Chapter 1

General Introduction

A general introduction on nanomaterials, magnetism of nanoparticles and spinel ferrites has been presented. Some of the known peculiar properties of nanomaterials including surface plasmon resonance and quantum size effect have been discussed. Magnetism of nanoparticles is outlined, touching up on anisotropy and superparamagnetism. Classification of ferrites and the crystal structure of spinel ferrite, the focal theme of the thesis, are given in detail. Magnetism of ferrites has been discussed in terms of Neel’s theory of ferrimagnetism using super exchange interactions. A brief description of electrical conduction in ferrites, with special reference to the hopping model of electrons and small polaron model is given.
Material science and technology is a field that is evolving at a very fast pace, and is currently making the most significant contributions to nanoscale research. Nanomaterials and nanostructures, a new branch of material research is attracting a great deal of attention because of its potential applications in areas such as electronics, optics, catalysis, ceramics, information storage, medicine and health care etc. It is driven by the desire to fabricate materials with novel or enhanced properties. The discovery of novel materials, processes and phenomena at the nanoscale, as well as the development of new experimental and theoretical techniques for research provide opportunities for the development of innovative nanosystems and nanostructured materials. In order to design nanomaterials for the next generation nanodevices, it is essential to understand their structural, electrical, electronic, chemical and magnetic properties. Researches are progressing all over the world towards the development of nanomaterials that are expected to perform more complex and efficient tasks; for example materials with a higher rate of decomposition of pollutants, selective and highly sensitive sensors, effective contrast agents in medical imaging, efficient carriers for targeted drug delivery and hyperthermia treatment of cancer, tougher and harder cutting tools, high density information storage or more efficient energy storage systems [1]. Thus the development of completely new technologies and innovative nanomaterials with desirable functional properties may lead to a new generation of products that will improve the quality of life and environment in the near future.

1.1 Nanomaterials

Nanomaterials can be defined as those, whose characteristic length scale lies within the nanometric range, i.e. in the range between 1 and 100nm [2]. Atoms have a size of 1 to 4Å. Therefore nanostructured materials could hold tens or thousands of atoms together. These particles often display properties
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intermediate between quantum and bulk materials. Nanostructured organic, inorganic and biological materials may have existed in nature since the evolution of life on earth. Some evident examples are micro organisms, fine grained minerals in rocks, nanoparticles in bacteria and smoke [3]. Nature makes nanomaterials of varying kind. For instance, magnetite (Fe₃O₄) particles of nanometre size are made by the bacteria, Magnetosperillum Magnetotacticum and the magnetism caused by the particles helps in finding a direction favourable for its growth. There are several bacteria like the familiar Lactobacillus which can absorb metal ions added in to butter milk, and reduce them inside the cell and make nanoparticles. Fungi and viruses are also known to make nanoparticles [4].

Table 1.1 Typical nanomaterials.

<table>
<thead>
<tr>
<th>Type</th>
<th>Size (approx.)</th>
<th>Materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Nanocrystals &amp; Clusters (quantum dots)</td>
<td>diameter 1-10nm</td>
<td>Metals, semiconductors, magnetic materials</td>
</tr>
<tr>
<td>Other nanoparticles</td>
<td>diameter 1-100nm</td>
<td>Ceramic oxides</td>
</tr>
<tr>
<td>(b) Nanowires</td>
<td>diameter 1-100nm</td>
<td>Metals, semiconductor oxides, sulfides &amp; nitrides</td>
</tr>
<tr>
<td>Nanotubes</td>
<td>diameter 1-100nm</td>
<td>Carbon, layered metal chalcogenides</td>
</tr>
<tr>
<td>(c) 2-Dimensional arrays (of nanoparticles)</td>
<td>several nm²-μm²</td>
<td>Metals, semiconductors, magnetic materials</td>
</tr>
<tr>
<td>Surfaces &amp; thin films</td>
<td>thickness 1-1000nm</td>
<td>Various materials</td>
</tr>
<tr>
<td>(d) 3-Dimensional structures (superlattices)</td>
<td>Several nm in all three dimensions</td>
<td>Metals, semiconductors, magnetic materials</td>
</tr>
</tbody>
</table>

The application of nanoparticles can be historically traced back to even before the generation of modern science and technology. Nanoparticles were used as dye
materials in ceramics by ancient people [5]; colloidal gold was used in the medical treatment of dipsomania, arthritis etc, as early as from nineteenth centuries. Systematic experiments on nanomaterials were started from the known Faraday experiment in 1857 [6].

