of surfactants and controlled reaction conditions. Sintering of $\text{Mn}_3\text{O}_4 - \text{La}(\text{OH})_3$ has resulted in the formation $\text{Mn}_3\text{O}_4\text{-La}_2\text{O}_3$ nanocomposite in variable stoichiometry depending on the ratio of both precursors.. TEM image showed 5-8 nm diameter of manganese oxide, nanorods of lanthanum hydroxide of 30-50 nm in length having aspect ratio 2 to 5 and the size of sintered nanocomposite vary between 40 – 80 nm.

Mn_3O_4 nanoparticles were synthesized by reducing KMnO_4 at about 70°C in the presence of long chain cetyltetrabutylammonium bromide (CTAB) surfactant and short chain tetra-n-butylammonium bromide (TBAB) co-surfactant. Structural characterisation showed monodispersity and capping with surfactant molecules. The presence of some amount of Mn_2O_3 was also found from TGA and XRD studies. These nanoparticles showed the temperature dependent behaviour of DC resistivity with reproducible NTC characteristics over a range of $40\text{--}200^\circ\text{C}$ with two thermister constants ($\beta_1 = 10,897\text{ K}$ for $40^\circ\text{C} < T < 107^\circ\text{C}$ and $\beta_2 = 1,529\text{ K}$ for $107^\circ\text{C} < T < 200^\circ\text{C}$). This study implies an enhanced sensitivity in nano ceramic-powder for its use in the fabrication of continuous thermisters. The impedance behaviour of this powder was evaluated over a temperature range of $40\text{--}140^\circ\text{C}$ in the frequency range of 1 kHz to 1 MHz delineates the role of electron hopping process between Mn^{2+} and Mn^{3+} in the conduction process. This study shows that Mn_3O_4 nanoceramic is promising material for NTC thermister in the low temperature range $40^\circ\text{C} < T < 107^\circ\text{C}$ as well as $107^\circ\text{C} < T < 200^\circ\text{C}$. Temperature and frequency dependent impedance behaviour implies the role of electron hopping between Mn^{2+} and Mn^{3+} as the conduction mechanism at lower temperatures and grain boundary conduction is proposed as the limiting mechanism at higher temperature. The significantly high thermister constant and reproducible

properties imply an enhanced sensitivity and stability of the nanoceramics powder for NTC principle based thermister.

Anisotropic $\text{La}(\text{OH})_3$ nanorods were synthesized through facile route in aqueous solution of lanthanum nitrate, mixture of above cationic surfactants and hydrazine hydrate solution. From TEM image, morphology has been found in the form of rods with narrow size distribution. TBAB/CTAB played a key role in the formation of nanorods and to limit the growth process for which a mechanism has been proposed. Thermal analysis (TGA & DSC) showed how $\text{La}(\text{OH})_3$ was reduced to La_2O_3 powder. A.C conductance measurements showed conductivity in the level of nano seimen. Such range in conductivity is present in various bio- fluids, hence this nano compound may be helpful in comparing A.C. Conductance values and designing new systems having such nanomaterial. Due to pF Capacitance of this compound, its use can be considered to design capacitors having low losses.

Nanocomposite of $\text{Mn}_3\text{O}_4 - \text{La}(\text{OH})_3$ have been synthesized by simultaneous reduction of KMnO_4 and $\text{La}(\text{NO}_3)_3$ solution in presence of above surfactant and reducing agent. Precursors ratios of both these compounds were varied during the synthesis, to make several combinations of nanocomposite. These nanocomposites were characterized using XRD, FTIR, TEM, TGA and DSC techniques. The XRD patterns confirms the presence of Mn_3O_4 and $\text{La}(\text{OH})_3$ together. After sintering at 1000°C , this nanocomposite converts into ceramic mixture $\text{Mn}_3\text{O}_4 - \text{La}_2\text{O}_3$. The crystallite size was also increased as a result of annealing. It was found that after heating the nano-particles at 1000°C the size increases due to agglomeration of nano-particles because of loss of surfactant. TEM image of the composite material showed the presence of Mn_3O_4 nanoparticles embedded on the surface of $\text{La}(\text{OH})_3$ nanorods. Average length and diameter of the nanoparticles and nanorods were also reported by TEM images. The capping behaviour of CTAB and TBAB on the nanoparticles has been explained with the help of FTIR. TGA studies showed that the conversion of $\text{Mn}_3\text{O}_4 - \text{La}(\text{OH})_3$ nanocomposite to $\text{Mn}_3\text{O}_4 - \text{La}_2\text{O}_3$ on heating above 600°C . The XRD data reveals that the $\text{Mn}_3\text{O}_4 - \text{La}(\text{OH})_3$ nanocomposites prepared using equimolar ratio of precursors completely undergoes complete conversion into $\text{Mn}_3\text{O}_4 - \text{La}_2\text{O}_3$ ceramic on annealing whereas in other cases a part of Mn_3O_4 left unconverted. Crystallite size of $\text{Mn}_3\text{O}_4 - \text{La}_2\text{O}_3$ ceramic calculated from the most intense peak ($2\theta \sim 32^\circ$, 110 plane) is found to be nearly 50 nm.

TEM image of sample shows the presence of globular Mn_3O_4 nanoparticles in the close vicinity of nanorods La_2O_3 .

NTC study of $\text{Mn}_3\text{O}_4 - \text{La}_2\text{O}_3$ nanocomposite has been carried out. The decrease in resistance with increasing temperature is in total agreement with the NTC behaviour, which shows that the $\text{Mn}_3\text{O}_4 - \text{La}_2\text{O}_3$ nanocomposite composite is a promising material to be used for thermister over a wide range of temperature with different cut-off temperature 300-460°C. Value of thermister constant for $\text{Mn}_3\text{O}_4 - \text{La}_2\text{O}_3$ nanocomposite is found between 7668–4928 K^{-1} in the temperature range 200 to 350°C for different concentrations.

Parameter such as conductance, capacitance and resistance follow a similar trend for all the three, as prepared of Mn_3O_4 nanoparticles, $\text{La}(\text{OH})_3$ nanorods and $\text{Mn}_3\text{O}_4 - \text{La}(\text{OH})_3$ nanocomposite with frequency change. Capacitance and resistance of the samples show an inverse relation with frequency. On the contrary, conductance of the sample increases with increase in frequency.

The study of NTC behaviour shows that the nanocomposite of $\text{Mn}_3\text{O}_4 - \text{La}_2\text{O}_3$ can be a promising material to be used for NTC thermister over a wide range of temperature. As the value of β is greater than 3000 K^{-1} , it will find a wide variety of applications in thermisters, hot air leak detection system and fire safety sensors. These thermisters will find applications to monitor and control critical systems like aero engine, armor tank and other strategic devices from overheating and fire conditions with temperature variations.

REFERENCES

References:

[1]	R. Feynman, " <i>There's plenty of room at the bottom</i> " Engineering and Science 23, 22-36 (1960)
[2]	J.Von Neumann, " <i>Theory of Self-Reproducing Automata</i> " ed. By A.W. Burks, University of Illinois Press, Urbana (1966)
[3]	K.E.Drexler, " <i>Engines of Creation</i> " Anchor Press, New York (1986)
[4]	D.M. Eigler, E.K. Schweizer, "Positioning single atoms with a scanning tunneling microscope" <i>Nature</i> , 344, 524-526 (1990)
[5]	J.F. Tremblay, " <i>Fullerenes by the Ton Mitsubishi's Frontier Carbon expects a big market for buckyballs</i> " Chemical and Engg News, 81, 13-14 (2003)
[6]	E. Roduner "Size matters: why nanomaterials are different" Chem. Soc. Rev.35, 583–592 (2006)
[7]	Y. K. Gunko, D. F. Brougham "Magnetic Nanomaterials as MRI Contrast Agents" Nanotechnologies for the Life Sciences, DOI: 10.1002/9783527610419. NtIs0166 (2011)
[8]	M. Valden, X. Lai, and D. W. Goodman, "Onset of Catalytic Activity of Gold Clusters on Titania with the Appearance of Nonmetallic Properties" <i>Science</i> , 281, 1647 (1998)
[9]	S. W. Chen R.S. Ingram, M.J. Hostetler and J.J. Pietreon, R. W. Murray, T .G. Schaaff', J. T. Khoury, M.M. Alvarez and R.L. Whette "Gold Nanoelectrodes of Varied Size: Transition to Molecule-Like Charging" <i>Science</i> , 280, 2098-2102 (1998).
[10]	P. J. Thomas, G.U. Kulkarni, C.N.R. Rao "Effect of size on the Coulomb staircase phenomenon in metal anocrystals" <i>Chemical Physics Letters</i> , 321,163–168, (2000)
[11]	P.M. Ajayan, L.S. Schadler, P. V. Braun "Nanocomposite science and technology", Wiley , ISBN 3527303596 (2003)
[12]	A K Singh,M.Sakil,G.S Roy "Study the Characteristics of CdSe\Polythiophene Nanocomposite By TGA/DTA, XRD, UV-VIS Spectroscopy, SEM-EDXA & FTIR"Researcher,4, 16-20 (2012)
[13]	G.P. Kelkar, K.E. Spear, A.H. Carim "Thermodynamic evaluation of reaction products and layering in brazed alumina joints" <i>Journal of Materials Research</i> 9, 2244-2250 (1994)

[14]	P. K. Rohatgi and B. Schultz “ <i>Lightweight Metal Matrix Nanocomposites – Stretching the Boundaries of Metals</i> ” <i>Material Matters</i> , 2.4, 16, (2007)
[15]	N.K. Tolochko, A.A. Andrushevich, Y.A. Shienok “ <i>Fabrication of Metal Matrix Nanocomposites</i> ” <i>Advanced Materials Research</i> 79 , 425-428, (2009)
[16]	K.R. Rayan, J.R.Gourley, S.E. Jones “ <i>Environmental anomalies at the World Trade Center: evidence for energetic materials</i> ”, <i>The Environmentalist</i> , 29,56-63 (2009)
[17]	E.Manias, “ <i>Nanocomposites: Stiffer by design</i> ”. <i>Nature Materials</i> 6, 9-11, (2007)
[18]	U. Arimitsu, K. Masaya, K. Yoshitsugum, O. Akane, K. Toshio, K. Osami, “ <i>Swelling behaviour of montmorillonite cation exchanged for co-amino acids by ϵ-caprolactam</i> ”, <i>Journal of Materials Research</i> , 8, 1174 (1993)
[19]	U. Arimitsu, K. Yoshitsugu, K. Masaya, O. Akane, F. Yoshiaki, K. Toshio, K. Osami, 1993, “ <i>Synthesis of nylon 6-clay hybrid</i> ”, <i>Journal of Materials Research</i> , 8, 1179, (1993).
[20]	A. B. Morgan, C. A. Wilkie , “ <i>Flame Retardant Polymer Nanocomposites</i> ” Wiley, 2007, ISBN 978-0-471-73426-0.
[21]	J.Fraden “ <i>Handbook of Modern Sensors: physics, designs and applications</i> ” 3 rd edn. Springer , New York (2003)
[22]	B.M.Zeffert, S. Hormats, “ <i>Applilcation of thermister to cryoscopy</i> ” <i>Anal. Chem.</i> 21, 1420-1422 (1949).
[23]	E.A.Boucher, “ <i>Theory and applications of thermisters</i> ” <i>J.Chem. Educ.</i> 44, 625-702 (1967)
[24]	K. Majid, S. Awasthi, M.L. Singla “ <i>Low temperature sensing capability of polyaniline and Mn_3O_4 composite as NTC material</i> ” <i>Sens. Actuators A Physical</i> . 135, 113–118 (2007)
[25]	K. Park, D.Y. Bang “ <i>Electrical properties of Ni–Mn–Co–(Fe) oxide thick-film NTC thermisters prepared by screen printing</i> ” <i>J. Mater. Sci. Mater. In Electronics</i> . 14, 81–87 (2003)
[26]	H. Einaga, A. Ogata “ <i>Benzene oxidation with ozone over supported manganese oxide catalysts: effect of catalyst support and reaction conditions</i> ” <i>J. Hazard. Mate.</i> 164, 1236 (2009)

[27]	L.C. Wang, X.S. Huang, Q. Liu, Y.M. Liu, Y. Cao, H.Y. He, K.N. Fan, J.H. Zhuang “ <i>Gold nanoparticles deposited on manganese(III) oxide as novel efficient catalyst for low temperature CO oxidation</i> ” J. Catal. 259, 6 -74(2008)
[28]	M. Kang, E.D. Park, J.M. Kim, J.E. Yie “ <i>Manganese oxide catalysts for Nox reduction with NH₃ at low temperatures</i> ” Appl. Catal. A:General, 327, 261-269 (2007)
[29]	N. Imamura, T. Mizoguchi, H. Yamauchi, M. Karppinen “ <i>Multivariate data analysis approach to understand magnetic properties of perovskite manganese oxides</i> ” J. Solid State Chem. 181, 1195-1203 (2008)
[30]	SB Ma, KW Nam, WS Yoon, SM Bak, XQ Yang, BW Cho, KB Kim “ <i>Nano-sized lithium manganese oxide dispersed on carbon nanotubes for energy storage applications</i> ” Electrochemistry Communications, 11, 1575 (2009)
[31]	K.W. Nam, C.W. Lee, X.Q. Yang, B.W. Cho, W.S. Yoon, K.B. Kim “ <i>Electrodeposited manganese oxides on three-dimensional carbon nanotube substrate: Supercapacitive behavior in aqueous and organic electrolytes</i> ” J. Power Sources 188, 323-331 (2009)
[32]	M.L.Singla, S.Sharma, B.Raj, V.R.Harchekar “ <i>Characterisation of transition metal oxide ceramic material for continuous thermocouple & its use as NTC fire wire sensor</i> ” Sens. Actuators A: Phys. 120, 337-342 (2005)
[33]	M. Lee, M. Yoo “ <i>Detectivity of thin-film NTC thermal sensors</i> ” Sens. Actuators A : Phys. 96, 97–104 (2002)
[34]	S. Komaba, S.T. Myung, N. Kumagai, T. Kanouchi, K. Oikawa, T. Kamiyama “ <i>Hydrothermal synthesis of high crystalline orthorhombic LiMnO₂ as a cathode material for Li-ion batteries</i> ” Solid State Ionics 152, 311 (2002)
[35]	Akbari, Jafar, Heydari, Akbar “ <i>Synthesis of Mn₃O₄ Nanoparticles with Controlled Morphology Using Ionic Liquid</i> ” Current Nanoscience, 8, 398-401 (2012)
[36]	BL Cushing, VL Kolesnichenko, C.O’Connor, “ <i>Recent advances in the liquid-phase syntheses of inorganic nanoparticles</i> ” J. Chem. Rev. 104, 3893 (2004)
[37]	L. Tao, C.G. Sun, M.L. Fan, C.J. Huang, H.L. Wu, Z.S. Chao, H.S. Zhai, “ <i>A redox-assisted supramolecular assembly of manganese oxide nanotube</i> ” Mater. Res. Bull. 41, 2035 (2006)

