CHAPTER 1

INTRODUCTION
Magnetism and magnetic materials have a long and illustrious history. In the modern era magnetism influences many aspects of our lives. Magnetic materials and magnetic phenomenon inconspicuously appear in many complex devices. One of such well known magnetic material family is ferrite.

1.1 Ferrites

"Ferrites represent a class of magnetic materials with a plethora of fascinating, intrinsic functionalities. The intriguing interplay of charge, spin, and orbital ordering in these systems superimposed by lattice effects opens a scientifically rewarding playground for both fundamental and application-oriented research. In particular, the possibility of externally modifying the properties of these complex oxides and thus potentially generating novel practical applications opens a new perspective."

Ferrites are the mixed metal oxides containing iron oxide as their main component. Though, ferrites are known to exist since hundreds of years, the research in ferrites was initiated at the end of Second World War. Kato & Takei [1], Kawai [2] and Snoek [3] were the first to start work on ferrimagnetic materials. In 1945 Snoek [4] laid the foundation of the science and technology of ferrites. The paper by Néel in 1948 [5] in which theory of a new class of magnetic materials, ferrimagnets, was put forward, initiated a great stream of experimental and theoretical investigations of ferrites and other ferrimagnets. Ferrite possesses good magnetic properties along with very high d.c. resistivity [6]. Among various magnetic materials, ferrites are the best in high frequency circuits and they cannot be replaced by other magnetic elements. In addition, they are relatively inexpensive. Ferrites have found wide applications as effective magnetic materials in radio engineering, microwave technology and some other fields of technology. They are extensively used as core materials for inductances and transformers in telecommunication industry, audio and video recording heads, memory devices, digital systems, tapes and electronic devices which are operated from low to high frequency range. The increasing demand due to the specific applications of ferrites have changed remarkably and kept pace with the developments in electronic technologies. Therefore, the diversity of applications make ferrites an active area of research. It is well known that changing its composition or the method or condition of preparation could modify the
properties of ferrites. Materials science and technology have been steadily applied to improve properties as well as new products by appropriate choice of composition and method of preparation.

1.1.1 Classification of ferrites

Depending on the nature of magnetic behavior of the ferrite materials, they are classified into two broad categories, soft ferrites and hard ferrites. Soft ferrites are easy to magnetize and demagnetize and have low coercive fields. Hard ferrites retain their magnetization once they are magnetized, having large coercive field and are used for permanent magnet. Soft ferrites are used to construct electromagnet. The characterization of soft and hard ferrites in general is based upon some important factors like:
(a) The residual magnetism (remanence/coercivity), $M_R$ that the material retains when the external magnetic field is removed.
(b) The saturation flux or the maximum magnetic field that can be induced in the materials i.e., saturation magnetization $M_s$.
(c) The demagnetization field or the value of the external magnetic field applied in the negative direction that removes the residual magnetic field i.e. coercive force $H_c$ [7].

Taking into the crystal structure and the magnetic ordering, ferrites can be grouped into four different categories [8] namely spinel, garnet, magnetoplumbite and ortho ferrites (Table 1.1).

Table 1.1 Different types of ferrites with their structures, chemical formula and examples

<table>
<thead>
<tr>
<th>Type</th>
<th>Structure</th>
<th>General Formula</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spinel</td>
<td>Cubic</td>
<td>$MFe_2O_4$</td>
<td>$M = Ni, Zn, Mn$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$Mg, Cu, Co, Li$</td>
</tr>
<tr>
<td>Garnet</td>
<td>Cubic</td>
<td>$Ln_3Fe_3O_{12}$</td>
<td>$Ln = Y, Sm, Eu, Gd$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$Tb, Dy, Ho, Er$</td>
</tr>
<tr>
<td>Magnetoplumbite</td>
<td>Hexagonal</td>
<td>$MFe_{12}O_{19}$</td>
<td>$M = Ba, Sr$</td>
</tr>
<tr>
<td>Orthoferrite</td>
<td>Pervoskite</td>
<td>$LnFeO_3$</td>
<td>$Ln =$ same as in garnet</td>
</tr>
</tbody>
</table>
The spinel ferrites are named after the naturally occurring mineral spinel, having the chemical formula MgAl₂O₄ and the general chemical formula written as MFe₂O₄, where M is a divalent transition metal or a suitable combination of these ions. The spinel lattice is composed of a close packed oxygen arrangement in which 32 oxygen ions form the unit cell (the smallest repeating unit in the crystal network). These anions are packed in a face centered cubic (FCC) arrangement leaving two kinds of spaces between anions: tetrahedrally coordinated sites (A), surrounded by four nearest oxygen atoms, and octahedrally coordinated sites (B), surrounded by six nearest neighbor oxygen atoms. These are illustrated in figure 1.1. In total, there are 64 tetrahedral sites and 32 octahedral sites in the unit cell, of which only 8 tetrahedral sites and 16 octahedral sites are occupied, resulting in a structure that is electrically neutral [9,10].