Table 1.1 [7] summarizes the typical nanomaterials, which include zero dimension nanostructures such as metallic, semiconducting and ceramic nanoparticles; one dimension nanostructures such as nanowires, nanotubes, and nanorods; two dimension nanostructures such as thin films. Besides these individual nanostructures, ensembles of these nanostructures form high dimension arrays, assemblies and super lattices.

1.1.1 Synthesis: Bottom-up and Top-down Approaches

There are two different approaches to the synthesis of nanomaterials and the fabrication of nanostructures: top-down and bottom-up. Top-down method is to start with a chunk of the material and successive cutting it into nanoscale; however bottom up method is to start with individual atoms and building up to a nanostructure. Milling is a typical top-down method where as the colloidal dispersion is a good example of bottom-up approach. Both approaches play very important role in nanotechnology for the fabrication of nanomaterials.

The top-down approach is extremely powerful and can deliver microscale objects effectively and reproducibly. However this strategy becomes increasingly challenging, as the dimensions of the target structures approach the nanoscale. Another disadvantage of top-down approach is the imperfection of the surface structure. It is well known that the conventional top-down techniques such as lithography can cause significant crystallographic damage to the processed patterns, and additional defects can happen during the etching steps. Such imperfections could have a significant impact on physical properties and surface chemistry of nanomaterials due to the increased surface to volume ratio. The
surface imperfections would result in a reduced conductivity due to inelastic
surface scattering, which in turn would lead to the generation of excessive heat
and thus impose extra challenges to the device design and fabrication.

Bottom-up approach refers to the build up of a material from the bottom: atom-by-atom, molecule-by-molecule or cluster-by-cluster. Although this method is nothing new, it plays an important role in the fabrication of nanostructures and nanomaterials. Bottom-up methods provide nanomaterials with less defects, more homogeneous chemical composition and better short and long range ordering [8].

1.1.2 Properties

Nanomaterials have the structural features in between those of atoms and the bulk materials. While most microstructured materials have properties similar to the corresponding bulk materials, the properties of materials with nanometre dimensions are significantly different from those of atoms and bulk materials. This is mainly due to the nanometre size of the materials which render them: (i) large fraction of surface atoms; (ii) high surface energy; (iii) spatial confinement and (iv) reduced imperfections, which do not exist in the corresponding bulk materials [8]. Due to their small dimensions, nanomaterials have extremely large surface area to volume ratio, which makes a larger fraction of atoms of the materials to be on the surface, resulting in more surface dependent material properties [9, 10]. Some of such peculiar properties are known, but there may be a lot more to be discovered.

The nanometre feature sizes of nanomaterials have spatial confinement effect on the materials, which bring the quantum effects. The quantum confinement has profound effects on the properties of nanomaterials. The energy band structure and charge carrier density in the nanomaterials are quite different from their bulk counterpart and this in turn will modify the electronic and optical properties of the materials. Reduced imperfections are also an important factor
which determines the properties of nanomaterials. Nanostructures and nanomaterials favour a self purification process in which the impurities and intrinsic material defects will move up to near the surface on annealing. This increased material perfection affects the properties of nanomaterials\[11\]. The properties of nanomaterials are described below.

\textbf{(a) Melting Point}

Nanoparticles of metals, inert gases, semiconductors and molecular crystals are all found to have lower melting temperatures as compared with their bulk forms, when the particle size decreases below 100nm. The decrease in the melting point can be of the order of tens to hundreds of degrees for materials with nanometre dimensions [12,13]. For example, melting point of bulk gold is of 1337K and decreasing rapidly for nanoparticles with sizes below 5nm as shown in figure 1.1[14]. Melting point depression occurs for almost all free nanoparticles [15,16], with anomaly in few cases[17,18]. The melting temperature higher than that of bulk- a phenomenon called superheating has also been reported for some cases [19].

The decrease in the phase transition temperature can be attributed to the changes in the ratio of surface energy to volume energy as a function of particle size. Surface energy increases with a decrease in particle size. From the atomistic point of view, as the size of the nanostructures decreases, an increased proportion of atoms occupy surface or interfacial sites. These atoms are more loosely bound than inner ones, which facilitates the melting of nanostructure [20]. Melting point depression is a very important issue for applications involving nanoparticles, as it decreases the functional range of the solid phase.
Figure 1.1 Variation of melting point with particle diameter of gold

(b) Mechanical Properties

Many of the mechanical properties including hardness, elastic modulus, fracture toughness, scratch resistance, fatigue strength etc are modified due to the structural perfection occurring in nanomaterials. The small size often renders them free of internal structural imperfections such as dislocations, micro twins and impurity precipitates or the few defects present cannot multiply sufficiently to cause mechanical failure. The imperfections within the nanodimension are highly energetic and will migrate to the surface to relax themselves under annealing. Moreover, the external surfaces of nanomaterials have less defects or are free of defects compared to bulk materials, serving to enhance the mechanical properties of nanomaterials[8].

