Chapter 1

Introduction to ferrites

1.1 Introduction

Now a day’s nanotechnology is an important branch of science and technology and has taken a lead role in the 21st century. In current material science, nano scale materials have stimulated great interest due to their importance in basic scientific research and potential technology applications such as microelectronic devices [1], chemical and biological sensors [2], light emitting displays [3], catalysis [4], energy storage and conversion devices [5], water splitting [6], dye sensitized solar cells (DSSCs) [7, 8], photo catalysis [9] etc. In the past decade, nano materials have been the subject of enormous interest because fundamental physical, chemical, electronic, magnetic and optical properties are also quite different at this nano level when compared to larger scale materials and they have potential applications in nano scale devices [10-13]. This opens the new era for scientist, researchers, technologist and engineers to study the nano materials with different properties.

The chemical and physical properties of nano materials can significantly differ from those of bulk materials of same chemical composition. The uniqueness of the structural characteristics, energetics, response, dynamics and chemistry of nanostructures constitutes the experimental and conceptual background for the field of nanoscience. Suitable control of properties and response of nanostructures can lead to new devices and technologies. The underlying themes of nano science and nanotechnology are dual: first, the bottom-up approach of the self-assembly of molecular components where each molecular or nano structured component plugs itself into a superstructure [14]; second, the top-down approach of miniaturization of the components [15]. The deviation of properties of the nano sized materials from the bulk material properties are due to surface effects which mainly depend upon the ratio of surface area to volume and size of the particles along with the chemical
composition and interaction between particles. The increase in surface to volume ratio, which is a gradual progression as the particle gets smaller, leads to an increasing dominance of the behavior of atoms on the surface of particles over that of those in the interior of particle as these atoms have lower coordination number than the interior atoms. In addition, depending on the geometry, different sites on the surface will be different in local coordination number [16]. In the last two decades; a class of materials with a nanometer-sized microstructure have been synthesized and studied. These materials are assembled from nanometer-sized building blocks, mostly crystallites. The building blocks may differ in their atomic structure, crystallographic orientation or chemical composition. In cases where the building blocks are crystallites, incoherent or coherent interfaces may be formed between them, depending on the atomic structure, the crystallographic orientation, and the chemical composition of adjacent crystallites. In other words, materials assembled of nanometer-sized building blocks are micro-structurally heterogeneous, consisting of the building blocks (e.g. crystallites) and the regions between adjacent building blocks (e.g. grain boundaries). The inherently heterogeneous structure on a nanometer scale that is crucial for many of their properties and also distinguishes them from glasses, gels etc., that are micro structurally homogeneous [17].

1.2 Magnetic nano particles

Magnetic nano particles are a class of nano particle which can be manipulated using magnetic field. Such particles commonly consist of magnetic elements such as iron, nickel and cobalt and their chemical compounds. While nano particles are smaller than 1 micrometer in diameter (typically 5–500 nanometers), the larger micro beads are 0.5–500 micrometer in diameter. The magnetic nano particles have been the focus of much research recently because they possess attractive properties which could see potential use in catalysis including nano material-based catalysts [18], biomedicine [19], magnetic resonance imaging [20], magnetic particle imaging [21], data storage [22],
environmental remediation [23], nano fluids [24], and optical filters [25], defect sensor [26] and cation sensors [27].

1.2.1 Types of magnetic nano particles

Currently, three different kinds of magnetic nano particles are being produced and used

i) Oxides: ferrite

Ferrite nano particles are the most explored magnetic nano particles up to date. Once the ferrite particles become smaller than 128 nm [28] they become super paramagnetic which prevents self-agglomeration since they exhibit their magnetic behavior only when an external magnetic field is applied. With the external magnetic field switched off, the remanence falls back to zero. Just like non-magnetic oxide nano particles, the surface of ferrite nano particles is often modified by surfactants, silicones or phosphoric acid derivatives to increase their stability in solution [29]

ii) Metallic

Metallic nano particles have the great disadvantage of being pyrophoric and reactive to oxidizing agents to various degrees. This makes their handling difficult and enables unwanted side reactions.