![Figure 1.1 Schematic of two subcells of a unit cell of the spinel structure, showing octahedral and tetrahedral sites](image)

The localization of ions either in the tetrahedral or octahedral sites depends fundamentally on the ion and lattice sizes. Also it has been observed to depend on the temperature and the orbital preference for specific coordination. The ionic distribution of this kind of structure may be represented by eqn. (1.1)

\[(M_x^{2+}Fe^{3+}_{1-x})[M_x^{2+}Fe^{3+}_{1-x}]O_4^{2-}\] ...............................(1.1)

where the cations enclosed by parenthesis occupy tetrahedral sites comprising the tetrahedral sublattice, while the cations enclosed by the square bracket occupy octahedral sites comprising the octahedral sublattice and $x$ is the inversion parameter and $x = 0$ and $1$ stand for the inverse and normal spinel and for mixed spinel, $0 < x < 1$. The factors, which
can influence the distribution of the metal ions over tetrahedral and octahedral sites: the electronic configuration of the metal ions, the ionic radii and the electrostatic energy of the spinel lattice and more recently the preparation condition [11,12].

1.2 Nanoferrites

Nanoscience is an ever expanding field of scientific research that involves materials that have at least one dimension in the nanometer size regime. What is usually termed “Nanostructured systems” mainly comprises those materials, whose properties are determined by entities (particles, crystallites or clusters) with characteristic lengths between 1 to 100 nm in at least two dimensions. The field of nanoscience encompasses various types of materials such as thin films (1 dimensional), nanotubes (2 dimensional), and nanoparticles (3 dimensional). Nanosized materials can display enhanced surface and size dependent properties. Although the unique properties of nanosized materials have been known as far back as 1700’s (e.g. Venetian glass blowers used colloidal gold to produce a red color), recognition of size related properties was not achieved until the past 60 years. It is the pursuit of novel size related properties that fuels nanoscience research. Nanostructured materials represent a fast evolving application of recent research in physics and chemistry. Among the most promising nanomaterials being developed are magnetic nanomaterials including magnetic nanoparticles and magnetic nanosensors.

In recent years the scientific literature has been replete with reports of magnetic nanoparticle synthesis, properties and novel applications [13,14]. This has largely been driven by the hope, and in some instances realization, of surface enhanced properties. By producing materials on the nanoscale, there exists the possibility that surface based properties (e.g. catalysis and reactivity), magnetism, and electronic properties may be enhanced. In most nanoparticulate materials, and specifically in the case of metal oxides, there are several properties can be influenced by the particle size.

In nanoparticle systems the surface disorder can influence the lattice symmetry and cell parameters throughout the particle due to the limitation in the size of the particle itself [15,16]. The thermodynamic stability can also change due to decreasing size and this in turn can induce modification of the cell parameters and/or structural
transformations. Structures that are not stable in the bulk can be at the nanoscale range; for example $\gamma$-Al$_2$O$_3$ [17], MoO$_x$ oxides [18] and BaTiO$_3$ [19].

In case of magnetic nanoparticles, the disruption in crystal structure at the surface can greatly influence the magnetic properties [20,21]. The truncation of the lattice at the surface weakens exchange interactions, and in many cases reduces coupling with neighboring particles. In particular, for magnetic oxide systems such as spinel ferrites the magnetic exchange is dependent on the cation-anion-cation bond angles that are affected by the surface truncation. The bond bending commonly experienced on surfaces can produce profound changes in the magnetic properties of nanoparticles and the solids based on these particles [22,23].