The excellent mechanical properties of nanomaterials could have many potential applications both in nanoscale such as mechanical nanoresonators, mass sensors, microscope probe tips and nanotweezers for nanoscale object manipulation[21,22,23] and in macroscale applications like structural reinforcement of polymer materials, light weight high strength materials, flexible conductive coatings, wear resistance coating, tougher and harder cutting tools etc.
(c) Optical Properties

The reduction of material dimension has pronounced effects on their optical properties. The size dependence can be generally classified into two groups. One is due to the increased energy level spacing as the system becomes more confined, and the other is related to surface plasmon resonance [8].

(i) Surface Plasmon Resonance.

Surface plasmon resonance is the coherent excitation of all the free electrons within the conduction band, leading to an in-phase oscillation [24,25]. When the size of a metal nanocrystal is smaller than the wavelength of incident radiation, a surface plasmon resonance is generated and figure 1.2 shows how a surface plasmon oscillation of a metallic particle is created [8]. The electric field of an incoming radiation induces polarization of the free electrons relative to the cationic lattice. The net charge difference occurs at the nanoparticle surface, which in turn acts as a restoring force. Thus a dipolar oscillation of electrons is created with a certain frequency. The energy of the surface plasmon resonance depends on both the free electron density and the dielectric medium surrounding the nanoparticle. The width of the resonance varies with the characteristic time before electron scattering. Plasmon resonance depends on the particle size and the plasmon band red shifts with increase in particle size.

Nanoparticles or nanowires of noble metals exhibit strong absorption bands in the ultraviolet-visible light regime that are not present in the bulk metal. This extraordinary absorption increase has been exploited to increase light absorption in photovoltaic cells by depositing metal nanoparticles on the cell surface. The energy of this absorption is different when light is polarized along or perpendicular to the nanowire. Shifts in this resonance due to changes in the local index of refraction upon adsorption to the nanoparticles can also be used to detect biopolymers such as DNA or proteins.
(ii) Quantum size effect

The electronic energy levels of nanomaterials are significantly different from that of their bulk counterpart. Nanocrystals lie in between the atomic and molecular limit of discrete density of energy states and the extended crystalline limit of continuous band [27]. In any material there will be a size below which there is substantial variation of fundamental optical and electrical properties with size, when energy level spacing exceeds thermal energy. This variation is more distinct for semiconductor nanoparticles, where the band gap increases with a decrease in size, resulting in the inter band transition shifting to higher frequencies [27, 28]. When the size of a semiconductor nanocrystal is smaller than
the de Broglie wavelength, electrons and holes are spatially confined and discrete energy levels would be formed. Similar to a particle in a box, the energy separation between adjacent levels increases with decrease in dimension. Transitions between any two levels are seen as discrete peaks in the optical spectra and the system is then referred to as ‘quantum confined’. If all the dimensions of a semiconductor crystal are shrunk down to a few nanometres, the resultant system is termed as quantum dot.

The quantum size effect is known for metal nanoparticles as well [29,30]; however, it is observable only if the size is well below 2nm, as the level spacing has to exceed the thermal energy.

(d) Electrical and thermal conductivity

Reduction in material’s dimensions would have two different effects on electrical conductivity. One is an increase in crystal perfection or reduction of defects, which results in a decrease in defect scattering and thus an increase in conductivity. The other is to create an additional contribution to the total resistivity due to surface scattering, which plays a very important role in determining the total electrical resistivity of nanosized materials. Further, if the particle size reduces below a critical value, quantum size effects due to change in electronic structure lead to an increase in electrical resistivity. Some metal nanowires may undergo a transition to become semi conducting as their diameters are reduced below certain values, and semiconductor nanowires may become insulators. Such a change can be partially attributed to the quantum size effect.