[38]	A.J.Moulson, J.M.Herbert “ <i>Electroceramics: Materials, Properties and Applications</i> ” Chapman & Hall, London,256-263 (1990)
[39]	D.C.Hill, H.L. Tuller “ <i>Ceramic Sensors: Theory and practice</i> ” ed. By R.Buchanan , Marcel Dekker, New York (1986)
[40]	D.Saha, A.D. Sharma, A. Sen, H.S.Maiti “ <i>Preparation of bixbytes phase (Mn_xFe_{1-x})₂O₃ for NTC thermister applications</i> ” Mat. Lett. 55,403 (2002)
[41]	M. Hosseini “ <i>The effect of cation composition on the electrical properties and aging of Mn-Co-Ni thermisters</i> ” Ceramics. Int. 26, 245–249 (2000)
[42]	J. Ryu, K.Y. Kim, J.J. Choi, B.D. Hahn, W.H. Yoon, B.K. Lee, D.S. Park, C. Park, “ <i>Highly dense and nanograined NiMn₂O₄ negative temperature coefficient thermister thick films fabricated by aerosol-deposition</i> ” J. Am. Ceram. Soc. 92, 3084–3087 (2009)
[43]	N.N. Greenwood, A. Earnshaw, Chemistry of the Elements, Publisher Pergamon Press, New York (1984)
[44]	Y.Chen, Y.Zhang, Q.Yao, G.T.Zhou, S. Fu, H. Fan. “ <i>Formation of α-Mn₂O₃ nanorods via a hydrothennal-assisted cleavage-decomposition mechanism</i> ”, J. Solid State Chemistry, 180, 1218-1223 (2007)
[45]	P. Gibot, L.Laffont, “ <i>Hydrophilic and hydrophobic nano sized Mn₃O₄ particles</i> ”. J. Solid State Chemistry, 180, 695-701 (2007)
[46]	T. Ozkaya, A. Baykal, H. Kavas, Y. Koseoglu, M.S. Toprak,” <i>A novel synthetic route to Mn₃O₄ nanoparticles and their magnetic evaluation</i> ”. Physica B: Condensed Matter, 403, 3760-3764, (2008)
[47]	J. Yun, C. Dub, N. Browning “ <i>Characterisation of manganese oxide nanowhiskers</i> ” J. Ceramic Processing Research, 9, 678-682 (2008).
[48]	S. Fritsch, J. Sarries, A. Rousset, G.U. Kulkarni “ <i>Low temperature oxidation of Mn₃O₄ hausmannite</i> ” Mater. Res. Bull. 33 , 1185 -1194 (1998)
[49]	M.L. Singla, R. Baldev, H.V. Rajaram, R.P. Bajpai, “ <i>Ceramic mixture having negative temperature coefficient, a thermister containing the ceramic mixture and the process for preparing same</i> ”, US Patent No 6878311 (2005)
[50]	J. Mu, Z.Gu, H.Sun, Q.Wei “ <i>Low Temperature Synthesis of Mn₃O₄ Nanoparticles Using Starch as Capping Agent</i> ” J. Dispersion Science and Technology, 27, 307–309, (2006)

[51]	K. Singh, Ashish, K. Sen, R. K Kotnala, M. Kumar, P. Gautam, M. Singh, "Room Temperature Long Rang Ordering in $(\text{BiFeO}_3)_{1-x}(\text{PbTiO}_3)_x$ " NanoCrystallites, J. Appl. Phys. 109, 123911 (2011)
[52]	A. Baykal, Y. Koseoglu, M. Senel, Central Eur. "Low temperature synthesis and ehavior ization of Mn_3O_4 nanoparticles". J.Chem. 5, 169-176 (2007)
[53]	Z. W. Chen, J.K.L. Lai, C.H. Shek, "Shape-controlled Synthesis and Nanostructure Evolution of Single-crystal Mn_3O_4 Nanocrystals"Scripta Material 55, 735-738 (2006)
[54]	M-S Wu, R-H. Lee, "Nanostructured manganese oxide electrodes for lithium-ion storage in aqueous lithium sulfate electrolyte" J. Power Souces, 176, 363-368 (2008)
[55]	T.D.Schladt,T. Graf,W.Tremel "Synthesis and Characterisation of Monodisperse Manganese Oxide Nanoparticles–Evaluation of the Nucleation and Growth Mechanism" Chemistry of materials, 21, 3183–3190 (2009)
[56]	M. S. Hassan, T. Amna, D. R. Pandeya, A. M. Hamza,Y. Y. Bing, H.ChelKim, M. Khil "Controlled synthesis of Mn_2O_3 nanowires by hydrothermal method and their bactericidal and cytotoxic impact: a promising future material" Applied Microbiology and Biotechnology, 95, 213-222, (2012)
[57]	W.He, Y. Zhang, X.Zhang, H. Wang, H. Yan "Low temperature preparation of nanocrystalline Mn_2O_3 via ethanol-thermal reduction of MnO_2 " Journal of Crystal Growth, 252, 285–288, (2003)
[58]	X.Chen, X. Li, Y. Jiang, C. Shi, X.Li, "Rational synthesis of $\alpha\text{-MnO}_2$ and $\gamma\text{-Mn}_2\text{O}_3$ nanowires with the electrochemical characterisation of $\alpha\text{-MnO}_2$ nanowires for supercapacitor" Solid State Communications,136, 94-96(2005).
[59]	Y. Han, F. Chen, Z. Zhong, K. Ramesh, L.Chen, E. Widjaja "Controlled Synthesis, Characterisation, and Catalytic Properties of Mn_2O_3 and Mn_3O_4 Nanoparticles Supported on Mesoporous Silica SBA-15" J. Phys. Chem. B, , 110, 24450–24456, (2006).
[60]	J. Moon, M. Awano, H. Takagi, Y. Fujishiro "Synthesis of nanocrystalline manganese oxide powders: Influence of hydrogen peroxide on particle characteristics" J. Mater. Res., 14, 4594 (1999)

[61]	Y. Li, H. Tan, X. Yang, B. Goris, J.Verbeeck, S. Bals, P. Colson, R. Cloots, G. V.Tendeloo, B.Su “ <i>Well Shaped Mn₃O₄ Nano-octahedra with Anomalous Magnetic Behaviour and Enhanced Photodecomposition Properties</i> ” Small 7, 475–483, (2011)
[62]	M. Arora, A. Sachdeva, V. Luthra, R.P. Tandon, R.P. Pant “ <i>Sol-gel Derived Nanocrystalline Lanthanum Doped Lead Zirconate Titanate Thin Films Studied for Solitary Waves Propagation</i> ”, Integrated Ferroelectrics, 122, 1, p. 144 – 151. (2010)
[63]	L.Yang, Y. Zhu, R.Tong, W. Wang, G. Cheng “ <i>Low temperature synthesis of Mn₃O₄ polyhedral nanocrystals and magnetic study</i> ” J. Solid State Chemistry, 179, 1225-1229 (2006)
[64]	Y.U Taekyung, M. Jaewon, P. Jinkyung, Y. I. Park, H.Bin NA ; B. H. Kim, C. Song, W. K. Moon, H. Taeghwan; “ <i>Various-Shaped Uniform Mn₃O₄ Nanocrystals Synthesized at Low Temperature in Air Atmosphere</i> ” Chemistry of materials, 21, 2272-2279 (2009)
[65]	T. Yamashita, A. Vannice, “ <i>NO Decomposition over Mn₂O₃ and Mn₃O₄</i> ”, J. Catalysis, 163, 158–168 (1996)
[66]	Y. Wang, H. Liu, M. Bao, B. Li, H Su, Y Wen, F Wang “ <i>Structural-controlled synthesis of manganese oxide nanostructures and their electrochemical properties</i> ”, J. Alloys and Compounds, 509, 8306– 8312 (2011)
[67]	S. Xing, Z. Zhou, Z. Ma, Y. Wu “ <i>Facile synthesis and electrochemical properties of Mn₃O₄ nanoparticles with a large surface area</i> ” Materials Letter, 65, 517–519 (2011)
[68]	Z. Gui, R. Fan, X. Chen, Y.C. Wu, “ <i>A simple direct preparation of nanocrystalline γ-Mn₂O₃ at ambient temperature</i> ”, Inorganic Chemistry Communications, 4, 294–296 (2001)
[69]	Y.Q. Chang, X.Y. Xu, X.H. Luo, C.P. Chen, D.P. Yu, “ <i>Synthesis and characterisation of Mn₃O₄ nanoparticles</i> ”, Journal of Crystal Growth, 264, 232–236 (2004)
[70]	A.Morsali, H. H. Monfared, “ <i>Synthesis and characterisation of Mn₃O₄ nanoparticles via thermal decomposition of a new synthesized hydrogen bonded polymer</i> ” Science Journal, 938, 10–14 (2009)

[71]	MM Thackeray, WIF David, P.G. Bruce, J.B. Goodenough, “ <i>Lithium insertion into manganese spinels</i> ”, Materials Research Bulletin, 18, 461–472 (1983)
[72]	M.V. Reddy, K.Y.H. Kenrick, Tang Ying Wei, Goh Yeow Chong, Goh Hock Leong, B.V.R. Chowdari “ <i>Nano-ZnCo₂O₄ material preparation by molten salt method and its electrochemical properties for Lithium batteries</i> ” Journal of Electrochem. Soc. 158 (12) (2011) A1423-A1430.
[73]	T. Yamashita, A Vannice, “ <i>Temperature-programmed desorption of NO absorbed on Mn₂O₃ and Mn₃O₄</i> ”, Applied Catalysis B: Environmental, 13, 141-155 (1997).
[74]	S.Komaba, S.T.Myung, N. Kumagai, T.Kanouchi, K.Oikawa, T.Kamiyama “ <i>Hydrothermal synthesis of high crystalline orthorhombic LiMnO₂ as a cathode material for Li-ion batteries</i> ” Solid State Ionics, 152, 311 (2002).
[75]	S.Chauhan,M.Kumar, S.Chhoker, S.C. Katyal, H. Singh, M. Jewariya, K.L. Yadav “ <i>Multiferroic, magnetoelectric and optical properties of Mn doped BiFeO₃ nanoparticles</i> ” Solid State Communications, 152, 525-529 (2012)
[76]	Menaka, N.Garg, S. Kumar, D.Kumar, K.V. Ramanujachary, S.E. Lofland, A.K.Ganguli “ <i>Nanostructured nickel manganese oxide: aligned nanostructures and their magnetic properties</i> ” J. Mater. Chem., 22, 18447-18453 (2012)
[77]	H. Gupta, A. Mahajan, R. K. Bedi “ <i>Synthesis and Characterisation of silver phthalocyanine nanowires and nanobelts</i> ”European Physical Journal of Applied Physics, 42(2008) 81-85
[78]	T.Nathan, M. Cloke, S.R.S. Prabakaran, “ <i>Electrode Properties of Mn₂O₃ nanospheres Synthesized by Combined Sonochemical/Solvothermal Method for Use in Electrochemical Capacitors</i> ” J. Nanomaterials.1-8 (2008)
[79]	R. Schmidt, A. Basu, A.W.Brinkman “ <i>Production of NTCR thermister devices based on NiMn₂O₄</i> ” J.European Ceramic Society 24, 1233–1236, (2004)
[80]	P. Billik, M.C. aplovicova, J. Janata, V.S. Fajnor “ <i>Direct synthesis of nanocrystalline, spherical α-Mn₂O₃ particles by mechanochemical reduction</i> ” mat. Lett. 62, 1052-1054 (2008)

[81]	A. Dierstein, H. Natter, F. Mayer, H-O. Stephan, Ch. Kropf, R. Hempelmann “ <i>Electrochemical deposition under oxidizing conditions : A new synthesis for nanocrystalline metal oxides</i> ” Scripta Mater, 44 2209-2212 (2001)
[82]	BL Cushing, V L Kolesnichenko, C. O’Connor “ <i>Recent advances in the liquid phase synthesis of inorganic nanoparticles</i> ” J. Chem. 104, 3893-3946 ((2004)
[83]	P. Tartaj, M.P. Morales, S.V.Verdaguer, T.G.Carreño, C.J.Serna “ <i>The preparation of magnetic nanoparticles for applications in biomedicine</i> ” Journal of Physics D: Applied Physics, 36 (2003)
[84]	M. Jain, S. B. Majumder, R. S. Katiyar, F. A. Miranda, F. W. Van Keuls “ <i>Improvement in electrical characteristics of graded manganese doped barium strontium titanate thin films</i> ” Applied Physics Letters, 82, 1911(2003)
[85]	Cristina Buzea, Ivan Pacheco and Kevin Robbie “ <i>Nanomaterials and Nanoparticles Sources and Toxicity</i> ”. Biointerphases, 2, Publisher: National Academies Press (2007)
[86]	C. Lu, Y.W. Mai, Y.G. Shen “ <i>Recent advances on understanding the origin of superhardness in nanocomposite coatings: A critical review</i> ” Journal of Materials Science, 41, 937-950 (2006)
[87]	S.V.N.T. Kuchibhatla, AS Karakoti, D. Bera, S Seal , “ <i>One dimensional nanostructured materials</i> ” Progress in Materials Science, 52, 699-913, (2007)
[88]	M. Alsawafta , S.Badilescu , A. Paneri , V.Truong , M.Packirisamy “ <i>Gold-Poly(methyl methacrylate) Nanocomposite Films for Plasmonic Biosensing Applications</i> ” Polymers, 3, 1833-1848 (2011)
[89]	M. Gunay, A. Baykal, M. S. Toprak, H. Sozeri “ <i>A Green Chemical Synthesis and Characterisation of Mn₃O₄ nanoparticles</i> ” Journal of Superconductivity and Novel Magnetism, 25, 1535-1539 (2012)
[90]	C.J.Murphy, T.K.Sau, A.M.Gole. C.J.Orendorff, J.Gao, L.Gou, S.E.Hunyadi, T.Li, “ <i>Anisotropic Metal Nanoparticles: Synthesis, Assembly, and Optical Applications</i> ” J.Phys. Chem. B 109,13857-13870 (2005)
[91]	W. Wang, Y. Liu , C. Xu, C. Zheng, G. Wang, “ <i>Synthesis of NiO nanorods by a novel simple precursor thermal decomposition approach</i> ” Science journal, 362, 119–122 (2002)