iii) Metallic with a shell

The metallic core of magnetic nano particles may be passivated by gentle oxidation, surfactants, polymers and precious metals [30]. In an oxygen environment, Co nano particles form an anti-ferromagnetic CoO layer on the surface of the Co nano particle. Recently, work has explored the synthesis and exchange bias effect in these Co core CoO shell nano particles with a gold outer shell [31]. Nano particles with a magnetic core consisting either of elementary Iron or Cobalt with a non reactive shell made of graphene have been synthesized recently [32]. The advantages compared to ferrite or elemental nano particles are:

• Higher magnetization
• Higher stability in acidic and basic solution as well as organic solvents
• Chemistry [33] on the graphene surface via methods already known for carbon nano tubes

1.2.2 Applications of magnetic nano particles

i) Medical diagnostics and treatments

Magnetic nano particles are used in an experimental cancer treatment called magnetic hyperthermia [34] in which the fact that nano particles heat when they are placed in an alternative magnetic field is used.

Another potential treatment of cancer includes attaching magnetic nano particles to free-floating cancer cells, allowing them to be captured and carried out of the body. The treatment has been tested in the laboratory on mice and will be looked at in survival studies [35, 36].

Magnetic nano particles can be used for the detection of cancer. Blood can be inserted onto a micro fluidic chip with magnetic nano particles in it. These magnetic nano particles are trapped inside due to an externally applied magnetic field as the blood is free to flow through. The magnetic nano particles are coated with antibodies targeting cancer cells or proteins. The magnetic nano particles can be recovered and the attached cancer-associated molecules can be assayed to test for their existence.

Magnetic nano particles can be conjugated with carbohydrates and used for detection of bacteria. Iron oxide particles have been used for the detection of Gram negative bacteria like Escherichia coli and for detection of Gram positive bacteria like Streptococcus Suis [37, 38].

ii) Magnetic immunoassay

Magnetic immunoassay[39] (MIA) is a novel type of diagnostic immunoassay utilizing magnetic beads as labels in lieu of conventional, enzymes, radioisotopes or fluorescent moieties. This assay involves the specific binding of an antibody to its antigen, where a magnetic label is conjugated to one element of the pair. The presence of magnetic beads is then detected by a magnetic reader (magnetometer) which measures the magnetic field change induced by the beads. The signal measured by the magnetometer is proportional
to the analyte (virus, toxin, bacteria, cardiac marker, etc.) quantity in the initial sample.

iii) Waste water treatment

Thanks to the easy separation by applying a magnetic field and the very large surface to volume ratio, magnetic nano particles have a good potential for treatment of contaminated water [40]. In this method, attachment of EDTA-like chelators to carbon coated metal nano magnets results in a magnetic reagent for the rapid removal of heavy metals from solutions or contaminated water by three orders of magnitude to concentrations as low as micrograms per litre.

iv) Chemistry

Magnetic nano particles are being used or have the potential use as a catalyst or catalyst supports [41]. In chemistry, a catalyst support is the material, usually a solid with a high surface area, to which a catalyst is affixed. The reactivity of heterogeneous catalysts occurs at the surface atoms. Consequently great effort is made to maximize the surface area of a catalyst by distributing it over the support. The support may be inert or participate in the catalytic reactions. Typical supports include various kinds of carbon, alumina, and silica.

v) Biomedical imaging

There are many applications for iron-oxide based nano particles in concert with magnetic resonance imaging [42]. Magnetic CoPt nano particles are being used as an MRI contrast agent for transplanted neural stem cell detection [43].

vi) Information storage

Research is going into the use of using MNPs for magnetic recording media. The most promising candidate for high-density storage is the face-centered tetragonal phase FePt alloy. Grain sizes can be as small as 3 nanometers. If it's possible to modify the MNPs at this small scale, the information density that can be achieved with this media could easily surpass 1 Terabyte per square inch [44].
vii) Genetic engineering