Interest in nanosized spinel ferrites has greatly increased in the past few years due to their importance in understanding the fundamentals in nanomagnetism [24] and their wide range of applications such as high-density data storage, ferrofluid technology, sensor technology, spintronics, magnetocaloric refrigeration, heterogeneous catalysis, magnetically guided drug delivery and magnetic resonance imaging [14,24-27]. The physics of nanoscale magnetic particles is an area of enduring interest. From a fundamental perspective the study of nanoparticles sheds light on how bulk properties transforms to atomic as size decreases. In fact, the behavior of bulk magnetic materials is determined and influenced by the formation of domains and domain wall movement. The magnetic behavior of bulk materials is complicated by the fact that domain wall moment can be impeded or pinned by impurities, grain boundaries, etc. due to this; a direct correlation between the observed magnetic behavior and the quantum origins of magnetism is not readily achievable. However, if the size of the magnetic materials is decreased below a critical characteristic length, domain formation is no longer energetically favored and the particles behave like single domains [28]. Moreover, the large surface fraction opens the opportunity for manipulation of properties via interfacial interaction. Knowledge of these fundamental properties is essential for creative use of nanoparticles in important technical applications [29-33].

Magnetism is the result of inert-atomic exchange and in case of nanoferrites, this requires well defined bond angles and lengths, and hence, the particles must be crystalline. A successful synthetic technique for this system should produce particles that
are single crystallites. The surface of any crystallite, however, by its very nature is disordered. An amorphous outer layer of the particles may be detrimental to the magnetic properties. In systems such as core shell nanoparticles minimizing the effect of the "amorphous layer" may be important not only from a chemical point of view, but also in terms of enhancing the magnetic properties.

Many disciplines including biology, physics, chemistry and engineering are pursuing a wide variety of methodologies for producing nanomaterials. To carefully study and exploit the potential and possibilities associated with nanomaterials, the key point is to create well-defined, monodisperse structures of predictable size, shape, crystallinity, and morphology through a straightforward synthesis. As is well known, in the preparation of nanocrystalline oxide samples, mainly following two approaches: (1) Top to bottom approach: physical methods (2) Bottom to top approach: chemical methods are followed.

Physical methods are commercially attractive because it is generally easier to produce larger volumes of product, but they tend to impact physical stresses in the materials which can require further processing and result in wider size distributions. The most popular physical methods are ball milling, laser pyrolysis and plasma torch. Chemical techniques are generally better for the synthesis of mixed cation nanoparticles because they can provide control over the particle stoichiometry, shape, size distribution, crystallinity and phase purity [13]. Numerous chemical methods have been developed that have proven viable for the synthesis of nanoparticles. The most popular chemical methods of synthesis of nanomaterials [34-40] include formation through a chimie douce solution chemistry methodology, a sol-gel processing mechanism, the use of microemulsions, the utilization of hydrothermal and solvothermal methods, the kinetic control of growth through the use of capping reagents, the application of template inspired methodologies, and Lastly, biomimetic synthesis. These methods have their own set of advantages and disadvantages in terms of ease of preparation, duration of synthesis, extent of instrumentation required and also the availability of the precursors and their economic viability. In contrast to physical methods, which often require breaking a larger sample into smaller components, these methods grow particles from the constituent atoms. In general, these synthesis routes utilize some form of solution chemistry thereby
providing pathways to kinetically stable phases that can be different from those obtained using traditional bulk preparation methods [17-19,41]. As a result, chemical methods are sometimes used to produce a pre-cursor material which is then annealed to yield the final product.

Energy-efficient synthesis and processing routes of nanocrystalline spinel ferrites are prerequisite for technological applications [14]. Among many types of preparation and processing techniques, reverse micelles, which are essentially nanosized aqueous droplets that exist in microemulsions with certain compositions, are known to present an excellent medium for the synthesis of nanoparticles [42-44]. It is the inherent ability of this reaction system to control the size and size distribution that makes it attractive for the synthesis of nanoparticles [45].