[92]	Y.C. Zhang, X.Y. Hu, T. Qiao, “ <i>Shape-controlled synthesis of CuS nanocrystallites via a facile hydrothermal route</i> ”, Science journal, 132, 779–782 (2004)
[93]	F. E. Kruis, H. Fissan, A. Peled. “ <i>Synthesis of nanoparticles in the gas phase for electronic, optical and magnetic applications – a review</i> ”. J. Aerosol Sci. 29, 511-535 (1998)
[94]	I.V. Kityk, A.A Majchrowski, E.E Michalski, D.D Kasprowicz, M .M Drozdowski, J.J Kisielewski, T.T Lukasiewicz, B.B Sahraoui “ <i>UV-induced nonlinear absorption in lanthanum calcium borate single crystals</i> ” J. Phys Chem B 110 , 9090-4 (2006)
[95]	S.K. Behera, P.K. Sahu. S.K. Pratihara, S. Bhattacharyya “ <i>Low temperature synthesis of spherical lanthanum aluminate nanoparticles</i> ” Materials Letters, 58, 3710-3715 (2005)
[96]	L.Lin, Y.Huang, J.Zhang, X. Ding. Q.Shouren, C.Tang ” <i>Preparation and characterisation of lanthanum borate nanowires</i> ” Materials Letters, 61, 1596-1600 (2007)
[97]	M.Mazloumi, S.Zanganeh, A.Kajbafvala, M.R.Shayegh, D.S.K.Sadrnezhaad “ <i>Formation of Lanthanum Hydroxide Nanostructures: Effect of NaOH and KOH solvents</i> ” IJE Transactions B: Applications, 21, 169 (2008)
[98]	X.Ma, H.Zhang, Y.Ji, J.Xu, D. Yang “ <i>Synthesis of ultrafine lanthanumhydroxide nanorods by a simple hydrothermal process</i> ” Materials Letters, 58, 1180–1182 (2004)
[99]	A. Neumann, D. Walter, “ <i>The thermaltransformation from lanthanum hydroxide to lanthanumhydroxide oxide</i> ” Thermochim Acta 445, 200 (2006)
[100]	A. V. Murugan, S.C. Navaleand, V. Ravi “ <i>Synthesis of nanocrystalline La₂O₃ powder at 100°C</i> ”, Materials Letters, 60, 848-849, (2006)
[101]	N.Imanaka, T. Masui, Y.Kato, “ <i>Preparation of the cubic-type La₂O₃ phase by thermal decomposition of LaI₃</i> ,” J. Solid State Chemistry,178,395-398, (2005).
[102]	X.Wang, Y.Li, “ <i>Synthesis and Characterisation of Lanthanide Hydroxide Single-Crystal Nanowires</i> ” Angew. Chem. Int. Edition. 41, 4790,(2002)
[103]	D. V. Pawar,T. S. Magdum,S. H. Chavan ,“ <i>Lanthanum oxide doping effect on dc electrical conductivity of ferroelectrics sodium vanadate and rubidium vanadate</i> ” Bulletin of Materials Science,18,141-146 (1995)

[104]	D. Berger, C. Matei, F. Papa, D. Macove; V. Fruth and J.P. Deloume, “ <i>Pure and doped lanthanum manganites obtained by combustion method</i> ” J. European Ceramic Society, 7, 4395-4398 (2007)
[105]	I.Djerdj, G. Garnweitner, D.S.Su, M. Niederberger, “ <i>Morphology-Controlled Nonaqueous Synthesis of Anisotropic Lanthanum Hydroxide Nanoparticles</i> ”. J. Solid State Chem.180, 2145 (2007)
[106]	C. A. C.Escobedo, F. S.Jesús, A. M. Bolarínmiró, J.M.Saldaña1 “ <i>Mechanosynthesis of LaMnO₃ from different manganese oxides</i> ” phys. Stat. sol. 4, 4054–4063 (2007)
[107]	S. B. Majumder, M. Jain , and R. S. Katiyar “ <i>Investigations on the optical properties of sol-gel derived lanthanum doped lead titanate thin Films</i> ”, Thin Solid Films, 402, 90 (2002)
[108]	A. Arulraj, R. Mahesh, G.N. Subbanna, R. Mahendiran, A.K. Ray-chaudhuri, C.N.R. Rao, “ <i>Insulator-metal transitions, giant magneto resistance & related aspects of the cation-deficient</i> ” J. Solid State Chem. 127, 87-91, (1996)
[109]	I.K. Gopalakrishnan, O.D. Jayakumar, C. Sudakar, R.M. Kadam, S.K. Kulshreshtha, “ <i>Significant Enhancement of Room Temperature Ferromagnetism in surfactant coated polycrystalline Mn doped ZnO particles</i> ” J. Alloys and Compounds, 438, 258-262 (2007)
[110]	A.A.Dakhel, “ <i>Growth and ac-Properties of Lanthanum-Manganese Oxide Films on Si Substrates</i> ” Microelectronic, 25 th International Conference publications, 109-112 (2006)
[111]	P. K. Datta, Z. Klusek, A. Basu, A. W. Brinkman “ <i>Nanoscale studies of morphological and electrical properties of NixMn3_xO3_d (0.4VxV1) thin films by in-situ high temperature scanning tunneling microscopy and spectroscopy</i> ” Surf. Coat. Technol., 187, 161-166 (2004)
[112]	S.M.Savic, M.V.Nikolic, O.S.Aleksic, M. Slankamenac, M. Zivanov, P. M. Nikolic “ <i>Intrinsic Resistivity of Sintered Nickel Manganite vs. Powder Activation Time and Density</i> ” Science of Sintering, 40, 27-32 (2008)
[113]	Q. Zhang and F. Saito “ <i>Mechanical synthesis of LaMnO₃ from La₂O₃ and Mn₂O₃ powder</i> ” J. Alloys Compd. 297, 99 (2000)

[114]	R.W.A. Scarr, R.A. Settrington, “ <i>Thermister, their theory, manufacture and application</i> ”, Proceedings of the IEE-part B: Electronic and communication engineering, 107, 395-405 (1960)
[115]	P. Umadevi, C.L. Nagendra, G.K.M. Thutupalli “ <i>Structural, electrical and infrared optical properties of vanadium pentoxide (V_2O_5) thick-film thermisters</i> ” Science journal, 39, 59–69 (1993)
[116]	P. Murugaraj, D. Mainwaring, N. M.Huertas “ <i>Thermister behaviour in a semiconducting polymer–nanoparticle composite film</i> ” J. Physics D: Applied Physics, 39, 2072 (2006)
[117]	D. A. Kukuruzyak, J.G.Moyer, F.S. Ohuchi “ <i>Improved Aging Characteristics of NTC Thermister Thin Films Fabricated by a Hybrid Sol–Gel–MOD Process</i> ” J. American Ceramic Society, 89, 189–192, (2006)
[118]	R. Schmidt, A.W. Brinkman “ <i>Studies of the Temperature and Frequency Dependent Impedance of an Electroceramic Functional Oxide NTC Thermister</i> ” Advanced Functional Materials, 17, 3170–317 (2007)
[119]	M. Leea, M. Yoo “ <i>Detectivity of thin-film NTC thermal sensors</i> ” Sensors and Actuators, 96, 97–104 (2002)
[120]	S.M. Hosseini, B.Ghanbari Shahany, N.Azad, A.Kompany “ <i>Low temperature synthesis and electronic properties of ntc temperature sensor spinel-type oxides nanopowders</i> ” Int. J. Nanosci. 10, 479 (2011)
[121]	Y.Sun, B.Mayers, Y.Xia, “ <i>Transformation of Silver Nanospheres into Nanobelts and Triangular Nanoplates through a Thermal Process</i> ” Nano Lett. 3, 675-679 (2003)
[122]	F.Kim, K.Sohn, W.Huang, “ <i>Chemical synthesis of gold nanowires in acidic solutions</i> ” J.Am.Chem.Soc.130,14442-14443 (2008)
[123]	X.M.Sun, X.Chen, Z.X.Deng, Y.D.Li, “ <i>A CTAB-Assisted Hydrothermal Orientation Growth of ZnO Nanorods</i> ”Mater, Chem.Phys. 78, 99-104 (2003)
[124]	W.J.Li, E.W.Shi, W.Z.Zhong, Z.W. Yin, “ <i>Growth mechanism and growth habits of oxide crystal</i> ”J. Crys, Growth 203,186-196 (1999)
[125]	L.Yan, Y.D.Li, Z.X.Deng, J.Zhuang, X.Sun, “ <i>Surfactant assisted hydrothermal synthesis of hydroxyapatite nanorods</i> ” Int. J. Inorg. Mater. 3, 633-637 (2001)

[126]	O. Bricker, “ <i>Some stability relations in the system MnO_2-H_2O at 25°C and one atmosphere total pressure</i> ” Am.Mineral. 50,1296-1354 (1965)
[127]	BL Cushing, VL Kolienichenko, CJO’Connor “ <i>Recent advances in the liquid-phase syntheses of inorganic nanoparticles</i> ” J.Chem.Rev.104,3893 (2004)
[128]	S.Ashoka, G.Nagaraju, G.T.Chandrappa “ <i>Reduction of $KMnO_4$ to Mn_3O_4 via hydrothermal process</i> ” Mater. Lett.64,2538-2540 (2010)
[129]	M. Mazloumi, S. Zanganeh, A Kajbafvala, M.R. Shayegh, S.K. Sadrnezhad, “ <i>Formation of Lanthanum Hydroxide Nanostructures: Effect of NaOH and KOH Solvents</i> ”, IJE Transactions A: Basics, 21, 169-176 (2008)
[130]	X.Ma, H.Zhang, Y.Ji, J.Xu, D.Yang, “ <i>Synthesis of Ultrafine Lanthanum Hydroxide Nanorods by a Simple Hydrothermal Process</i> ”, Mater. Lett. 58,1180-1182 (2004).
[131]	M. Ishii, M. Nakahira, T. Yamanaka, “ <i>Infrared absorption spectra and cation distributions in $(Mn, Fe)_3O_4$</i> ”. Solid State Commun. 11, 209 (1972)
[132]	Y.Borodko, L.Jones, H.Lee, H.Frei, G.Somorjai “ <i>Spectroscopic study of tetradecyltrimethylammonium bromide Pt-C14TAB nanoparticles: structure and stability</i> ” Langmuir 25,6665-71 (2009)
[133]	M.L. Singla, A. Negi, V. Mahajan, K.C. Singh, D.V.S. Jain, “ <i>Catalytic behaviour of nickel nanoparticles stabilized by lower alkylammonium bromide in aqueous medium</i> ”. Appl. Catal. A-Gen. 323, 51–57 (2007)
[134]	L. Wang, X. Wu, M. Pei, Z. Wu, X. Li, X. Tao, “ <i>Facile synthesis of multi-branched gold nanostructures through a TBAB-assisted route in aqueous solution and their SERS property</i> ” Chinese J. Chem. 29, 185–190 (2011)
[135]	J.C.Southard, G.E.Moore “ <i>High temperature heat content of Mn_3O_4, $MnSiO_3$ and Mn_3C</i> ” J.Am.Chem. Soc.64,1769(1942)
[136]	A. Neumann, D.Walter “ <i>The thermal transformation from lanthanum hydroxide to lanthanum hydroxide oxide</i> ” Thermochim Acta 445,200 (2006)
[137]	E.Fuglein, D.Walter, Z.Anorg, “ <i>Thermal Behaviour of Lanthanum Hydroxide in Dependency of Pressure</i> ” Allg. Chem. 632,2154(2006)
[138]	A. Azam, A.S. Ahmed, M. Chaman, A.H. Naqui “ <i>Investigation of electrical properties of Mn doped tin oxide nanoparticles using impedance spectroscopy</i> ” J. Appl. Phys. 108, 094329 (2010)

[139]	A.M.M. Farea, S. Kumar, K.M. Batoo, “ <i>Influence of the doping of Ti_4 ions on electrical and magnetic properties of $Mn_{1-x}Fe_{2-x}Ti_xO_4$ ferrite</i> ” J. Alloys Compd. 464, 361 (2008)
[140]	A. Baykal, N. Bitrak, B. Unal, H. Kavas, Z. Durmus, S. o’Zden, M.S. Toprak, “ <i>Polyol synthesis of (polyvinylpyrrolidone) $PVPMn_3O_4$ nanocomposite</i> ” J. Alloys Compd. 502, 199 (2010)
[141]	M.G. Bellino, D.G. Lammas, N.E.W. De Reza, “ <i>A mechanism for the fast ionic transport in nanostructured oxide-ion solid electrolytes</i> ” Adv. Mater. 18, 3005–3009 (2006)
[142]	S.S. Umare, B.H. Shambharkar, R.S. Ningthoujam “ <i>Synthesis and characterisation of polyaniline-Fe_3O_4 nanocomposite: Electrical conductivity, magnetic, electrochemical studies</i> ” Synth. Met. 160, 1815–1821 (2010)
[143]	R. Regmi, R. Tackett, G. Lawes “ <i>Suppression of low-temperature magnetic states in Mn_3O_4 nanoparticles</i> ” J. Mater Sci: Mater Electron 321, 2296 (2009)
[144]	R.Shmidt, A.W. Brinkman “ <i>Preparation and characterisation of $NiMn_2O_4$ films</i> ” J. Inorg. Mater. 3,1215-1217 (2001)

Synthesis and electrical behavior study of Mn_3O_4 nanoceramic powder for low temperature NTC thermistor

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Abstract Monodispersed Mn_3O_4 nanoparticles (NPs) were synthesized by reducing KMnO_4 at room temperature in the presence of cetyltributylammonium bromide surfactant and short chain tetra-n-butylammonium bromide co-surfactant. Structural characterization done through XRD, TEM and FT-IR analysis techniques showed mono dispersity (5–8 nm) and capping of the NPs with surfactants. The temperature dependent behavior of dc resistivity of the nanopowder pellets showed reproducible NTC characteristics over a range of 40–200 °C with two thermistor constants ($\beta_1 = 10,897$ K for 40 °C < T < 107 °C and $\beta_2 = 1,529$ K for 107 °C < T < 190 °C) and a negative temperature coefficient of resistance ($\alpha = -0.111$ K⁻¹ at 40 °C). The thermistor constant (β_1) and NTC values are found to be higher than that of bulk Mn_3O_4 in range of 40 °C < T < 107 °C. This observed behavior implies an enhanced sensitivity in nano-powder based thermistors. Temperature and frequency dependent impedance behavior of the as-synthesized samples evaluated over a temperature range of 40–140 °C and a frequency range of 1 kHz to 1 MHz delineates the role of electron hopping between Mn^{2+} and Mn^{3+} in the conduction process. These studies present monodispersed Mn_3O_4 NPs as promising material for NTC thermistor in the low temperature range 40 °C < T < 107 °C.