Magnetic nano particles can be used for a variety of genetics applications. One application is the isolation of mRNA. This can be done quickly – usually within 15 minutes. In this particular application, the magnetic bead is attached to a poly T tail. When mixed with mRNA, the poly A tail of the mRNA will attach to the bead’s poly T tail and the isolation takes place simply by placing a magnet on the side of the tube and pouring out the liquid. Magnetic beads have also been used in plasmid assembly. Rapid genetic circuit construction has been achieved by the sequential addition of genes onto a growing genetic chain, using nano beads as an anchor. This method has been shown to be much faster than previous methods, taking less than an hour to create functional multi-gene constructs in vitro [45].

1.3 Magnetic materials

Magnetic materials can be divided into two group soft and hard magnetic materials. The soft magnetic materials are those materials which are magnetized and demagnetized easily while the hard magnetic materials are those which are difficult to magnetize and demagnetize. The hard magnetic materials have high coercivily, because the high coercivity resists the magnetization action. The basic difference of two types of permanent magnets was described on the basis of hysteresis loop. The soft magnetic materials exhibit a narrow hysteresis loop, whereas; the hard magnetic materials show a broad hysteresis loop. In the narrow hysteresis loop magnetization follows the variation of the applied field without significant loss. The broad hysteresis loop shows the magnetic energy that can be stored in the materials [46].

1.3.1 Soft magnetic materials

Soft magnetic materials can be easily magnetized and demagnetized. They retain their magnetization only in presence of a magnetic field. They show a narrow hysteresis loop, so that the magnetization follows the variation of applied field nearly without hysteresis loss [47]. They are used to enhance the flux, produced by an electric current in them. The quality factor of a soft
magnetic material is to measure of its permeability with respect to the applied magnetic field. The other main parameter is the coercivity, saturation magnetization and the electrical conductivity. An ideal soft magnetic material would have low coercivity (Hc), a very large saturation magnetization (Ms), zero remanence (Br), zero hysteresis loss and very large permeability [48].

### 1.3.2 Hard magnetic materials

Hard Magnetic materials also called as permanent magnets are used to produce strong field without applying a current to coil. Permanent magnets required high coercivity, so they should exhibit a strong net magnetization and is stable in the presence of external fields, which requires high coercivity. In hard magnetic materials uniaxial magnetic anisotropy is necessary and the following magnetic properties are required[49]. Important properties of hard magnetic materials are mentioned below:

**i) High coercivity:**

The coercivity, also called the coercive field, of a ferromagnetic material is the intensity of the applied magnetic field required to reduce the magnetization of that material to zero after the magnetization of the sample has been driven to saturation. Coercivity is usually measured in oersted or ampere/meter units and is denoted Hc. Materials with high coercivity are called hard ferromagnetic materials, and are used to make permanent magnets [50].

**ii) Large magnetization:**

The process of making a substance temporarily or permanently magnetic, as by insertion the material in a magnetic field.

**iii) Rectangular hysteresis loop:**

A hysteresis loop shows the relationship between the induced magnetic flux density (B) and the magnetizing force (H). hard magnetic materials have rectangular hysteresis loop [51].
1.4 Ferrites

Ferrites are magnetic ceramics containing iron oxide as a major constituent in it. It is now some 70 years since ferrites debuted as an important new category of magnetic materials. These are now very well established group of magnetic materials. Today ferrites are employed in a truly wide range of applications, and have contributed materially to the advances in electronics. In the area of new materials, ferrites with permeabilities up to 30,000 and power ferrites for frequencies up to 10 MHz have been made available commercially. Even though, improvements and innovations continue to take place; many new applications, theories and preparation technologies are currently under development in field of ferrites.

Ferrites are iron based oxides with technologically fascinating magnetic properties, making them a prominent category in magnetic materials. The ferrite particles in nano-regime with significant change of physical properties provide more advantages over the bulk ferrites [52]. With regards to the rapidly mounting field of nanotechnology, ferrite nano particles have been the core of extensive research pertaining to their widespread applications, be it biomedical, techno-logical or industrial. Nano crystalline particles of magnetic materials show substantially enhanced magnetic properties.

