CHAPTER I
INTRODUCTION

All matters are collection of grains, which are in turn made up of atoms. Depending on their size, these grains could be perceptible or invisible. Nanomaterials are materials possessing grain sizes in the order of 1 – 100 nanometre (nm) in at least one coordinate. The average radius of an atom is of the order of 1 – 2 Å. One nm comprises 10 Å and hence, in one nanometre, there may be 3 – 5 atoms depending on the atomic radii. Nanomaterials may have spherical, triangular, hexagonal, pentagonal, tubular, plate-like, rod-like, needle shaped or more complex geometries. When the size of particles decreases to nanometre scale, the ratio of surface atoms increases. The total surface area per unit mass also increases as the size of any particle decreases and all the properties which depend on the surface-to-volume ratio change continuously. Thus, nanoparticles have unique beneficial properties when compared with their bulk counterparts and hence, the nanoparticle research has become a focused area of interest nowadays.

1.1 METAL OXIDE NANOPARTICLES

Metal oxide nanoparticles are one of the most useful inorganic compounds. Transition metal and rare earth oxides are important and of great interest due to their limited size and a high density of corner or edge surface sites. Transition metals exhibit several common oxidation states. This is because of their valence electrons or the electrons that use to combine with other elements are to be found in more than one shell.

The reduction of particle size and size distribution of metal oxide nanoparticles influences structural characteristics, namely the lattice symmetry and cell parameters [4-8]. As the particle size decreases, the increasing number of surface and interface atoms
generates stress/strain and structural perturbations [9]. Beyond this ‘intrinsic’ strain, there may be also ‘extrinsic’ strain associated with a particular synthesis method which may be partially removed by annealing or calcination [10]. The reduced particle size also influences the electronic properties in oxide materials. The presence of discrete, atom-like electronic states give rise to the quantum confinement effect, which is related to the energy shift of exciton levels and optical band gap. The optical band gap energy is inversely proportional to the square of the particle size. The size effect also influences the physical and chemical properties. In bulk state, many oxides have wide band gaps and low reactivity. A decrease in the average size of an oxide particle changes the magnitude of the band gap with strong influence in conductivity and chemical reactivity. The optical conductivity can be obtained from reflectivity and absorption measurements. Metal oxides are used for both redox and acid/base properties.

Nanocrystalline oxides have superplasticity due to the large interfaces between the nanosize grains. Some have superconducting and giant magnetic resistance properties. Metal oxide nanoparticles have high hardness, thermal stability and chemical resistance. Because of these special properties the metal oxide nanoparticles, especially the transition metal oxides have wide applications in modern technology [11-22].

1.2 MAGNETIC NANOPARTICLES

Magnetic nanoparticles are commonly composed of either metallic elements or their oxides. Metal magnetic nanoparticles are very sensitive to oxidation. They have higher magnetic moment. Iron, nickel and cobalt are the most common magnetic elements. Metal oxide magnetic nanoparticles consist of oxides with a complex distribution of phases within the particles.
The magnetic properties of the magnetic nanoparticles can be changed by varying the size of the nanoparticles and by varying the applied external magnetic field. The magnetic moment per atom, the relaxation time, Curie temperature ($T_C$), Neel temperature ($T_N$), coercivity field ($H_C$) and the magnetic anisotropy of nanoparticles can be different than those of a bulk material [23, 24].

Magnetic nanoparticles have potential modern applications in various fields. In the medical realm, scientists hope to use magnetic nanoparticle in targeted drug delivery [26-28], cancer therapy by magnetic hyperthermia [29], magnetic resonance imaging [30-32], biomolecules separation [33], detoxification of biological fluids, tissue repair and DNA detection [34]. Magnetic nanoparticles are used in the development of magnetic storage [35], electro-photographic developer [36], dynamic sealing [37] and in spintronic devices. They can also be used as pigments [38], catalysts [39] and for the removal of metal ions [40].

1.3 MAGNETIC IRON OXIDE NANOPARTICLES

Iron oxide is one of the most important transition metal oxides, which is widespread in nature and can also be readily synthesized in the laboratory. The iron with 26 protons in nucleus is a component of transition elements group. The iron has eight electrons in the valence shell and due to oxygen’s electronegativity it can form bivalent and trivalent combinations. The magnetic iron oxide nanoparticles have unique biochemical, magnetic, catalytic and other properties which provide suitability for many applications.

The most common anhydrous oxides of iron are trivalent oxides of iron. They are inorganic compound with the general formula $\alpha$-Fe$_2$O$_3$, named hematite. $\alpha$-Fe$_2$O$_3$ is widely used as catalysts, pigments and gas sensors due to its low cost and high resistance to
corrosion. It can be used as starting material for the synthesis of magnetite (Fe$_3$O$_4$) and maghemite (γ-Fe$_3$O$_4$). α-Fe$_2$O$_3$ nanocrystals are considered to be the promising material in water splitting [43], gas sensor [44], Li-ion battery [45] and sewage treatment [46]. Hematite nanostructures have been explored in the development of electrochromic devices [47] and in the construction of photoelectrochemical systems [48]. α-Fe$_2$O$_3$ nanoparticles have a wide range of applications in pigments [49], magnetic recording materials [50] and drug delivery [51].