Several factors such as small size, special shape, large interfaces etc modify thermal properties of the nanomaterials, rendering them quite different behaviour as compared to the macroscopic materials. As the dimension goes down to nano scales, the size of the nanomaterials becomes comparable to the wavelength and mean free path of phonons, so that the phonon transport within
the materials will be changed significantly due to the phonon confinement and quantization of phonon transport, resulting in modified thermal properties. For example, nanowires of silicon have a much smaller thermal conductivity compared to bulk silicon [31]. The special structure of nanomaterials also affects the thermal properties. For example, because of its tubular structures of carbon nanotubes, they have extreme high thermal conductivity in axial directions, leaving high anisotropy in the heat transport [32]. Moreover, surface inelastic scattering of phonons and electrons can reduce thermal conductivity. As a result, nanomaterials with high interface densities will have reduced thermal conductivity [33].

1.2. Magnetic nanomaterials

Among many known nanomaterials, a special position belongs to magnetic nanoparticles and nanostructures owing to their important technological and biomedical applications. Magnetic nanoparticles have been the subject of continuous and growing interest from both fundamental and technological point of view, in the last 50 years, since the pioneering work of Louis Neel. Nanoparticles are unique physical objects with remarkable magnetic properties which differ greatly from their parent massive materials. They are due to finite size effects of the magnetic core related to the reduced number of spins co-operatively linked within the particle and to surface and interface effects related to the lack of coordination for the surface ions, inducing broken exchange bonds which can result in frustration and spin disorder [34]. As the particle size decreases, surface and interface effects are enhanced since the surface to volume ratio becomes larger. This determines completely different magnetic properties, raising basic and challenging questions for their theoretical description, being the ‘giant spin’ model, which assumes that all the spins participate in a single domain and that the magnetic energy is only determined by the particle volume and shape. Surface and
interface driven properties play a dominant role in all applications of magnetic nanoparticles.

1.2.1. Classification

Based on the physical mechanisms responsible for the magnetic behaviour, magnetic nanostructures can be classified as follows [35].

![Figure 1.3](image.png)

Figure 1.3 Schematic representations of the different types of magnetic nanostructures.

Figure 1.3 schematically illustrates four classes of magnetic nanostructured materials ranging from non interacting particles (type A) which derive their unique magnetic properties strictly from the reduced size of the components, to fine grained nanostructures (type D), in which interaction dominates magnetic properties. Two forms of each of these types are indicated: the ideal type A material is one in which the particles are separated and can be treated as non interacting. Ferrofluids in which long surfactant molecules provide separation of particles, are subset of type A. Type D materials consist of small crystallites dispersed in a noncrystalline matrix. The nanostructure may be of two phases, one in which nanocrystallites are a distinct phase from the matrix, and the
second being the ideal case in which both the crystallites and the matrix are made of same material. Type B materials are ultra fine particles with a core-shell morphology. The presence of a shell can help to prevent particle-particle interactions, but often at the cost of interactions between the core and the shell. Type C nanocomposites are composed of magnetic particles distributed throughout a matrix, and the magnetic interactions are determined by the volume fraction of the magnetic particles and the character of the matrix. The matrix may or may not be magneto active.

1.2.2 Magnetism of nanoparticles

Magnetic nanoparticles exhibit many unique phenomena such as superparamagnetism [36], quantum tunnelling of magnetization [37], enhanced magnetic coercivity [38] etc. In case of bulk materials, their intrinsic magnetic properties like saturation magnetization ($M_s$), coercive force ($H_C$) and Curie temperature ($T_C$) depend only on chemical and crystallographic structure. The size and shape of bulk samples are not crucially important. Magnetic nanoparticles show a wide variety of unusual magnetic properties as compared to the respective bulk materials. Magnetic characteristics of nanoparticles are strongly influenced by so-called finite-size and surface effects.

In the view of the condensed matter physics, finite-size effects [39] are originated due to cutting off of characteristic length (exchange length, domain size, etc, [40]), resulting from the geometric limitation of particle volume. For example, macroscopic ferromagnetic single-crystal materials have well defined $T_C$ values depending exclusively on their composition [41]. As a specimen characteristic dimension $d$ approach nano size values and since the magnetic correlation length diverges at $T_C$, the correlated fluctuating magnetic moments in a volume are influenced by the finite size of the specimen. The $T_C$ is then reduced as
\[ \frac{T_C(d) - T_C(\infty)}{T_C(\infty)} = \pm \left( \frac{d}{d_0} \right)^{-\lambda} \]  

Where, \( T_C(\infty) \) is the bulk Curie temperature, \( \lambda \) is related to a correlation length exponent, and \( d_0 \) is an order of the characteristic microscopic dimension [42]. Hence, if the particle size decreases, we can anticipate that the Curie temperature should also decrease. However, changing of crystallographic parameters or composition, either in the particle core or its surface layer, can mask or even inverse this effect [43, 44].