The unit cell of the spinel ferrite is formed by doubling the face centered cubic oxygen sub lattice along each of the three dimensions. In this arrangement 64 tetrahedral or A-sites and 32 octahedral or B-sites are created in the unit cell. In stoichio metric spinels only 8 A-sites and 16 B-sites are filled by divalent transition-metal ions. The spine compounds belong to the space group Fd3m (F4/m3m, No. 227 in the International Tables for X-ray Crystallography) with lattice parameter 8.5 Å. In mixed spinel ferrites the concentrations of ferrous, ferric and substituted metal ions and their distribution over tetrahedral and octahedral sites play a vital role in determining their magnetic and electrical properties. In normal spinels, all the A-sites are occupied by divalent transition metal ions while in inverse spinels; the divalent ions occupy B-sites. In disordered spinels the divalent ions are present on both
A and B-sites. The normal and inverse spinels are two extremes between which the cation distribution may vary. When the origin of the unit cell is taken at the centers of symmetry $4\bar{3}m$ and $\bar{3}m$, then oxygen positional parameter ‘$u$’ (the distance between the oxygen ion and the face of the cube edge along the cube diagonal of the spinel sub cell) has ideal values 0.375 (3/8) and 0.250 (1/4) respectively, for a perfect cubic close-packed arrangement of oxygen ions. In this case the octahedral cation–anion distance or bond length is 1.155 times larger than the tetrahedral bond length. A deviation from the ideal structure occurs when oxygen is displaced along [111] direction to accommodate the constituent cations, the tetrahedral site with smaller volume enlarges at the expense of the octahedral site and then $u$ a value greater than 0.375. In order to control the domain of ferrite’s applications, the investigation of cation distribution on A and B sites and oxygen positional parameter $u$, is most important [53, 54].

1.4.1 Applications of ferrites

The field of spinel ferrites is well cultivated because of their various potential applications and the interesting physics involved in it. Even after more than half of the century the scientist, researchers, technologist, and engineers are still excited in various types of bulk as well as nano crystalline ferrite materials. The recent trend is focused on the doped ferrites prepared using various synthesis techniques with different cation concentrations which intern affects the various properties like, electrical, dielectric, and magnetic behavior. Ferrite materials are important magnetic materials, which have various applications in power conditioning and conversion. Due to their distinct magnetic properties, ferrite materials have been widely used to prepare many electromagnetic devices such as inductors, converters, phase shifters and electromagnetic wave absorbers [55, 56].

Industrial applications of magnetic nano particles cover abroad spectrum such as magnetic seals in motors, magnetic inks for bank cards, magnetic
recording media and biomedical applications such as magnetic resonance contrast media and therapeutic agents in cancer treatment [57-61]. Each potential application requires the magnetic nanoparticles to have different properties. For example, in data storage applications, the particles need to have a stable, switchable magnetic state to represent bits of information, a state that is not affected by temperature fluctuations.

**Inductors:** Ferrites are primarily used as inductive components in a large variety of electronic circuits such as low noise amplifiers, filters, voltage-controlled oscillators, impedance matching networks, for instance. Their recent applications as inductors obey, among other tendencies, to the general trend of miniaturization and integration as ferrite multilayers for passive functional electronic devices. The multilayer technology has become a key technology for mass production of integrated devices; multilayers allow a high degree of integration density. Multilayer capacitors penetrated the market a few decades ago, while inductors started in the 1980s.

**High Frequency:** There has been an increasing demand of magnetic materials for high-frequency applications such as telecommunications and radar systems, as microwave technology requires higher frequencies and bandwidths up to 100 GHz. Ferrites are non conducting oxides and therefore allow total penetration of electromagnetic fields, in contrast with metals, where the skin effect severely limits the penetration of high-frequency fields [62].