In addition to trivalent iron oxides, there is another important form of iron oxide called iron (II, III) oxide. Fe$_3$O$_4$ has unique properties including magnetic properties, chemical stability, biocompatibility and low toxicity. It attracts research interest in materials science owing to its low producing cost, environmental benignity, natural abundance and potential applications. It has applications in magnetic fluids [52], information storage [53], lithium-ion batteries [54] and catalysis [55]. Nanoparticles of Fe$_3$O$_4$ have unique size and morphology dependent physical and chemical properties. They depend on several other factors including preparation method, experimental conditions like pH, precursors, solvent, temperature, duration, gas atmosphere, post treatment, etc. They possess numerous applications in biomedicine because of their unique superparamagnetic properties with higher saturation magnetization. Well dispersed Fe$_3$O$_4$ particles have been widely used as an ideal candidate for biological applications such as a tag for sensing and imaging [56], drug-delivery carrier for antitumour therapy [57], immunosensor for the detection of carcinoembryonic antigen in clinical immunoassay [58].

1.4 PROPOSED STUDY

Plenty of work has been done on the magnetic iron oxide nanoparticles so far, but the studies on doped magnetic iron oxide nanoparticles are not adequate. Few works have
been reported on magnetic iron oxide nanoparticles doped with transition metal elements, and the reports on magnetic iron oxide nanoparticles doped with rare earth metal elements are still fewer. The present study, therefore, stipulates the synthesis of pure and rare earth metal elements doped magnetic iron oxide nanoparticles and extraction of their physical properties by characterizations. The following chapter II presents the synthesis methods that have been used for the formation of the magnetic iron oxide nanoparticles and the methods adopted for identifying their properties. Chapter III gives the list of previous amount of work and also explains the material properties of the selected magnetic metal oxides. Chapters IV to VIII are the original research investigating the formation and characterization of the pure and rare earth metal elements doped magnetic iron oxide nanoparticles. Chapter IX is the formal conclusions attained through the research made on these materials and the possible scopes available for the future research.

1.5 SCOPE OF THE STUDY AND METHODOLOGY ADOPTED

The aim of proposed study is to synthesize and characterize pure and rare earth metal elements doped iron oxide nanoparticles using the simple chemical precipitation method.

During synthesis, the effect of pH on phase formation of both hematite and magnetite is to be elucidated. The effect of annealing on phase transformation from magnetite to hematite has to be analyzed. Various characterization techniques are to be carried out on the prepared pure and rare earth metal elements doped iron oxide nanoparticles, to unveil the unique structural, morphological, optical, electrical and magnetic properties. The decomposition behavior of the starting precursor and the prepared pure iron oxide nanoparticles are to be studied through the thermogravimetry analysis. The need for calcination is also to be confirmed from the TGA analysis.
Structural characterization for the prepared pure and doped iron oxide nanoparticles is to be done using the authentic tool, XRD analysis. The obtained data will be compared with the standard JCPDS values to identify the crystal structure, phase purity and the incorporation of dopant ion into the lattice site. The structural parameters are to be calculated using suitable formulae. The metal-oxide phase formation is to be further identified by employing the FTIR analysis. The shape and size of the nanoparticles are to be exposed with the help of SEM and TEM. The structural information of the nanoparticles is to be further proved by SAED analysis. The elemental composition is to be elucidated using EDX analysis; whereas the XPS is to be used to obtain the information on the near surface of the nanoparticles. UV-Vis-NIR spectroscopy is to be used to obtain the knowledge about the optical absorption of the nanoparticles. A standard two probe set up has to be used to study the electrical properties of the nanoparticles. As the DC electrical conductivity of iron oxides are usually very low, it was proposed to measure the dielectric constant of the prepared hematite and magnetite nanoparticles, and their variations with respect to temperature also. Magnetic properties of the nanoparticles have to be assessed at room temperature and low temperature with the aid of Vibrating Sample Magnetometer. The properties of the pure nanoparticles are to be compared with the doped nanoparticles to inspect the effect of doping. Especially, this work is to examine the effect of doping on the magnetic properties of the iron oxide nanoparticles.

1.6 SIGNIFICANCE OF THE STUDY

The study comprises the synthesis of iron oxide nanoparticles, $\alpha$-Fe$_2$O$_3$ and Fe$_3$O$_4$ by varying the pH value of the facile solution. Chosen preparative method is very simple and cost-effective. Realized role of pH on phase formation of hematite and magnetite will be helpful for future researchers. The study further helps to comprehend the effect of
calcination and the phase transformation of the prepared nanoparticles. Systematic characterization to evaluate their structural, morphological, optical, electrical and magnetic properties will be surely an eye opener for beginners of research. The preparation of rare earth ions doped iron oxide nanoparticles and their study help to understand the property modifications due to the incorporated dopant ions. This work provides magnetic properties of hematite, magnetite and their doped counter parts with respect to applied field and temperature.

The unique properties of these nanoparticles will pave new ways for the fabrication of innovative devices that promotes the range of technological developments.

1.7 IMPACT OF THE STUDY

Concluded findings of the study will provide information about the properties of the magnetic iron oxide nanoparticles. Further, the study will provide understandings about the effect of rare earth metal ions doping into the iron oxide crystal lattice. Since the study is aimed to vary the phase formation by adjusting the pH and calcination along with property modification by rare earth ion doping, the study will surely make an impact among the researchers those who involve in similar studies.