Surface effects are due to the lack of translational symmetry at outer boundaries of a particle, reduced coordination number, and broken magnetic exchange bonds of surface atoms [45]. Decreasing the particle size gradually increases the ratio of surface spins to the total number of spins and hence increases spin disorder. For instance, in a maghemite \((\gamma - \text{Fe}_2\text{O}_3)\) particle of radius about 4 nm, 500% of atoms lie on the surface [46]. Thus due to surface effects saturation magnetization values generally decrease with decrease in particle size. The coercive force of nanoparticles is observed to increase with decrease in particle size, at least until extremely small dimensions are reached. This has been considered as a substantial evidence for the existence of single domain particles.

Shape of the nanoparticle also can influence its magnetic properties. According to classical Electrodynamics, homogeneous magnetization is achievable only for ellipsoidal bodies and so ideal single domain particle must be ellipsoidal. Distortion in particle shape can induce additional anisotropy, stabilizing or destabilizing the single domain state. Small deviations from uniformity in the magnetization field within the nanoparticles can play a crucial role in determining its magnetic properties. In addition to this, the surface effects can be shape dependant since the relative number of surface atoms depends on the particle shape [47].

Macroscopic magnetic materials consist of a large number of magnetic domain - groups of spins all pointing in the same direction and acting
cooperatively - that form in an effort to minimize the magnetostatic energy of the material.

Domains are separated by domain walls, which have a characteristic width and energy associated with their formation and existence. The motion of domain walls is a primary means of reversing magnetization. Experimental investigation on the dependence of coercivity on particle size showed behaviour similar to that schematically illustrated in figure 1.4. In large particles, energetic considerations favour the formation of domain walls. As the particle size decreases towards some critical particle diameter, $D_c$, the formation of domain walls becomes energetically unfavourable and the particles are of single domain. Changes in the magnetization can no longer occur through domain wall motion and instead require the coherent rotation of spins, resulting in larger coercivities. As the particle size continues to decrease below single domain value, the spins are increasingly affected by thermal fluctuations and the system becomes super paramagnetic.

**Figure 1.4** Qualitative illustration of the behaviour of the coercivity in ultra fine particle systems as the particle size changes [35]
1.2.3. Anisotropy in nanomaterials

The two most common anisotropies in nanomaterials are crystalline anisotropy and shape anisotropy. The anisotropy can often be modelled as uniaxial in character and represented by \[ E = KV \sin^2 \theta \] (in its simplest form)

Where, \( K \) is the effective uniaxial anisotropy energy per unit volume, \( \theta \) is the angle between the moment and the easy axis, and \( V \) is the particle volume.

Magnetocrystalline anisotropy arises from spin-orbit coupling and energetically favours alignment of the magnetization along a specific crystallographic direction. The direction favoured by the magnetocrystalline anisotropy is called the easy axis of the material. The magnetocrystalline anisotropy is specific to a given material and independent of particle shape. The coercivity is proportional to the anisotropy constant and so high anisotropy materials are attractive candidates for high coercivity applications.

A polycrystalline sample with no preferred grain orientation has no net crystal anisotropy due to averaging over all orientations. A non spherical polycrystalline specimen can possess shape anisotropy. A cylindrical sample, for example, is easier to magnetize along the long direction than along the short direction. A symmetric shape, like spherical shape, will have no net shape anisotropy. Shape anisotropy is predicted to produce the largest coercive forces.

1.2.4 Superparamagnetism

Consider an assembly of identical single domain particles with uniaxial anisotropy. The energy per particle is

\[ U = -K_i V \sin^2 \theta \]

Where, \( \theta \) is the angle between the single particle magnetic moment \( \mu \) and the easy axis. The energy barrier that must be overcome for a magnetic nanoparticle to rotate its magnetization is \( E_b = K_i V \). As first pointed out by Neel[48], thermal
fluctuations could provide the required energy to overcome the anisotropy barrier and spontaneously reverse the magnetization of a magnetic nanoparticle from one easy direction to the other. The assembly shows paramagnetic behaviour; however, it is the giant magnetic moments of the nanoparticles that fluctuate rather than the atomic moments of a classical bulk paramagnetic material. This magnetic behaviour of nanoparticles is termed as superparamagnetism[36]. At high enough temperature, \( k_\text{B} T \gg K_1 V \), the anisotropy energy can be neglected and the assembly magnetization can be described by the well-known Langevin function \( M = nM_s L(x) \), where \( n \) is the particle number density and \( x = \mu_0 \mu H/k_\text{B} T \).