**Power Application:** Power applications of ferrites are dominated by the power supplies for a large variety of devices such as computers, all kinds of peripherals, TV and video systems, and all types of small and medium instruments. The main applications in the systems known as switched-mode power supplies (SMPS). In this application, the mains power signal is first rectified it is then switched as regular pulses (typically rectangular) at a high frequency to feed into a ferrite transformer, and finally it is rectified again to provide the required power to the instrument. An increase in power delivery and efficiency can be obtained by increasing the working frequency of the
Electromagnetic Interference (EMI) Suppression: The significant increase in the amount of electronic equipment such as high-speed digital interfaces in notebooks and computers, digital cameras, scanners, and so forth, in small areas, has seriously enhanced the possibility of disturbing each other by electromagnetic interference (EMI). In particular, the fast development of wireless communications has led to interference induced by electric and magnetic fields. Electromagnetic interference can be defined as the degradation in performance of an electronic system caused by an electromagnetic disturbance [63]. The noise from electric devices is usually produced at frequencies higher than circuit signals. To avoid, or at least reduce EMI, suppressors should work as low-pass filters, that is, circuits that block signals with frequencies higher than a given frequency value. There are several approaches to build EMI suppressors: soft ferrites [64], ferromagnetic metals [65], ferromagnetic metal/hexaferrite composites [66], encapsulated magnetic particles [67], and carbon nano tube composites [68].

High-density write-once optical recording: Thin films of defect spinel ferrites can be used as write-once read-many media working with blue wavelengths. In fact, because these non-stoichio metric ferrites are meta stable, they can be transformed into corundum phases at moderate temperatures by a laser spot. The transformed regions have different optical indices from the starting ferrite film, making the readout process possible.

Magnetic sensors: These are used for temperature control and these can be made using ferrite with sharp and definite Curie temperature. Position and rotational angle sensors (proximity switches) have also been designed using ferrites.

Magnetic shielding: A radar absorbing paint containing ferrite has been developed to render an aircraft of submarine invisible to radar.

Pollution control: There are several Japanese installations which use precipitation of ferrite precursors to scavenge pollutant materials such as
mercury from waste streams. The ferrites produced subsequently can be separated magnetically along with the pollutant.

**Ferrite electrodes:** Because of their high corrosion resistance, ferrites having the appropriate conductivities have been used as electrode in applications such as chromium plating.

**Entertainment ferrites:** Ferrites are widely used in radio and television circuits. Typically applications include deflection Yokes, fly back transformers and SMPS transformer for power applications.

### 1.5 Literature survey and aim of the present work

The structural, magnetic and dielectric properties of ferrites are of great importance to select materials for specific applications. Some factors which affect the properties of ferrites are the type and amount of substitution, chemical composition, methods of preparation and different types of irradiation. Since the research on ferrites is so vast, it is very difficult to collect all the experimental results and information’s about all types of ferrites in every aspect that’s why restrict our self to present a systematic review of different theoretical and experimental facts related to this present study. This literature survey not only highlights the various modifications attempted by various researchers and to mention the updated research activities in this important field but also to recognize the possible potential applications for which this material is of crucial significance.

Cobalt ferrite (CoFe$_2$O$_4$) a well-known hard ferromagnetic material, in its bulk form crystallizes in mixed spinel structure with space group Fd3m represented as \((Co_{x}^{2+}Fe_{1-x}^{3+})[Co_{1-x}^{3+}Fe_{x}^{3+}]O_4\), where round and square brackets indicate A and B sites, respectively, and x depends on the thermal history and preparation conditions [69]. The anti parallel alignment of magnetic moments of A-site with B-site is coupled by super exchange interaction through the O$^{2-}$ ions, which shows ferri magnetism [70]. Since the \(Fe_{3}^{3+} - Fe_{5}^{3+}\) super exchange interactions differs from the \(Co_{3}^{2+} - Fe_{5}^{3+}\) interactions, variation of
the cation distribution over the A and B sites in the spinel leads to different magnetic properties of this ferrite even though the chemical compositions of the compounds do not change [71]. It has a curie temperature around $\sim 520$ °C, and exhibits high coercivity, moderate saturation magnetisation and good chemical stability [72]. Hence this material is a promising candidate for most technological applications at room temperature such as data storage devices, magnetic sensors, actuators, targeted drug delivery, medical diagnosis, etc. [73-76]. The cubic CoFe$_2$O$_4$ has large magneto crystalline anisotropy energy with positive anisotropy constant. It has six easy directions along the cube edges of the crystal represented as <100>, four hard directions across the body diagonals denoted as <111> and twelve saddle points across the face diagonals, which lead to positive magneto crystalline anisotropy constant [77,78]. The large magneto crystalline anisotropy energy of cobalt ferrite is mainly attributed to the Co$^{2+}$ ions on the B sites of the spinel. As the crystal field is not capable to quench the orbital magnetic moment, there is a strong spin-orbit coupling (L-S coupling) and due to this coupling there is large magneto crystalline anisotropy energy (MAE) [79].