As magnetic materials, soft ferrites are best suited for high frequency applications. Among soft spinel ferrites nickel-zinc ferrites are found to be very attractive and versatile magnetic materials, which have applications in both low and high frequency devices and play significant role in technological applications such as microwave devices, power transformers in electronics, rod antennas, read/write heads for high speed digital tapes etc. because of their high resistivity [46], low dielectric losses, high curie temperature and chemical stability. Structural and magnetic properties of nickel-zinc ferrites are highly sensitive to composition, sintering condition, grain size, type and amount of additives, impurities and the preparation methodology [47-49]. The various compositions of the bulk system Ni$_{1-x}$Zn$_x$Fe$_2$O$_4$ ($x = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9$) [50-59] have been investigated and reported in literature. This system has also been extensively studied for various properties as well as for structural and characterization techniques in nanometric range. The material can be synthesized by numerous different chemical and physical methods [60-70]. A very few numbers of investigations have been made on structural and magnetic properties of nickel-zinc ferrite particles synthesized via reverse micelle technique [71-75].

A large number of investigations have been made on trivalent impurities (Al$^{3+}$, Cr$^{3+}$, In$^{3+}$) substituted spinel ferrite to understand their magnetic and electric properties [53,67,76-81]. It has been shown that the magnetic and other properties of ferrite particles can be upgraded by incorporating suitable diamagnetic impurities [53,78-81]. Very little
work has been reported on the Mössbauer investigations in case of trivalent indium (In$^{3+}$) ions doped in stoichiometric compositions of nickel-zinc ferrites. Parvatheeswara Rao et al [80] have studied the substitution of indium ions in the nickel-zinc system. They found that saturation magnetization increases slightly for a certain concentration of indium ions thereafter it decreases. Their assertion on this type of anomalous behavior of magnetization as a function of indium ions concentration in nickel-zinc ferrite systems was corroborated by the experiments of Lakshman et al [78] and Ghosh et al [79] on indium substituted Mg-Mn ferrite. They interpreted this effect in terms of distribution of the indium ions behavior at tetrahedral and octahedral sites. Kirichok et al [76] have studied the Mössbauer investigations of magnesium ferrite doped with indium ions. They found that indium ions replace primarily the iron ions in the tetra-positions and with further increase in concentration of indium ions they partially occupy octa-positions.

Very little work has been reported on the bulk ferrite particles prepared by annealing nano particles at high temperature [62,64,67,81-83]. Upadhyay et al [64] have investigated nickel-zinc ferrite (Ni$_{1-x}$Zn$_x$Fe$_2$O$_4$, $x = 0.0$, 0.25, 0.50, 0.75, 1.0) systems prepared by chemical precipitation followed by hydrothermal treatment, using Mössbauer spectroscopy and found that the occupancy of nano particles returns to normal values after heat treatment.

1.3 Aim of present work and outline of thesis

In the present work, we have chosen nickel-zinc ferrite as basic material. Due to the inherent ability of reverse micelle technique to control the size and size distribution of nanoparticles in comparison to other techniques, we have chosen this technique for synthesis of nanoparticles. Among the different possible compositions of nickel-zinc ferrites, low value of dielectric constant and dielectric loss obtained in Ni$_{0.58}$Zn$_{0.42}$Fe$_2$O$_4$ ferrites show its applicability at high frequencies [46]. The Ni$_{0.58}$Zn$_{0.42}$Fe$_2$O$_4$ has, therefore, been used as the basic ferrite material. We have successively substituted diamagnetic In$^{3+}$ ions in place of Fe$^{3+}$ ions to achieve a possible upgrading of the magnetic properties. Bulk samples have been prepared by annealing the reverse micelle synthesized nanoparticles at high temperature (~1473 K).
The magnetic hyperfine structure of the nickel-zinc ferrites $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ have been the subjects of many years [51-53,58], but we have not found any Mössbauer investigations on nano nickel-zinc ferrite systems synthesized via reverse micelle technique. It would be interesting to investigate the site preference of nickel and zinc ions in nickel-zinc ferrite system where one of the cations has a strong preference for tetrahedral and the other for octahedral sites. It is widely appreciated that the cation distribution in spinel ferrites, upon which many physical and chemical properties depend, are a complex function of processing parameters and depends on the preparation method of the material [84,85]. It should be emphasized that in most of the papers on reverse micelle synthesis of spinel ferrites [71-75,86,87], not much work has been done to determine the structure of oxides, finite size effect and interparticle interactions among the nanoparticles. Especially, the evaluation of the cation distribution in reverse micelle synthesized spinel ferrites from Mössbauer spectra and/or X-ray diffraction patterns is not as straightforward as is frequently claimed in the literature. Because of the importance of the site inversion phenomena, we have first focused on the structural change at nano level. Once these site inversion phenomena are understood and controlled, we can use our particles for size dependent studies. We have investigated in detail the thermal and nanoparticle size dependence of the high field magnetization of ferrite particles. The small size of the nanoparticles indeed leads to enhanced finite-size and surface spin effects. We have analyzed the thermal variations of magnetization in high fields to investigate the finite-size effect and an extra surface contribution. The magnetic behavior of nanoparticles is strongly affected also by interparticle interactions. The magnetic interactions can be due to dipolar coupling and exchange coupling among surface atoms and play a fundamental role in the physics of these systems [88-90]. The role of interactions on the static and dynamic properties of ferrite nanoparticles is investigated.