1 Introduction

Temperature sensors used for measurement and control include thermo-couples, thermistors, and semiconductor band gap sensors. Among these, thermistor is widely used due to high sensitivity, accuracy, low cost and unique thermo electric properties [1, 2]. Thermistors have a wide array of applications in air-conditioners, refrigerators, freezers, water heaters, washing machines, computers, power supply facilities and communication equipment [3–6]. Negative temperature coefficient (NTC) thermistors are capable of measuring temperatures within a specific range with high accuracy and sensitivity thereby making them good candidates for applications in a number of electrical and electronic devices [7, 8]. Thermistor materials typically exhibit Arrhenius behavior over a wide temperature range and are characterized by a thermistor constant $\beta = \Delta E/K$, where ΔE is the activation energy and K is the Boltzmann constant.

Typically, materials with $\beta > 3,000$ K find applications in temperature sensors [9]. Oxides of Manganese, Cobalt and Nickel which typically exist as spinel crystal structures have been studied for applications in NTC thermistors due to their interesting electrical properties [10]. Various new materials and modifications of existing materials have been proposed to achieve better sensing devices [1, 11, 12]. Oxides of manganese have attracted much interest during the last decade for many industrial applications involving catalysis [13–15], magnetism [16], electrochemistry [17, 18], air decontamination and temperature sensing [19, 20]. Specifically, Mn_3O_4 is an important transition-metal oxide and is well known as a promising technological material for usage in NTC thermistors [20, 21]. It is a black mineral that forms a spinel structure with tetragonal distortion due to Jahn–Teller effect on Mn^{+2} . The oxide exists as

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$\text{Mn}^{+2}(\text{Mn}^{+3})_2\text{O}_4$ with Mn^{+2} and Mn^{+3} ions occupying the tetrahedral and octahedral sites respectively [22]. We have previously reported the NTC behavior of bulk Mn_3O_4 and its composite with La_2O_3 [18, 23]. However, it has been reported that nanopowders show a totally different behavior from their bulk counterparts and hence significantly change the performance of many functional materials [24]. Komoba et al. [25] have investigated the use of Mn_3O_4 as a precursor in the synthesis of Li–Mn–O electrode material for rechargeable Lithium batteries. Studies have been reported by several groups describing the synthesis of Mn_3O_4 nanoparticles with varying properties through various techniques [25–28].

In the present study, we have synthesized nanoceramic Mn_3O_4 by reducing KMnO_4 at room temperature in the presence of long chain CTAB surfactant and short chain TBAB co-surfactant. The synthesized material was then used to fabricate micron sized thermistors by pressed die chip technique, and continuous thermistors by cold drawn technique [29]. The fabricated thermistors were studied for their NTC behavior. The conductivity and impedance studies were performed as a function of temperature and frequency in order to understand the underlying conduction mechanism responsible for the material's observed electrical behavior.

2 Experimental

2.1 Synthesis and characterization

Analytical grade reagents: Potassium permanganate (Qualigens), Monohydrate hydrazine (Qualigens), N-cetyl-N,N,N-trimethylammoniumbromide (Loba chemie), Tetraethylammonium bromide (Loba chemie), and ethanol (99.9 %) were used for synthesis.

Synthesis of monodispersed Mn_3O_4 NPs was carried out by a procedure involving reduction of KMnO_4 by hydrazine monohydrate in the presence of a surfactant (CTAB) and an additional co-surfactant (TBAB). In a typical procedure, 0.5 mmol of CTAB, 0.1 mmol TBAB and 0.5 mmol of KMnO_4 were mixed together with 100 ml of distilled water in a round bottom flask. The reaction mixture was allowed to get homogenized for 10 min under slow stirring in order to avoid froth formation. Further, 0.5 mmol of monohydrated hydrazine was added rapidly to this solution under vigorous magnetic stirring. The color of the reaction mixture changed from dark purple to dark brown and finally to brown with a tinge of orange. It was further heated to 70 °C for 1 h and then cooled to room temperature resulting in complete precipitation. The precipitate was separated by centrifugation followed by several washing cycles with ethanol and then dried in vacuum for 3 h at 40 °C.

Powder XRD patterns of the samples were recorded at room temperature using Bruker powder X-ray diffractometer operated at 30 kV (Cu-K_α radiation, 40 mA, $\lambda = 1.5406 \text{ \AA}$) with a scan speed of 2° min^{-1} .

FT-IR spectra of the samples grounded with KBr and compressed into pellets were collected using a Perkin Elmer FT-IR spectrometer ($400\text{--}4,000 \text{ cm}^{-1}$). The microstructural analysis of NPs was done using TEM (JEOL; model JEM-2000CX) operated at 200 kV.

A thermo gravimetric analyzer (TGA; universal V4.1D TA instruments) was used to measure weight loss of the powder samples under nitrogen stream in the temperature range of 30–1,000 °C while keeping the temperature ramp at $5^\circ \text{ C min}^{-1}$.

To investigate the NTC behavior, dc conductivity studies of this material was done by in-house setups. NP powder was ramified in a glass capillary tube of length 2 mm with openings (0.5 mm diameter) at both ends. Metal contacts were provided through Chromel and alumel wires (0.1 mm diameter) inserted at opposite ends [ESI]. Resistivity measurement was performed with Fluke 177 digital multimeter. The temperature was controlled through a muffle furnace with digital temperature controller ($\pm 1.0^\circ \text{ C}$ accuracy). The temperature ramp was kept at $2^\circ \text{ C min}^{-1}$. Similarly, for ac conductivity measurements, the powder sample was compressed into a pellet (diameter $\sim 10 \text{ mm}$) and coated with silver paste on both sides to provide the metallic contacts. Impedance measurements were done using HIOKI 3532-50 LCR Hitester LCR in a frequency range of 1 kHz–1 MHz inside an in-house designed digitally controlled temperature assembly over a range of 40–200 °C.

3 Results and discussion

3.1 TEM analysis

The TEM images (Fig. 1) clearly show the monodispersed nature of nearly spherical as-synthesized nano-particles with a diameter range of 5–8 nm. The small size and monodispersity could be attributed to the presence of CTAB-TBAB system in the reaction mixture. Short chain TBA^+ ions function as filler molecules (through hydrophobic interactions between alkyl chains of CTAB and butyl chains of TBAB) in gaps of adsorbed long chain CTAB micelles and hence further stabilize the nanoparticles by preventing irregular growth into such gaps [30, 31].

3.2 FT-IR analysis

The FTIR spectrum of Mn_3O_4 NPs is depicted in Fig. 2 and the observed bands are described in Table 1. The presence

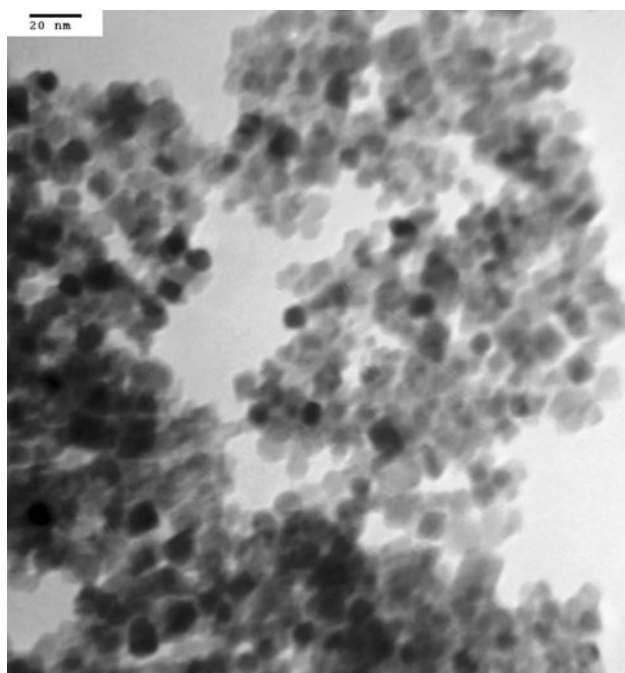


Fig. 1 TEM image of as-synthesized Mn_3O_4 NPs at higher resolution (794,000 $\times$)

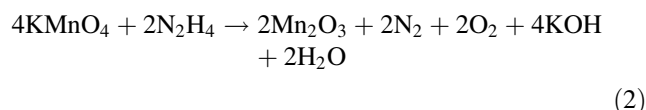
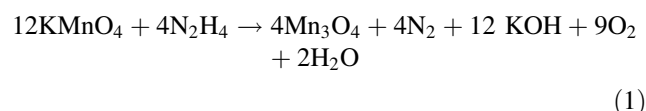
of C–H, N–H and C–N stretching vibration bands confirm the surfactant capping of Mn_3O_4 NPs.

3.3 XRD analysis

The XRD pattern of as synthesized Mn_3O_4 NPs (Fig. 3a) shows the tetragonal hausmannite nano-crystalline nature of the synthesized nanopowder. The crystalline phase of the synthesized particles seems to be better indexed as a

tetragonal structure [JCPDS-sample code 24-0734–Hausmannite], albeit some peaks corresponding to $\gamma\text{-Mn}_2\text{O}_3$ [JCPDS card no. 06-0540] were also observed. However, it is difficult to distinguish Mn_3O_4 Hausmannite [JCPDS card no. 24-0734] from $\gamma\text{-Mn}_2\text{O}_3$ [JCPDS card no. 06-0540] as a consequence of their highly similar XRD patterns [34]. The average crystallite size of the NPs in as synthesized samples was calculated using the Debye–Scherrer formula [35] for the most intense peak ($\theta = 36^\circ$) corresponding to the (211) plane and is found to be ~ 7.8 nm.

The presence of both Mn_3O_4 and Mn_2O_3 in as-synthesized material may be attributed to the reduction of KMnO_4 by hydrazine monohydrate through two competing mechanisms:



Formation of Mn_3O_4 and Mn_2O_3 was confirmed by the presence of their signatures in XRD as well as in TGA results (Sect. 3.4). Hydrazine being a powerful reducing agent releases nitrogen gas and hydrogen ions during its oxidation [36] while reducing KMnO_4 . Oxygen is one of the byproducts in potassium permanganate hydrolysis reaction [37].

The XRD pattern of thermally treated Mn_3O_4 NPs (at 1,000 $^\circ\text{C}$ in N_2 atmosphere) showed peaks corresponding to pure single phase Mn_3O_4 [JCPDS card no. 24-0734]

Fig. 2 FT-IR spectrum of as-synthesized Mn_3O_4 NPs

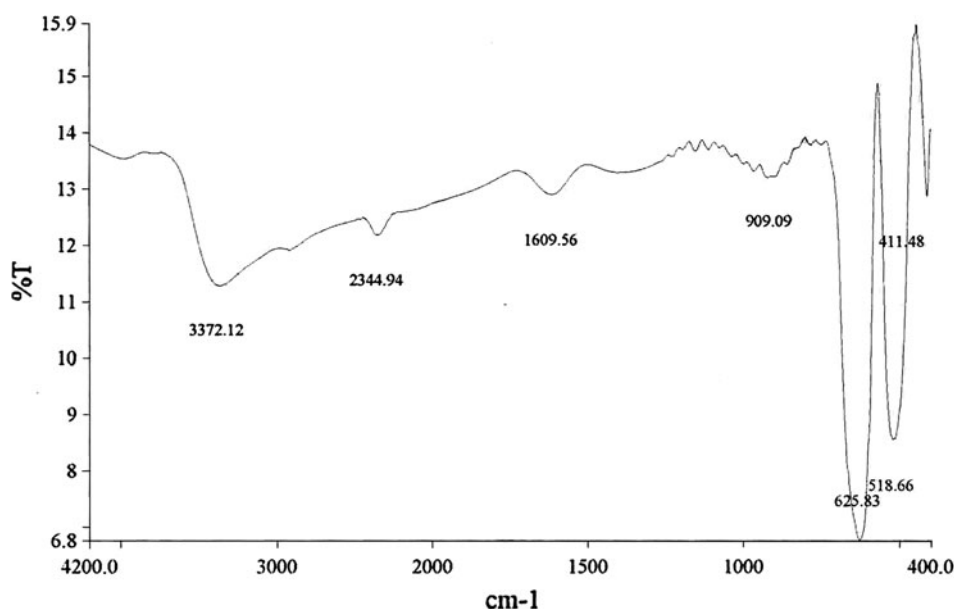
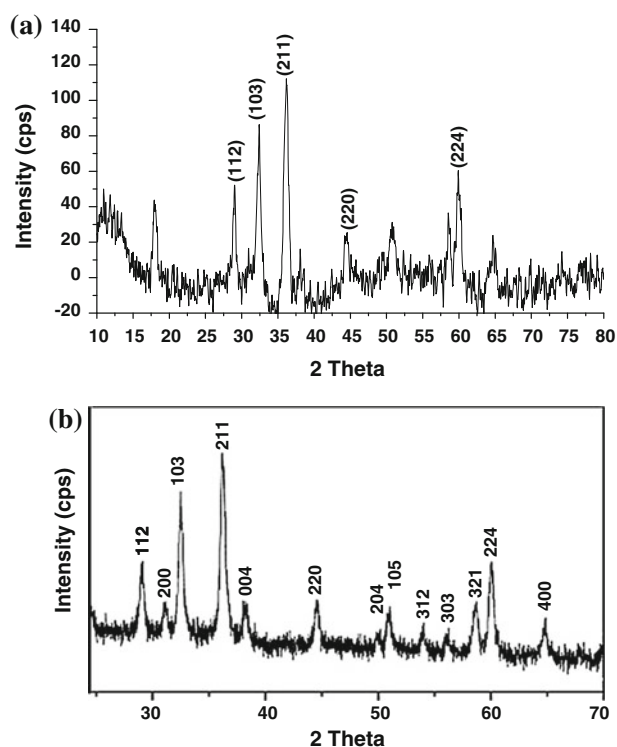