Thus, the features of superparamagnetism are the scaling of magnetization curves with \( H/T \), as dictated by the Langevin function, and the lack of hysteresis, that is, vanishing remanence and coercivity. Moreover, the major difference between classical paramagnetism of bulk materials and superparamagnetism is the weak fields (\( H = 0.1 \, \text{T} \)) required to achieve the saturation of nanoparticle assembly magnetization \( M \). This occurs because of the large particle moment (\( \mu \approx 10^4 \mu_B \)) compared to the atomic moments (\( \mu_{\text{at}} \approx \mu_B \)).

At low temperatures, \( k_\text{B} T \ll K_1 V \), the anisotropy barriers are very rarely overcome (weak thermal fluctuations), the assembly shows hysteresis, and this is called the blocked state. Following Neel’s arguments, we assume that thermal activation over the anisotropy barrier can be described within the relaxation time approximation (or Arrhenius law) as

\[
\tau = \tau_0 \exp \left[ \frac{K_1 V}{K_B T} \right]
\]

The intrinsic time \( \tau_0 \) depends on the material parameters (magnetostriction constant, Young's modulus, anisotropy constant, and saturation magnetization). Typical values are \( \tau_0 = 10^{-10} \) to \( 10^{-9} \) s as obtained by Neel. If \( \tau_m \) is the measuring time window, the condition for superparamagnetic behaviour is \( \tau_m \gg \tau \). The strong dependence of \( \tau \) on temperature permits us to define a temperature above
which the relaxation time is so small that superparamagnetic behaviour is observed. This is called the blocking temperature ($T_b$) of the assembly, and is given by

$$T_b = \frac{K_V}{K_B} \ln \left( \frac{\tau_m}{\tau} \right)$$

For $T < T_b$, the particle moments fluctuate without switching direction (on average) and the assembly is in the blocked state exhibiting hysteresis. For $T > T_b$, the assembly is in the superparamagnetic state, hysteresis disappears, and thermal equilibrium is established. It is remarkable that the value of $T_b$ depends on $\tau_m$, which is a characteristic of the experimental technique adopted.

### 1.3 Ferrites

Polycrystalline ferrites are the most widely used oxide magnetic nanomaterial, exhibiting interesting magnetic, electrical and optical properties and having applications in fields as diverse as catalysis, information storage, electronics, medical diagnostic, drug delivery and environmental protection.

Ferrite materials have been known to ancient cultures for many centuries. As early as the 12th century the Chinese were known to use lodestone (Fe$_3$O$_4$) in compasses for navigation. However, it was not until the 1930s that modern ferrites had been studied for their magnetic structure and electronic properties. The first systematic study on the relationship between the chemical composition and magnetic properties of various ferrites was reported by Hilpert in 1909 [49, 50]. About 20 years after Hilpert’s work Forestier [51] have reported a chemical study on the preparation of various ferrites and the measurements of their saturation magnetization as well as Curie temperature. However, he was not able to improve the magnetic properties of the ferrites to the commercial level. In 1932, Kato and Takei found that the permeability of mixed ferrites had been multiplied more than several tens of times and this was the birth of commercial ferrite cores [52]. Many Philips researchers in Netherlands have contributed significantly to the
development of science and technology of ferrites. The work of Verway and Heilmann [53] on the distribution of ions over the tetrahedral and octahedral sites in the spinel lattice has contributed to the progress in the physics and chemistry of ferrites. In 1935, Snoek [54] made a systematic investigation on ferrites and produced materials having low hysteresis, high resistivity and higher permeability suitable for the use as magnetic cores up to a few mega hertz. The mechanism for the enhancement of magnetization by the addition of zinc ferrite was explained successfully by Neel in 1948 [55]. The basic study by Anderson [56] on super exchange interaction was especially helpful in understanding the magnetic properties of ferrites. Extensive research work carried out by several researchers led to a clear understanding of the structure of ferrites and found that these can be generally classified into three based on their crystal structure. They are depicted in table 1.2.

The electrical and magnetic properties of ferrites are greatly dependent on the crystal structure. In the following section the structure of spinel ferrites is described very briefly.