The properties of ferrites are greatly depends upon the type and amount of dopant. Cr$^{3+}$ and Al$^{3+}$ ions are known to change the properties of ferrite and are invested by several workers. Jianxun Qiu et al. studied the Effect of Cr substitution on microwave absorption of BaFe$_{12}$O$_{19}$ [80]. Vasambekar et al. studied cation distribution and susceptibility study of Cd-Co and Cr$^{3+}$substituted Cd-Co ferrites [81]. Radhapiyari et.al. studied magnetic properties of Cr$^{3+}$ substituted Li-Sb ferrites [82]. The effect of Al-substitution on the magnetic and electrical properties of different ferrites was studied by many authors [83-87]. Influence of Al$^{3+}$ ion concentration on the crystal structure and magnetic anisotropy of nano crystalline spinel cobalt ferrite has been studied by Lawrence Kumar and Manoranjan Kar [88]. Gul et. al. studied Optical, magnetic and electrical investigation of cobalt ferrite nano particles synthesized by co-precipitation route [89].

The substitutional effect of Cr$^{3+}$ ions, when they replaces Fe$^{3+}$ ions show
some interesting results [90,91]. The effect of replacement of Fe\textsuperscript{3+} ions by Cr\textsuperscript{3+} ion have been studied by various workers [92, 93]. Lee et al. studied the magnetic properties and showed magnetic moment and Curie temperature decreases with Cr\textsuperscript{3+} substitution [94]. Magnetic properties like remanence and coercivity which are of utmost technological importance could be modified and controlled by Cr\textsuperscript{3+} substitution [95]. It was also found that the crystallographic transport and magnetic properties were also affected for Cr-substituted ferrites [96].

Manganese ferrite (MnFe\textsubscript{2}O\textsubscript{4}), Mn-Fe-O has received a great attention in the area of magnetic storage device, microwave, and electronic device because it has high magnetic permeability and high electrical resistance. Many research groups have investigated to enhance the magnetic property of magnetic materials such as manganese ferrite. MnFe\textsubscript{2}O\textsubscript{4} is a ferrimagnet (\( T_N = 560 \) K) having the spinel structure with two in equivalent sub lattices of tetrahedral (A) and octahedral [B] symmetries for the magnetic ions sites [97-100]. Mn cation in spinel is at its high spin state. Its five d electrons display the configurations \( e^2t_2^3 \) and \( t_{2g}^3e_g^2 \) at the tetrahedral and octahedral lattice site, respectively. As a result, the coupling between the electron spin and the angular momentum of its orbital should be rather small in Mn cations [101].

By considering the above facts and importance of cobalt ferrite, manganese ferrite and Al\textsuperscript{3+}/Cr\textsuperscript{3+} substitution it was decided that to prepare the CoMn\(_{1-x}\)Al\(_x\)FeO\(_4\) and CoMn\(_{1-x}\)Cr\(_x\)FeO\(_4\) ferrite systems where \( x = 0.0-1.0 \) in steps of \( x = 0.25 \), in order to investigate structural and magnetic properties.
References


[44] Natalie A. Frey and Shouheng Sun Magnetic Nano particle for Information Storage Applications