Table 1 FT-IR spectrum of as-synthesized Mn₃O₄ NPs

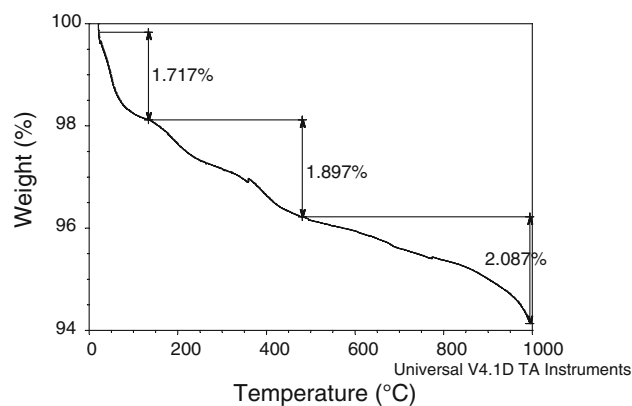
Band position (cm ⁻¹)	Description of vibration modes
411	Mn _{octahedral} ↔ O stretching [32, 33]
511 and 626	Due to coupling modes between Mn _{octahedral} ↔ O and Mn _{tetra} ↔ O [32]
1,000–1,250	Weak bands due to C–N stretching modes
1,609	O–H stretching in adsorbed water molecules on the surface of Mn ₃ O ₄ NPs [32(b)]
2,980–2,850	C–H stretching vibration
3,372	(a) N–H stretching vibration (b) O–H stretching of adsorbed water molecules

**Fig. 3** XRD spectrum of **a** as-synthesized Mn₃O₄ NPs and **b** thermally treated Mn₃O₄ NPs (at 1,000 °C in N₂ atmosphere)

(Fig. 3b) with larger grains. The increase in grain size (~33.50 nm) after thermal treatment is attributed to the agglomeration of NPs due to expulsion of the surfactant molecules from their surface.

3.4 TGA analysis

Thermal analysis of NPs in the temperature range of 30–1,000 °C in N₂ atmosphere reveals a typical graph with three gradual weight loss transition phases depicted in Fig. 4. The first transition with a 1.717 % weight loss in the temperature range 30–130 °C is ascribed to the expulsion of adsorbed water molecules. The second transition with a weight loss of 1.897 % in the temperature range 120–480 °C

**Fig. 4** TGA profile of as-synthesized Mn₃O₄ NPs in the temperature range of 30–1,000 °C in N₂ atmosphere

may be due to the loss of surfactant molecules capping the NPs. The final transition with 2.087 % weight loss is attributed to the release of O₂ due to conversion of higher oxides into lower oxides (E iii) at higher temperatures [38].



It can be concluded that the as-synthesized oxide mixture contained ~30 % Mn₂O₃ that completely transformed into Mn₃O₄ at higher temperatures in agreement with XRD results. On further heating beyond 1,000 °C, no further mass loss was observed.

3.5 Electrical characterization

3.5.1 Impedance studies

In order to determine the conduction mechanism, ac impedance of the as-synthesized nanopowder was measured over a wide range of frequencies at different temperatures. The plots of real (*Z'*) and imaginary (*Z''*) parts of the impedance are shown in Fig. 5a, b. The impedance is found to decrease with increase in temperature as expected in a thermally activated process. Additionally, from the impedance plots at lower temperatures, a decrease in both resistance and reactance with increase in frequency is observed. Such a behavior can be explained using the phenomenon of electron hopping between manganese cations (Mn²⁺ and Mn³⁺) of differing valencies. The increase in frequency of the applied voltage increases the probability of electron hopping [39–41]. However, at higher temperatures beyond 140 °C, a deviation from this behavior was observed in the reactance plot indicating additional contributions from other mechanisms.

3.5.2 DC conductivity analysis

The Arrhenius behavior is described by $\rho = \rho_0 \exp(\beta/T)$, where ρ is the resistivity, β is the thermistor constant and T

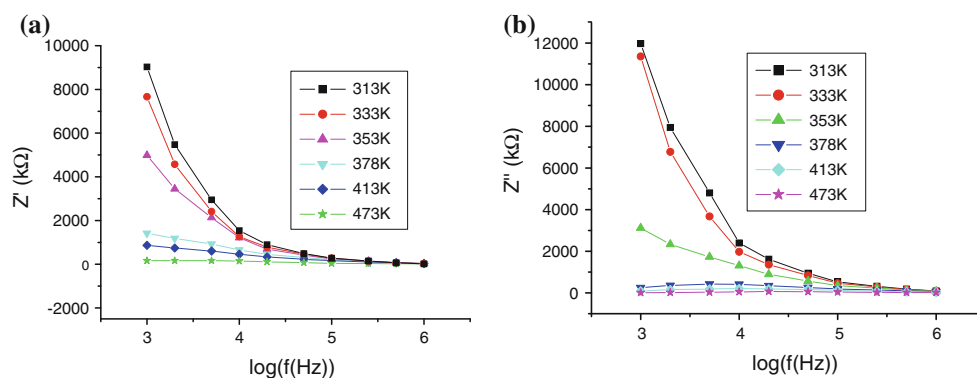
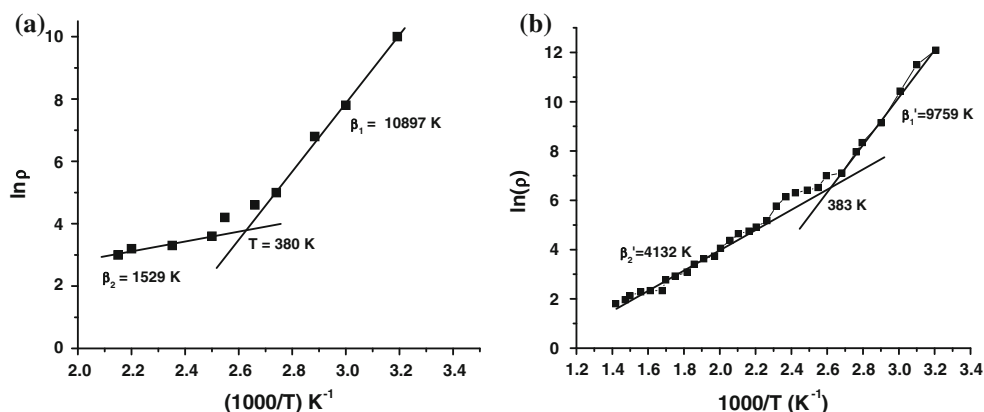


Fig. 5 Impedance spectra **a** real part (Z' (resistance)) versus frequency (logarithmic) **b** Imaginary part (Z'' (reactance)) versus frequency (logarithmic) of as-synthesized Mn_3O_4 NPs in the frequency range of 1 kHz to 1 MHz at a temperature range of 40–200 °C

Fig. 6 DC behavior ($\ln \rho$ vs. $1/T$ plot) for **a** as-synthesized Mn_3O_4 NPs and **b** thermally treated Mn_3O_4 NPs in the temperature range of 40–200 °C



is the temperature. The dc resistivity studies of the as-synthesized nanoparticles indicate thermally activated multiple conduction mechanisms that show Arrhenius behavior with two different activation energies. The values of the corresponding thermistor constants β_1 ($25\text{ }^\circ\text{C} < T < 107\text{ }^\circ\text{C}$) & β_2 ($107\text{ }^\circ\text{C} < T < 190\text{ }^\circ\text{C}$) were calculated from the plot of $\ln \rho$ versus $1/T$ (Fig. 6a) and are found to be 10,897 K ($\Delta E_1 = 939.02\text{ meV}$) and 1,529 K ($\Delta E_2 = 131.75\text{ meV}$) respectively. The temperature coefficient of resistance ($\alpha = -\beta/T^2$) is found to be -0.111 K^{-1} at 313 K. A similar study with the thermally treated NPs also showed two slopes with activation energies ($\beta'_1 = 9,759\text{ K}$ ($\Delta E'_1 = 813\text{ meV}$) and $\beta'_2 = 4,132\text{ K}$ ($\Delta E'_2 = 344\text{ meV}$) but with significantly larger resistivity (Fig. 6b). The temperature coefficient of resistance (α) at 313 K was found to be -0.0996 K^{-1} . This difference in behavior can be attributed to larger grain sizes in thermally treated NPs due to the removal of surfactant and co-surfactant that were stabilizing the NPs, leading to aggregation.

The DC conductivity studies corroborates with the previous impedance analysis in revealing the contribution of additional conduction mechanisms at higher temperatures.

It can also be concluded that these mechanisms are in series configuration as the mechanism with larger resistivity dominates. Hence, one may conclude that the additional resistivity is due to the grain boundaries. It is observed that this mechanism limits the conductivity at higher temperatures. The low limiting resistance observed in as-synthesized nanopowder can be attributed to higher grain boundary conductivity due to larger volume fraction of grain boundaries [42]. The apparent difference in the y-intercepts of the two slopes indicates different carrier densities. The larger carrier density for grain boundary conduction may be attributed to additional charge carriers or ions present in the grain boundaries in addition to those supplied by the grain. In addition, various other parameters like porosity, chemical composition, particle size and cation distribution have been reported to have significant effect on the conductivity and activation energies in spinel structures [43–45]. In order to study the reproducibility, the thermal behavior of the samples was studied by subjecting them to heating cycles and the behavior was found not to vary significantly hence implying applications in stable NTC thermistors.

4 Conclusion

Monodispersed Mn_3O_4 nanoparticles (NPs) were synthesized by reducing KMnO_4 at room temperature in the presence of long chain cetyltrimethylammonium bromide (CTAB) surfactant and short chain tetra-n-butylammonium bromide (TBAB) co-surfactant. Structural characterization showed mono dispersity (5–8 nm) and surfactant capping. The temperature dependent behavior of dc resistivity showed reproducible NTC characteristics over a range of 40–200 °C with two thermistor constants ($\beta_1 = 10,897$ K for 40 °C < T < 107 °C and $\beta_2 = 1,529$ K for 107 °C < T < 200 °C) and a negative temperature co-efficient of resistance ($\alpha = -0.111$ K⁻¹ at 40 °C). Temperature and frequency dependent impedance behavior of the as-synthesized samples indicates the role of electron hopping between Mn^{2+} and Mn^{3+} as the conduction mechanism at lower temperatures. Grain boundary conduction is proposed as the limiting mechanism at higher temperatures. The significantly high thermistor constant and reproducible properties imply an enhanced sensitivity and stable nanopowder based NTC thermistors.