**Table 1.2. Types of ferrites based on the crystal structure.**

<table>
<thead>
<tr>
<th>Type</th>
<th>Structure</th>
<th>General formula</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spinel</td>
<td>Cubic</td>
<td>$A^2\text{Fe}_2\text{O}_4$</td>
<td>$A^2 = \text{Cd, Co, Mn, Mg, Ni, Zn.}$</td>
</tr>
<tr>
<td>Garnet</td>
<td>Cubic</td>
<td>$\text{Ln}_3^3\text{Fe}<em>2\text{O}</em>{12}$</td>
<td>$\text{Ln}^3 = \text{Y, Sm, Eu, Gd, Dy, Ho, Er, Tm, Ln.}$</td>
</tr>
<tr>
<td>Magnetoplumbite</td>
<td>Hexagonal</td>
<td>$A^2\text{Fe}<em>{12}\text{O}</em>{19}$</td>
<td>$A^2 = \text{Ba, Sr.}$</td>
</tr>
</tbody>
</table>
1.3.1 Crystal structure of spinel ferrite

The spinel structure takes its name from the mineral, spinel (MgAl₂O₄), whose structure was elucidated by Bragg in 1915. Analogous to the mineral spinel, magnetic spinel ferrites have the general formula MFe₂O₄, where M is a divalent metal ion such as Mn²⁺, Ni²⁺, Cu²⁺, Co²⁺, Fe²⁺, Zn²⁺, Mg²⁺, Cd²⁺ or more often a combination of these[57,58]. The presence of Fe²⁺, Ni²⁺, Co²⁺ and Mn²⁺ can provide unpaired electron spins and therefore contribute to the magnetic moment of spinel. Other divalent ions such as Mg²⁺, Zn²⁺ or Cd²⁺ do not have unpaired electrons but them disproportionate the Fe³⁺ ions on the crystal lattice sites to increase the magnetic moment.

The crystal structure of spinel ferrite is best described by subdividing the unit cell into 8 octants with edge \( a/2 \) where ‘a’ is the lattice parameter, as shown in figure 1.5. The location of oxygen ions and metal ions in two adjacent octants are depicted in the figure. The oxygen ions are arranged in identical manner in all octants. Each octant contains four oxygen ions in the body diagonal and they lie at the corners of a tetrahedron. Positions of metal ions are different in the two octants sharing a face. In the case of octants sharing only an edge the location is the same.

![Figure 1.5](image-url). Crystal structure of spinel ferrite.
The distribution of metal ions is very important in determining the magnetic properties of these materials. In the case of mineral spinel, Mg$^{2+}$ ions are in the A sites and Al$^{3+}$ ions are in B sites. Such an arrangement in which the divalent ions are on A sites and trivalent ions are on the B sites is called normal spinel structure. ZnFe$_2$O$_4$ and CdFe$_2$O$_4$ are normal spinel in the micron regime. The structure in which divalent ions are in the B sites and trivalent ions are equally distributed on A and B sites, is called an inverse spinel structure. CoFe$_2$O$_4$ and NiFe$_2$O$_4$ ferrites have inverse structure and they are all ferrimagnetic. Completely normal and completely inverse spinel structures represent extreme cases and in most of the spinel ferrites, cation distribution is in between them, especially in the nanoregime.

1.3.2 Exchange Forces

To understand the ferrimagnetism of ferrites, it is necessary to know the interactions which result in the spin ordering. In order to explain the magnetic ordering in ferromagnetic materials, P. Weiss introduced his hypothesis of molecular field in 1906 [59]. However, the physical origin of the molecular field, which tends to align neighbouring spins, was not understood until 1928, when Heisenberg showed that it was caused by quantum mechanical exchange forces.
For a particular pair of atoms, situated at a certain distance apart, there are certain electrostatic attractive and repulsive forces which can be calculated by Coulomb’s law and the exchange force which depends on the relative orientation of the spins of the two electrons. The exchange force is a consequence of the Pauli’s exclusion principle, applied to the atoms as a whole.