To our knowledge, no systematic and comparative study of nano and bulk nickel-zinc ferrite and indium doped nickel-zinc ferrite samples prepared by reverse micelle technique has been reported yet. The structural, magnetic and Mössbauer characterization of the prepared nano and bulk samples is carried out using different techniques.
Chapter 1: Introduction

Considering all the above mentioned points, the present thesis aims

- To prepare uniform and spherical nanoparticles of nickel-zinc ferrite (Ni$_{0.58}$Zn$_{0.42}$Fe$_2$O$_4$) and indium doped nickel-zinc ferrite (Ni$_{0.58}$Zn$_{0.42}$In$_x$Fe$_{2-x}$O$_4$, x = 0.1, 0.2, 0.3) samples via reverse micelle technique followed by annealing at high temperature to make bulk samples.

- To study the effect of pH value of precipitation on the formation of spinel phase and on the particle size.

- To see the effect of co-substitution of diamagnetic (In$^{3+}$) ion at iron (Fe$^{3+}$) site in nickel-zinc ferrite system to understand the various magnetic exchange interactions.

- To study the structural properties of nano and bulk ferrite particles using X-ray diffraction, transmission electron microscopy (TEM), far-infrared transmission spectra (FTIR).

- To obtain the quantitative structural information about the nonequilibrium cation distribution and the noncollinear spin arrangement in nanosized particles using in-situ Mössbauer spectroscopy.

- To study the magnetic properties of nano and bulk ferrite systems using superconducting quantum interference magnetometer (SQUID) and vibrating sample magnetometer (VSM).

- To see the effects of the particle size and indium concentration on the physical properties of nano samples viz. surface effects, cation distribution, superparamagnetic relaxation, interparticle interaction, saturation magnetization, and coercivity.

- To study the finite size effect and an extra surface contribution at low temperature using Bloch’s law.

- To study the spin dynamics in nano particles using ac susceptibility measurements and role of interactions on the static and dynamic properties of nanoparticles using different models.

From the application point of view, a comparative study of nano and bulk samples is also carried out.
This thesis is divided into seven chapters.

Chapter 1 contains the introduction to ferrites, nanoferrites, literature survey, aim of the present work and outline of the thesis.

Chapter 2 presents the theoretical concepts used/developed in this work. Various models have been described to understand the magnetism of ferrite and nanoferrite particles. A brief description of technique used for preparation of nanocrystalline ferrite samples is included.

Chapter 3 describes the various experimental techniques used for the preparation and characterization of nano and bulk samples.

Chapter 4 focuses on the study of structural properties of nano and bulk samples using X-ray diffraction, transmission electron microscopy and fourier transform infrared spectroscopy measurements.

Chapter 5 includes the experimental results and observations obtained by Mössbauer spectroscopy. Effect of indium concentration, particles size and temperature on the Mössbauer parameters of nickel-zinc ferrite sample has been described. A comparative study on nano and bulk samples has also been illustrated.

Chapter 6 describes magnetic properties of nano and bulk samples using super conducting quantum interference device (SQUID) magnetometer, vibrating sample magnetometer (VSM) and ac susceptometer. Effect of particle size and indium concentration on the magnetic properties of nickel-zinc ferrite particles has been described. The thermal variation of magnetization in high fields in terms of a modified Bloch’s law, the role of interactions on the static and dynamic properties of nano samples have also been discussed.

Chapter 7 represents the summary and conclusions obtained through various studies. Suggestions for the future work on the samples studied have also been included in this chapter.
References


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