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References

1. J. Fraden, *Handbook of modern sensors: physics, designs, and applications*, 3rd edn. (Springer Science, New York, 2003)
2. <http://www.sequoia.co.uk/White%20papers/Advantages%20of%20NTC%20Thermistors%20-%20Dec%202003.pdf>. 13 Oct 2011
3. http://www.wuntronix.de/sensors/therm_appl.htm. 13 Oct 2010
4. <http://en.wikipedia.org/wiki/Thermistor>. 13 Oct 2010
5. B.M. Zeffert, S. Hormats, Application of thermistors to cryoscopy. *Anal. Chem.* **21**, 1420–1422 (1949)
6. E.A. Boucher, *J. Chem. Educ.* **44**, A935 (1967)
7. A.J. Moulson, J.M. Herbert, *Electroceramics: Materials, Properties and Applications* (Chapman & Hall, London, 1990), p. p141
8. D.C. Hill, H.L. Tuller, in *Ceramic Sensors: Theory and Practice*, ed. by R. Buchanan (Marcel Dekker, New York, 1986), p. 323
9. D. Saha, A.D. Sharma, A. Sen, H.S. Maiti, Preparation of bixbyite phase ($\text{Mn}_x\text{Fe}_{1-x}\text{O}_3$) for NTC thermistor applications. *Mat. Lett.* **55**, 403 (2002)
10. M. Hosseini, The effect of cation composition on the electrical properties and aging of Mn-Co-Ni thermistors. *Ceram. Int.* **26**, 245–249 (2000)
11. K. Majid, S. Awasthi, M.L. Singla, Low temperature sensing capability of polyaniline and Mn_3O_4 composite as NTC material. *Sens. Actuators A Phys.* **135**, 113–118 (2007)
12. K. Park, D.Y. Bang, Electrical properties of Ni–Mn–Co–(Fe) oxide thick-film NTC thermistors prepared by screen printing. *J. Mater. Sci. Mater. Electron.* **14**, 81–87 (2003)
13. H. Einaga, A. Ogata, Benzene oxidation with ozone over supported manganese oxide catalysts: effect of catalyst support and reaction conditions. *J. Hazard. Mater.* **164**, 1236 (2009)
14. L.C. Wang, X.S. Huang, Q. Liu, Y.M. Liu, Y. Cao, H.Y. He, K.N. Fan, J.H. Zhuang, Gold nanoparticles deposited on manganese(III) oxide as novel efficient catalyst for low temperature CO oxidation. *J. Catal.* **259**, 66 (2008)
15. M. Kang, E.D. Park, J.M. Kim, J.E. Yie, Manganese oxide catalysts for NOx reduction with NH_3 at low temperatures. *Appl. Catal. A* **327**, 261 (2007)
16. N. Imamura, T. Mizoguchi, H. Yamauchi, M. Karppinen, Multivariate data analysis approach to understand magnetic properties of perovskite manganese oxides. *J. Solid State Chem.* **181**, 1195 (2008)
17. S.B. Ma, K.W. Nam, W.S. Yoon, S.M. Bak, X.Q. Yang, B.W. Cho, K.B. Kim, Nano-sized lithium manganese oxide dispersed on carbon nanotubes for energy storage applications. *Electrochem. Commun.* **11**, 1575 (2009)
18. K.W. Nam, C.W. Lee, X.Q. Yang, B.W. Cho, W.S. Yoon, K.B. Kim, Electrodeposited manganese oxides on three-dimensional carbon nanotube substrate: Supercapacitive behaviour in aqueous and organic electrolytes. *J. Power Sources* **188**, 323 (2009)
19. M.L. Singla, S. Sharma, B. Raj, V.R. Harchekar, Characterization of transition metal oxide ceramic material for continuous thermocouple and its use as NTC fire wire sensor. *Sens. Actuators A Phys.* **120**, 337 (2005)
20. M. Lee, M. Yoo, Detectivity of thin-film NTC thermal sensors. *Sens. Actuators A Phys.* **96**, 97–104 (2002)
21. J. Ryu, K.Y. Kim, J.J. Choi, B.D. Hahn, W.H. Yoon, B.K. Lee, D.S. Park, C. Park, Highly dense and nanograined NiMn_2O_4 negative temperature coefficient thermistor thick films fabricated by aerosol-deposition. *J. Am. Ceram. Soc.* **92**, 3084–3087 (2009)
22. N.N. Greenwood, A. Earnshaw, *Chemistry of the Elements* (Pergamon, New York, 1984)
23. M.L. Singla, R. Baldev, H.V. Rajaram, R.P. Bajpai, Ceramic mixture having negative temperature coefficient, a thermistor containing the ceramic mixture and the process for preparing same, US Patent No 6878311 dated 12 Apr 2005
24. J.L. Dormann, D. Fiorani, Magnetic properties of fine particles: proceedings of the International Workshop on Studies of Magnetic Properties of Fine Particles and their Relevance to Materials Science, Rome, Italy, November 4–8, 1991, North-Holland, 1992
25. S. Komaba, S.T. Myung, N. Kumagai, T. Kanouchi, K. Oikawa, T. Kamiyama, Hydrothermal synthesis of high crystalline orthorhombic LiMnO_2 as a cathode material for Li-ion batteries. *Solid State Ionics* **152**, 311 (2002)
26. P. Gibot, L. Laffont, Hydrophilic and hydrophobic nano-sized Mn_3O_4 particles. *J. Solid State Chem.* **180**, 695 (2007)
27. B.L. Cushing, V.L. Kolesnichenko, C. O'Connor, Recent advances in the liquid-phase syntheses of inorganic nanoparticles. *J. Chem. Rev.* **104**, 3893 (2004)
28. L. Tao, C.-G. Sun, M.-L. Fan, C.-J. Huang, H.-L. Wu, Z.-S. Chao, H.-S. Zhai, A redox-assisted supramolecular assembly of manganese oxide nanotube. *Mater. Res. Bull.* **41**, 2035 (2006)
29. P. Umadevi, C.L. Nagendra, Preparation and characterisation of transition metal oxide micro-thermistors and their application to immersed thermistor bolometer infrared detectors. *Sens. Actuators A Phys.* **96**, 114–124 (2002)
30. M.L. Singla, A. Negi, V. Mahajan, K.C. Singh, D.V.S. Jain, Catalytic behavior of nickel nanoparticles stabilized by lower alkylammonium bromide in aqueous medium. *Appl. Catal. A-Gen.* **323**, 51–57 (2007)
31. L. Wang, X. Wu, M. Pei, Z. Wu, X. Li, X. Tao, Facile synthesis of multi-branched gold nanostructures through a TBAB-assisted route in aqueous solution and their SERS property. *Chinese J. Chem.* **29**, 185–190 (2011)

32. M. Ishii, M. Nakahira, T. Yamanaka, Infrared absorption spectra and cation distributions in $(\text{Mn}, \text{Fe})_3\text{O}_4$. *Solid State Commun.* **11**, 209 (1972)
33. W.Z. Wang, C.K. Xu, G.H. Wang, Y.K. Liu, C.L. Zheng, Preparation of smooth single-crystal Mn_3O_4 Nanowires. *Adv. Mat.* **14**, 837 (2002)
34. O. Bricker, Some stability relations in the system $\text{MnO}_2\text{-H}_2\text{O}$ at 25 °C and one atmosphere total pressure. *Am. Mineral.* **50**, 1296 (1965)
35. B.D. Cullity, S.R. Stock, *Elements of X-ray Diffraction*, 3rd edn. (Prentice Hall, New Jersey, 2001), p. p170
36. B.L. Cushing, V.L. Kolenichenko, C.J. O'Connor, *Chem. Rev.* **104**, 3893 (2004)
37. S. Ashoka, G. Nagaraju, G.T. Chandrappa, *Mater. Lett.* **64**, 2538–2540 (2010)
38. J.C. Southard, G.E. Moore, High-temperature heat content of Mn_3O_4 , MnSiO_3 and Mn_3C . *J. Am. Chem. Soc.* **64**, 1769 (1942)
39. A. Azam, A.S. Ahmed, M. Chaman, A.H. Naqui, Investigation of electrical properties of Mn doped tin oxide nanoparticles using impedance spectroscopy. *J. Appl. Phys.* **108**, 094329 (2010)
40. A.M.M. Farea, S. Kumar, K.M. Batoo, Influence of the doping of Ti⁴⁺ ions on electrical and magnetic properties of $\text{Mn}_{1+x}\text{Fe}_{2-2x}\text{Ti}_x\text{O}_4$ ferrite. *J. Alloys Compd.* **464**, 361 (2008)
41. A. Baykal, N. Bitrak, B. Unal, H. Kavas, Z. Durmus, S. özden, M.S. Toprak, Polyol synthesis of (polyvinylpyrrolidone) PVP- Mn_3O_4 nanocomposite. *J. Alloys Compd.* **502**, 199 (2010)
42. M.G. Bellino, D.G. Lammis, N.E.W. De Reza, A mechanism for the fast ionic transport in nanostructured oxide-ion solid electrolytes. *Adv. Mater.* **18**, 3005–3009 (2006)
43. S.S. Umare, U.S. Waware, S. Ingole, *Int. J. Polym. Anal. Charact.* **10**, 1 (2005)
44. S.S. Umare, B.H. Shambharkar, R.S. Ningthoujam, Synthesis and characterization of polyaniline- Fe_3O_4 nanocomposite: Electrical conductivity, magnetic, electrochemical studies. *Synth. Met.* **160**, 1815–1821 (2010)
45. R. Regmi, R. Tackett, G. Lawes, Suppression of low-temperature magnetic states in Mn_3O_4 nanoparticles. *J. Magn. Magn. Mater.* **321**, 2296 (2009)

Mechanism for the formation of low aspect ratio of $\text{La}(\text{OH})_3$ nanorods in aqueous solution: thermal and frequency dependent behaviour

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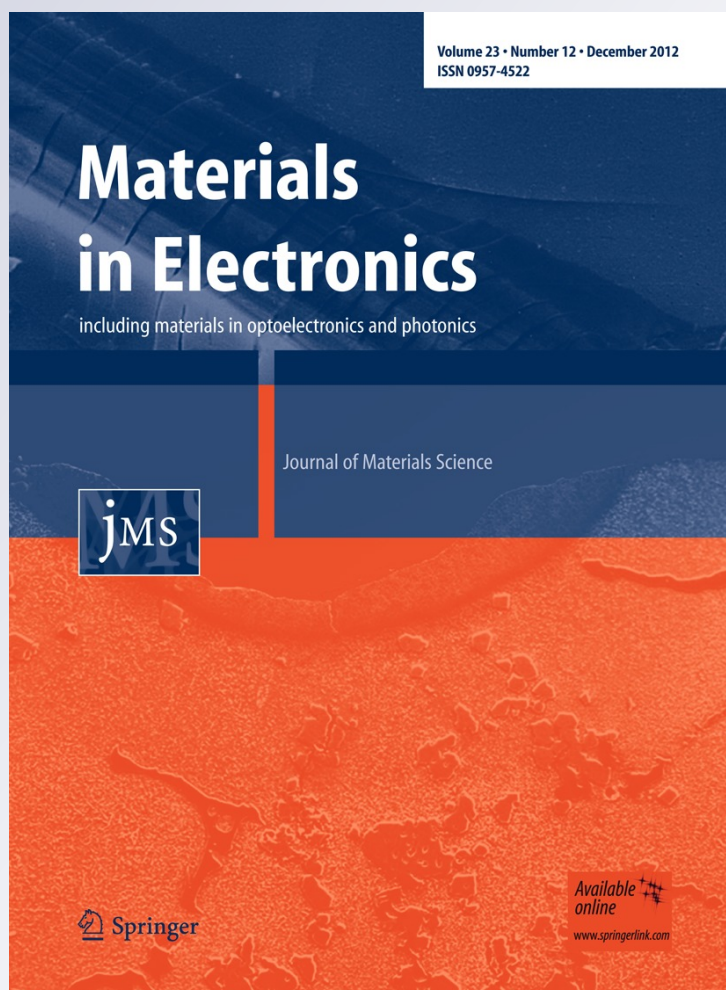
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Mechanism for the formation of low aspect ratio of $\text{La}(\text{OH})_3$ nanorods in aqueous solution: thermal and frequency dependent behaviour

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Abstract $\text{La}(\text{OH})_3$ nanorods of length varying between 30 and 50 nm with aspect ratio of 2–5 were synthesized in aqueous solution using hydrazine hydrate in presence of mixture of cationic *N*-cetyl-*N,N,N*,trimethylammonium bromide (CTAB) and tetra-*n*-butylammonium bromide (TBAB) surfactants. The resultant product was characterized for its morphology and structure using XRD, TEM and FT-IR. Thermal stability studied using TGA indicated good stability. Surfactants in reaction mixture reduces the surface tension of the solution which lowers the energy needed to form a new phase, resulting in the formation of $\text{La}(\text{OH})_3$ crystals of anisotropic shape with low aspect ratio. The A.C. conductivity was found to be of the order of nano-seimen (ns), which non-linearly increases with the increase in frequency (10^2 – 10^6 Hz) The capacitance behaviour was observed in pF in mid frequency region, which can be useful as low loss dielectric material. Nano rods may work as standard materials to monitor conductivity levels in biofluid proteins.

1 Introduction

The behaviour of nano sized materials strongly depends on their size, shape and morphology [1, 2]. Wet chemical methods have been reported for large scale production of nanomaterials. Solution phase synthesis of nanorods/wires

of controlled dimensions is still a challenging task as surface energy favours the spherical particle formation [3]. Synthesis of nanomaterials has been reported in which shape, size is controlled during synthesis by either deploying surfactants/polymer as capping agent or using templates. But still low dimension system such as nanocrystals, thin films, short aspect ratio rods are getting enormous attention due to their potential applications in nanoelectronics, photonics, data recording, fuel cells and sensors [4–6].

Lanthanum and its compounds have unique electronic structure and exhibit number of transition modes involving the 4f shell of these atoms/ions. These compounds have shown outstanding catalytic, optical, electrical and magnetic properties [7, 8]. $\text{La}(\text{OH})_3$ and La_2O_3 are rare-earth novel compounds which have been synthesized in various morphologies such as nanopowder, nanotubes, nanowires, nanorods and nanobelts using hydrothermal, solvothermal, precipitation and microwave assisted route in both aqueous and non aqueous medium [9–16]. $\text{La}(\text{OH})_3$ nanowires synthesized in these processes have dimensions of the order of microns in length and possess a low aspect ratio except a few reports on controlled size nanorods. More over it involves the use of elevated temperature, higher reaction time and strong alkaline solutions. To the best of our knowledge no electrical behaviour study has been reported on these nanorods. In this work we present a facile route for the synthesis of $\text{La}(\text{OH})_3$ nanorods of high aspect ratio and have proposed the mechanism for the same. Synthesis was carried out in aqueous medium using $\text{La}(\text{NO}_3)_3$ precursor and hydrazine hydrate as reducing agent under mild heating conditions. A mixture of CTAB and TBAB surfactant is used to control aspect ratio for which reaction mechanism has been discussed. A.C. conductance and capacitance of this material was measured in the frequency range

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of 10^2 Hz to 10^6 Hz. The material being di-electric may be used for fabrication of capacitors.

2 Experimental

2.1 Materials

Following chemicals were used without further purification. Lanthanum Nitrate ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), Loba Chemie, M.W = 433.02, monohydrate hydrazine ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$, 98 %), Rankem M.W. = 50.06, *N*-cetyl-*N,N,N*,trimethylammonium bromide (CTAB), Loba Chemie M.W. = 364.46, tetra-*n*-butylammonium bromide (TBAB), Spectrochem M.W. = 322.38, absolute ethanol ($\text{C}_2\text{H}_5\text{OH}$), Changshu Yanguan Chemicals, China. Throughout this study deionised (DI) water (18.6 Mohm) Millipore was used.

2.2 Synthesis of $\text{La}(\text{OH})_3$ nanorods

In a typical procedure, 5 mM of each CTAB (0.1822 g), TBAB (0.1612 g) and $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.2165 g) were dissolved together in DI water (100 ml) in a round bottom glass flask. The reaction mixture was homogenized under slow stirring for about 10 min, to avoid foam formation. 1.215 ml of hydrazine hydrate was added rapidly to this reaction mixture under vigorous magnetic stirring. The reaction mixture was kept at 70 °C for about 1 h in order to complete the precipitation. It was kept as such for some time to cool down to room temperature. The residue was separated from precipitation solution through centrifugation process. It was washed several times with DI water to make free from soluble impurities and finally rinsed with ethanol. The left out precipitation was dried under vacuum at 40 °C.

2.3 Analytical measurements

X-ray diffraction (XRD) patterns were determined with A Panalytical's X'Pert Pro powder X-ray diffractometer using Cu K α radiation ($\lambda = 1.5406$ Å) from a sealed tube operated at 30 kV and 40 mA. Transmission electron microscopy (TEM) studies were carried out using a Hitachi H-7500 operated at an accelerating voltage of 120 kV. The samples for TEM image were prepared by drop-casting the dispersed particles solution on a carbon coated copper grid. For Thermogravimetric Analysis (TGA/DSC; universal V4.1D TA instruments) was used. Mass change variations of the powered sample were recorded in the temperature range of ambient to 1,000 °C in nitrogen atmosphere, at the heating rate of 5 °C min⁻¹. A Fourier transformation infrared (FT-IR) spectrum was recorded on Perkin Elmer

RX-1FTIR spectrophotometer in frequency ranging from 500 to 4000 cm⁻¹. The spectra were taken in KBr powder in the form of pellets. Frequency dependence of this material was studied using HIOKI 13530-50 LCR Hi TESTER. All measurement were carried out under vacuum at room temperature, at constant operating voltage (5 V) in the frequency range of 10^2 – 10^6 Hz. Compressed pellets of 10 mm diameter were made using in house fabricated metal die system under hydraulic pressure of 5 tone load. Electrical contacts were made with silver paste coating at both opposite sides of the pellets.

3 Results and discussion

3.1 XRD analysis

From the XRD pattern (Fig. 1), it is clear that the product obtained is a pure crystalline compound of $\text{La}(\text{OH})_3$ phase with hexagonal crystal structure. All diffraction peaks can be indexed as hexagonal $\text{La}(\text{OH})_3$ with lattice constants $a = 6.5286$ Å, $c = 3.8588$ Å which belongs to $\text{P6}_3/\text{m}$ space group. Typical reflections were found to match JCPDS—international centre for diffraction data for sample code 36-1481. No peak could be attributed to the existence of any other impurity or of La_2O_3 . The average crystalline size of as synthesised product was calculated using Debye–Scherrer formula:

$$a = 0.9\lambda / \beta \cos \theta$$

where a , λ , β , and θ are the average crystalline size, Cu–K α wavelength of X-ray beam (0.1545 nm), full width at half maxima intensity (FWHM) of each peak in Radian and Bragg's diffraction angle respectively was found to be 8 nm from the average value of various reflection peaks, however for the most intense peak corresponding to (111) plane, it is to be 7 nm. Mazloumi et al. [13] observed average crystalline size between 50 and 65 nm, when synthesis was carried out in various alkaline solution where as in another study [9] size was reported to be fine when

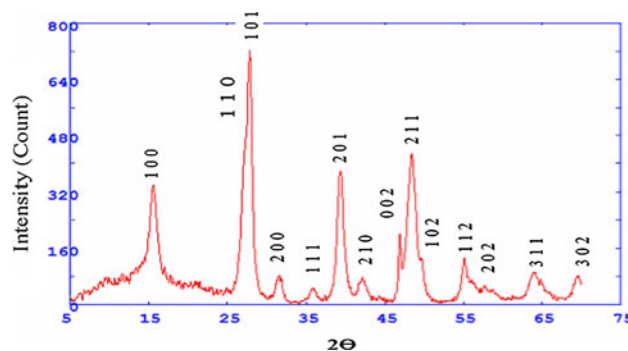


Fig. 1 XRD pattern of $\text{La}(\text{OH})_3$ nanorods

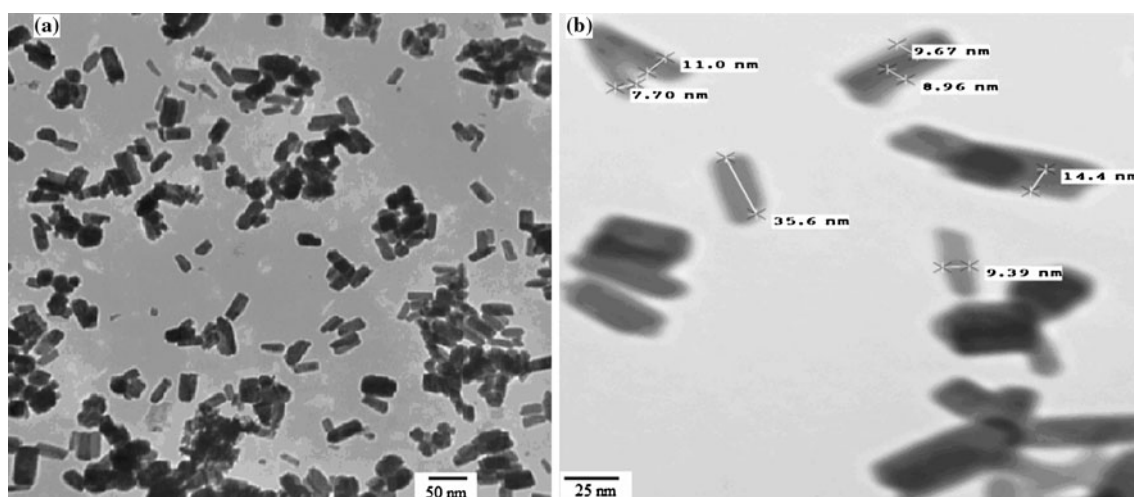


Fig. 2 **a** TEM micrographs of $\text{La}(\text{OH})_3$ nanorods, **b** TEM measurements of selected are displaying length and width of nanorods in nm

synthesis was carried out by hydrothermal method in KOH without the use of any surfactant. The broadening of diffraction peaks in the present study clearly indicates the fine crystalline size, which is due to controlled growth of nanocrystals in presence of mixture of surfactant.

3.2 Transmission electron microscope analysis

Figure 2 shows typical TEM image of $\text{La}(\text{OH})_3$ nanorods which clearly shows monodisperse nature of anisotropic nanorods with 7–12 nm in width and 30–50 nm in length. These are uniformly dispersed when viewed at different portions of the grid sample. Few rods are appearing as overlapping or in contacting each other, where as at some places only top surface of the rod is visible. From the image, it is clear that there is no agglomeration. The small size and monodispersity could be attributed to the presence of CTAB/TBAB system in the reaction mixture. Short chain TBA^+ ions function as filler through hydrophobic interactions between alkyl chains of CTAB and butyl chain of TBAB in the gaps of adsorbed long chain CTAB micelles and hence further stabilized nano materials by preventing irregular growth in such gaps [17–19].

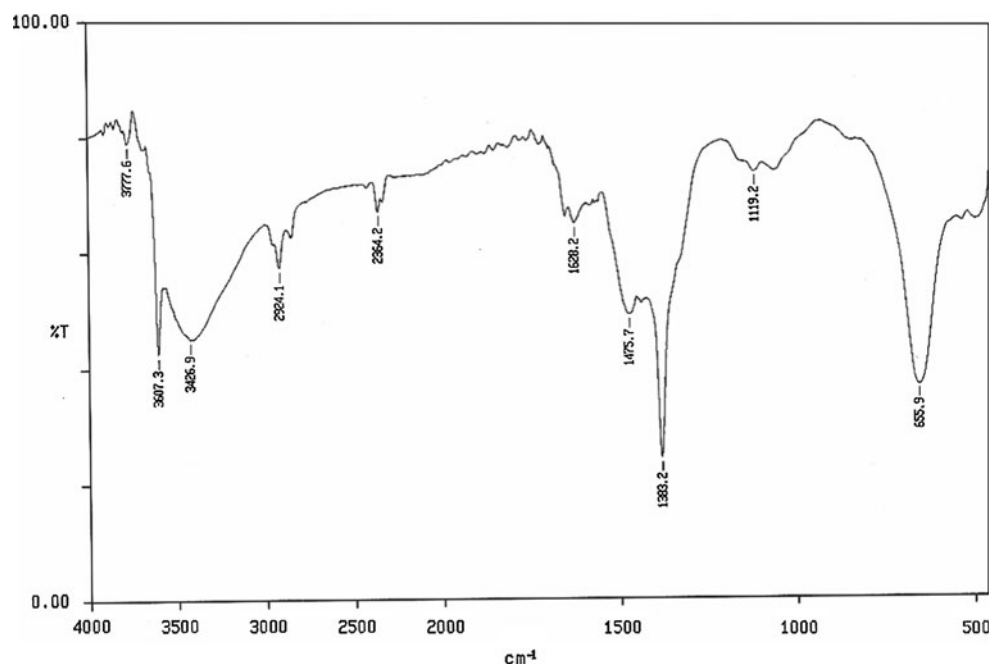
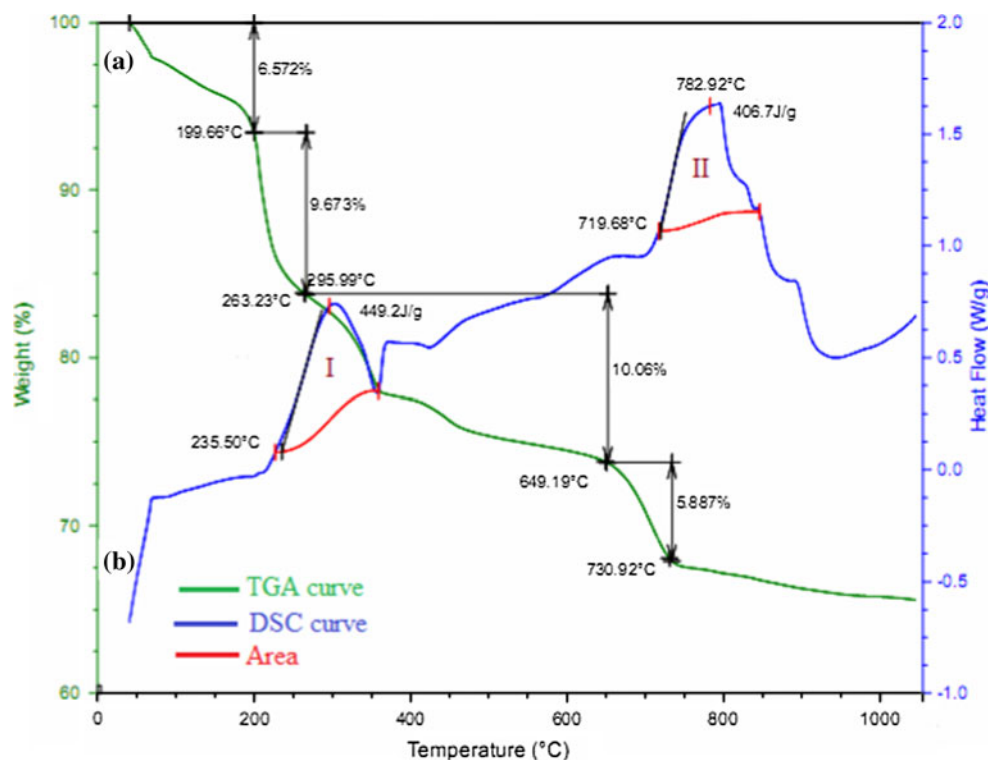
3.3 IR analysis

Adsorption behaviour of the surfactant molecules on nano rods surface was observed by taking FT-IR spectra in $4,000\text{--}500\text{ cm}^{-1}$ (Fig. 3). For pure CTAB/TBAB symmetric and asymmetric peaks were reported at $2,914.0$ and $2,864.0\text{ cm}^{-1}$ and C–H scissoring vibration of N–R moiety were reported at $1,550.0$ and $1,474.0\text{ cm}^{-1}$ [17, 20]. In the present study CH_2 stretching vibration lies at $2,924.0\text{ cm}^{-1}$ and $2,850.0\text{ cm}^{-1}$ indicating almost no shift in the head groups of the surfactant molecules. The N–C–H scissoring

vibration of N–R has shown a peak at $1,628.2\text{ cm}^{-1}$ which is a significant shift in comparison to pure surfactant molecule. However, a peak at $1,475.7\text{ cm}^{-1}$ indicates the presence of free surfactant CTAB molecule remained trapped inside the product [21]. Also peak appeared at $1,119.2\text{ cm}^{-1}$ is due to –C–N stretching from CTAB molecule have significantly shifted than pure CTAB molecules because adsorption of surfactant molecule. The peak at $1,383.2\text{ cm}^{-1}$ can be attributed to $-\text{CH}_3$ bending vibration of tertiary butyl of surfactant TBAB [17]. The bands at $3,426.9$ and $1,628.2\text{ cm}^{-1}$ may be due to physisorbed water molecules. A broad peak at 655.9 cm^{-1} clearly indicates L–OH deformation. This study shows that anisotropic rod formation may be due to the capping behaviour surfactant molecules.

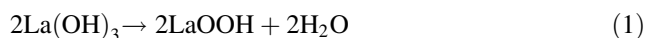
3.4 Thermogravimetric study

TGA/DSC plot of the product in the temperature range of ambient to $1000\text{ }^\circ\text{C}$ is given in Fig. 4a. The profile indicates the corresponding weight loss in various temperature range which is divided in four steps, (1) in the temperature range of ambient $199.66\text{ }^\circ\text{C}$. The weight loss of 6.572% is due to physisorbed water molecules as well as unbounded CTAB/TBAB molecules. In FT-IR spectra (Fig. 3) the broad band at $3,426.9$ and $1,628.2\text{ cm}^{-1}$ due to stretching vibration of physisorbed water molecules also confirms the presence of water moiety. A peak at $1,457.7\text{ cm}^{-1}$ also confirms the presence of free CTAB as reported [21] (2) further gradual weight loss of 9.673% in the temperature range $263.23\text{ }^\circ\text{C}$ is due to the decomposition of the bounded surfactant molecules into C, H and N moiety. Both CTAB/TBAB were got adsorbed on the surface of the nanorods during synthesis. (3) on further ramping in the temperature range from 263.23 to $649.16\text{ }^\circ\text{C}$ the weight loss of 10.66% was observed due to dehydration of

Fig. 3 FT-IR spectra of $\text{La}(\text{OH})_3$ nanorods**Fig. 4** Thermogravimetric analysis of $\text{La}(\text{OH})_3$ nanorods, **b** DSC plot of $\text{La}(\text{OH})_3$ nanorods

$\text{La}(\text{OH})_3$ to LaOOH (lanthanum hydroxide—oxide) [22]. (4) another weight loss of 5.88 % up to the temperature of 730.92 °C was due to complete dehydration of LaOOH into La_2O_3 . It has already been reported that the $\text{La}(\text{OH})_3$ phase first get transformed to the LaOOH phase in the temperature range of 330–400 °C which is an intermediate

phase with monoclinic crystal structure and P21/m (No.11) space group. It further gets dehydrate form La_2O_3 up to 600 °C as per Eqs. (1) and (2) [22, 23]. However, in the present study there is a possibility that both reaction (1) and (2) may be occurring simultaneously and clear cut distinction may not be possible.



According to Eqs. (1) and (2), the total thermal transformation weight loss for the conversion of $\text{La}(\text{OH})_3$ to La_2O_3 theoretically should be 13.4 %, which is somewhat higher in the present study and the decomposition temperature of $\text{La}(\text{OH})_3$ to La_2O_3 ranges in the temperature range of 330–730 °C. In the present study the shift in dehydration temperature may be the result of surface modification of particles due to CTAB/TBAB capping.

In DSC curve (Fig. 4b) two endothermic peaks were observed. First peak temperature is 295.99 °C having area 449.2 J/g amounting $\sim 85.3 \text{ kJ mol}^{-1}$. This reaction enthalpy change is due to first dehydration (transformation of $\text{La}(\text{OH})_3$ to LaOOH) and is in agreement with the results reported by Neumann and Walter [22]. The second peak temperature at 782.92 °C having peak area 406.7 J/g corresponds to 77.0 kJ mol^{-1} which is due to transformation of LaOOH to La_2O_3 . The second reaction enthalpy is higher than already reported [22] may be due to rigid and an isotropic nature of the compound form.

3.5 Frequency dependent electrical study

Figure 5a and b shows the variation in electrical conductivity of the material in the frequency ranging from 10^2 to 10^6 Hz and Table 1 comprises of capacitance and conductance values with respect to variable frequency range selected for the study. The A.C. conductivity was measured in ns, which non-linearly increases with the increase in frequency. Total conductivity of the system is given by

$$\sigma = \sigma_0(T) + \sigma(\omega, T) \quad (3)$$

Here, the first term is dc conductivity which is independent of frequency. The second term is A.C. conductivity may be due to auto ionisation or polarization which occurred due to electro negativity difference between the

Table 1 Capacitance and conductance data of $\text{La}(\text{OH})_3$ nanomaterial in the selected frequency range of 0.1–1000 KHz

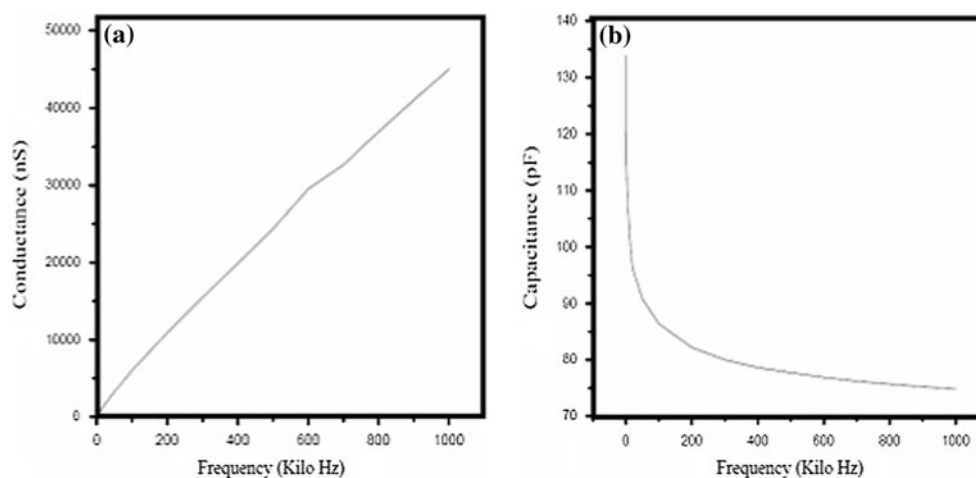
Frequency (Kilo Hz)	Capacitance (pF)	Conductance (nS)
0.1	142.432	1.2204
0.5	123.53	41
1	116.63	75.055
10	103.65	83.17
50	91.335	1437.7
100	86.995	3212.7
500	78.148	19,990
1,000	75.558	38,600

lanthanum and hydroxyl groups resulting in hopping between metal ions under the effect of electric field. It may also be possible that some of free La^{+3} ions left entrapped inside the crystal structure during the synthesis process which may generate defects in the $\text{La}(\text{OH})_3$ crystal. Electron transfer experiments in these materials involve the transfer of charge from one end to another end but no net flow of charge or associated current in between contacts or molecules. However more detailed study is needed to understand proper mechanism. It has observed that capacitance values first decreases sharply at lower frequency and then slowly and becomes nearly constant as shown in Fig. 5b. The capacitive behaviour may be due to space charge polarisation from inhomogeneous dielectric structure. Inhomogeneous structure may be due to nanopore defects in the crystal but exact cause is not clear. This type of electrical behaviour may be useful for designing low loss dielectric capacitors and sensors for monitoring and comparing the conductivity levels of bio-fluids.

4 Mechanism of formation

Surfactant assisted synthesis is considered an effective methodology for shape controlled synthesis in nanomaterials

Fig. 5 Frequency dependent electrical study **a** A.C. Conductance versus frequency, **b** Capacitance versus frequency plot of $\text{La}(\text{OH})_3$ nanorods in pellet form



in aqueous phase [24, 25]. Hydrazine hydrate is freely soluble in water but since N_2H_4 is basic, chemically free active ions are normally N_2H_5^+ and OH^- as per Eq. (4). Lanthanum ions in aqueous solution quickly react with hydroxyl ion to form lanthanum hydroxide due to electrostatic interactions. However presence of excess hot water, the formation of complex co-ordinate complex of $\text{La}(\text{OH})_4^{-1}$ occurs which immediately stabilized by the cationic group of surfactants molecules present in the reaction mixture. This reaction product acted as seeding crystal for the transformation into short anisotropic rods of $\text{La}(\text{OH})_3$.



Growth process of $\text{La}(\text{OH})_3$ rods/crystal in presence of CTAB/TBAB is different than the reaction system having no surfactants. A highly surface active blocks some of the crystal plane because of its preferential adsorption there by directing overall growth in specific direction. Surfactants in reaction mixture reduces the surface tension of the solution which lowers the energy needed to form a new phase, resulting in the formation of $\text{La}(\text{OH})_3$ crystals in a lower super saturation [26]. Both CTAB and TBAB are ionic compounds and completely soluble in aqueous medium. The resultant ions are positively charged tetrahedron with a long hydrophobic chain in case of CTAB and short butyl chains with TBAB. Growth unit for $\text{La}(\text{OH})_3$ crystal is considered as $\text{La}(\text{OH})_4^{-1}$ which have tetrahedron geometry, but negatively charged [27]. Thus $\text{La}(\text{OH})_4^{-1}$ and cation CTA^+ forms ion pair due to electrostatic interactions. The complementary between these ion pairs is to provide the surfactant the capability to act as ionic carrier [28]. The Lanthanum particles are negatively charged and CTA^+ got adsorbed on the surface to form a film. The film is floatable which acts as seeding source for assembly and growth of regular crystal structure in the form of rods. In the growth process the surfactant molecule serves as a growth controller as well as agglomeration inhibitor by the forming a covering film on the $\text{La}(\text{OH})_3$ rods. These seed crystals will become the nucleating centres and the surfactant molecule carrying the growing unit will be adsorbed on the seed surface. This lending process occurs on the surface of $\text{La}(\text{OH})_3$ (0001). As the surfactant forms the film and the molecule will be perpendicularly adsorbed on the surface. It has been earlier studied that the presence of CTAB alone in the reaction mixture has resulted in formation of long fibres with unsymmetrical growth. However, the addition of TBAB restricts the faster longitudinal growth to some extent, because of short butyl groups which possess large hydrophobic volume. TBA^+ ions get mingled in between CTA^+ and both got adsorbed on the top of growing crystal surface. Presence TBAB alone, in the reaction mixture may not be stabilize

nano-crystals because of short molecular structure [18]. It may not have stable adherence with another surface and can easily removed on repeated washing. Thus it has been become possible to grow short size anisotropic rods of almost uniform dimensions in presence of the both CTAB and TBAB mixture, more over no alkali hydroxide solution has been deployed in synthesis process.

5 Conclusion

Anisotropic $\text{La}(\text{OH})_3$ nanorods have been synthesized through facile route in aqueous medium using a mixture of cationic surfactants in presence of hydrazine hydrate. The morphology indicates narrow size distribution. The growth process CTAB serves as a carrier for $\text{La}(\text{OH})_4^{-1}$ and organise the regular structure. TBAB played a key role to limit the growth of nanorods to some extent. Thermal analysis of this material leads to higher stability than pure $\text{La}(\text{OH})_3$ crystals grown without surface capping. Repeated A.C. conductance measurements showed conductivity in the level of ns which has also been reported for various bio-fluids hence this material can be utilized to compare A.C. conductance behaviour of such compounds. Due to pF capacitance behaviour, it can be used to build capacitors with low loss.

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References

1. L.X. Yang, Y. Liang, H. Chen, Y.M. Meng, W. Jiang, *Mater. Res. Bull.* **44**, 1753 (2009)
2. L. Qiting, N. Jansen, W. Yiqing, D. Yanan, D. Weizhong, G. Shuhua, *J. Rare Earths* **29**, 416 (2011)
3. C.J. Murphy, T.K. Sau, A.M. Gole, C.J. Orendorff, J. Gao, L. Gou, S.E. Hunyadi, T. Li, *J. Phys. Chem. B* **109**, 13857 (2005)
4. X. Duan, Y. Huang, R. Agarwal, C.M. Lieber, *Nature* **421**, 241 (2003)
5. M.S. Fuhrer, J. Nygard, L. Shih, M. Forero, Y.G. Yoon, M.S.C. Mazzoni, H.J. Choi, *Science* **288**, 494 (2000)
6. Z.F. Ren, Z.P. Huang, J.W. Xu, J.H. Wang, P. Bush, M.P. Siegal, P.N. Provencio, *Science* **282**, 1105 (1998)
7. X. Wang, Y. Li, *Angew. Chem. Int. Ed.* **41**, 4790 (2002)
8. Y.D. Li, Y. Huang, T. Bai, L.Q. Li, *Inorg. Chem.* **39**, 3418 (2000)
9. X. Ma, H. Zhang, Y. Ji, J. Xu, D. Yang, *Mater. Lett.* **58**, 1180 (2004)
10. H. Zhang, X. Ma, Y. Ji, J. Xu, D. Yang, *Chem. Phys. Lett.* **377**, 654 (2003)
11. H. Zhang, Y. Ji, X. Ma, J. Xu, D. Yang, *Nanotechnology* **14**, 974 (2003)
12. I. Djerdj, G. Garnweitner, D.S. Su, M. Niederberger, *J. Solid State Chem.* **180**, 2145 (2007)
13. M. Mazloumi, S. Zanganeh, A. Kajbafvala, M.R. Shayegh, D.S.K. Sadrezhaad, *IJE Trans. B: Appl.* **21**, 169 (2008)

14. Q. Mu, T. Chen, Y. Wang, *Nanotechnology* **20**, 345602 (2009)
15. G. Li, C. Li, Z. Xu, Z. Cheng, J. Lin, *Cryst. Eng. Comm.* **12**, 4208 (2010)
16. F. Bouyer, N. Sanson, M. Destarac, C. Geradin, *New J. Chem.* **30**, 399 (2006)
17. M.L. Singla, A. Negi, V. Mahajan, K.C. Singh, D.V.S. Jain, *Appl. Catal. A-Gen.* **323**, 51 (2007)
18. L. Wang, X. Wu, M. Pei, Z. Wu, X. Li, X. Tao, *Chinese J. Chem.* **29**, 185 (2011)
19. P.S. Kohli, P. Devi, P. Reddy, K.K. Raina, M.L. Singla, *J. Mater. Sci.: Mater. Electron.* (2012). doi:[10.1007/s10854-012-0680-2](https://doi.org/10.1007/s10854-012-0680-2)
20. S.K. Mehta, S. Kumar, S. Chaudhary, K.K. Bhasin, M. Gradzielski, *Nanoscale Res. Lett.* **4**, 17 (2009)
21. Y. Borodko, L. Jones, H. Lee, H. Frei, G. Somorjai, *Langmuir* **25**, 6665 (2009)
22. A. Neumann, D. Walter, *Thermochim. Acta* **445**, 200 (2006)
23. E. Fuglein, D. Walter, *Z. Anorg. Allg. Chem.* **632**, 2154 (2006)
24. Y. Son, B. Mayers, Y. Xia, *Nano Lett.* **3**, 675 (2003)
25. F. Kim, K. Sohn, W. Huang, *J. Am. Chem. Soc.* **130**, 1442 (2008)
26. X.M. Sun, X. Chen, Z.X. Deng, Y.D. Li, *Mater. Chem. Phys.* **78**, 99 (2002)
27. W.J. Li, E.W. Shi, W.Z. Zhong, Z.W. Yin, *J. Crys. Growth* **203**, 186 (1999)
28. L. Yan, Y.D. Li, Z.X. Deng, J. Zhuang, X. Sun, *Int. J. Inorg. Mater.* **3**, 633 (2001)