Heisenberg showed that exchange energy plays a decisive role in the spin ordering of ferromagnetic and antiferromagnetic materials [57, 60, 61]. If two atoms i and j have spin angular momentum $S_i \frac{\hbar}{2\pi}$ and $S_j \frac{\hbar}{2\pi}$, then the exchange energy between them is given by

$$E_{\text{EX}} = -2J_{\text{EX}} S_i S_j \cos \phi$$  \hspace{1cm} (1.6)

Where $J_{\text{EX}}$ is called the exchange integral, which occurs in the calculation of exchange effect, and $\phi$ is the angle between the spins. If $J_{\text{EX}}$ is positive, $E_{\text{EX}}$ is a minimum when the spins are parallel ($\cos \phi = 0$) and if $J_{\text{EX}}$ is negative, the lowest energy state results from antiparallel spins ($\cos \phi = -1$). This explains ferromagnetic and antiferromagnetic ordering in materials. Now we are at a position to discuss the magnetism of ferrites with a particular reference to Neel’s sub lattice model.

1.3.3 Neel’s Theory of Ferrimagnetism

In ferromagnetic materials such as ferrites, the positive metal ions, which carry the magnetic moment, are far away for a direct exchange interaction to be possible, since the extent of overlapping of the wave functions decreases exponentially with distance. Hence in ferrites the exchange interaction between the metal ions will act through the oxygen ions by means of an indirect exchange mechanism called super exchange. Furthermore, the exchange energy $J_{\text{EX}}$...
between the spins of the neighbouring metal ions is found to be negative, so that antiparallel alignment gives the lowest energy.

![Exchange interactions between ions in an inverse cubic ferrite.](image)

**Figure 1.8** Exchange interactions between ions in an inverse cubic ferrite.

In ferrimagnetic materials A and B sites are crystallographically different, since an ion on A site has a different number and arrangement of neighbours than the same ion on B site. Figure 1.8(a) [62] shows the exchange interactions that would have to be considered in a rigorous treatment of an inverse spinel ferrite MO$_2$Fe$_2$O$_3$. These interactions are shown by arrows and there are 5 in all. To simplify the problem, Neel [55] replaced the real ferromagnetic material with a model composed of identical magnetic ions divided unequally between A and B sublattices. This still leaves 3 different interactions to be considered as shown in figure 1.8(b). These are A-A, B-B and A-B interactions and the strength of these negative interactions depends on the distances between the metal ions and the oxygen ion that links them and also on the angles between the three ions. The interaction is greatest for an angle of 180° and also where the inter-atomic distances are the shortest. In the A-A and B-B cases, the angles are too small or the distances between the metal ions and the oxygen ions are too long. The best combination of angles and distances are found in the A-B interaction and hence it is the strongest. As a result the magnetic moments on A sites are held anti parallel to those on B
 sites [55]. In ferrimagnets the A and B sub lattice magnetizations are not equal and hence this results in a net spontaneous magnetization.

The molecular field theory of ferrimagnetism with A and B sub lattices was developed by Neel [55]. He considered a simple ferrite with general formula MO.Fe$_2$O$_3$ in which M ions are diamagnetic.

The equivalent Weiss field acting on an ion at ‘A’ site is assumed to have the form

$$ H_A = n(\alpha \lambda M_A + \varepsilon \mu M_B) $$  \hspace{1cm} (1.7)

Similarly, for an ion at B site,

$$ H_B = n(\beta \mu M_B + \varepsilon \lambda M_A) $$  \hspace{1cm} (1.8)

Where, $M_A$, $M_B$ are the magnetizations of A and B sub lattices respectively, $n$ is a positive constant, $\lambda$ is the fraction of Fe ions on ‘A’ sites, $\mu$ is the fraction of Fe ions on ‘B’ sites (so that $\lambda + \mu = 1$), $\alpha$ and $\beta$ are positive constants for ferromagnets and negative for antiferromagnets coupling within the corresponding A or B group, $\varepsilon = +1$ for ferromagnets and $\varepsilon = -1$ for antiferromagnetic coupling between A and B groups of ions [63].

As we have seen, on account of the interactions between neighbouring magnetic ions and their different environments, the sub lattice magnetizations $M_A$ and $M_B$ are in general different from each other. The average magnetization is

$$ M = \lambda M_A + \mu M_B $$  \hspace{1cm} (1.9)

And this equation is essentially a vector equation.

When an external field $H$ is applied, the resultant magnetization is assumed to follow Curie law for the A and B sub lattices separately,

$$ M_A = C \left( \frac{H + H_A}{T} \right) $$  \hspace{1cm} (1.10)
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\[ M_B = C \frac{(H + H_B)}{T} \quad \text{(1.11)} \]

Where \( C \) is the Curie constant defined in the usual way for simple paramagnetic ions in weak field at not too low temperatures, and \( T \) is the absolute temperature. In the temperature range in which spontaneous magnetization does not occur, we may solve equations 1.7 to 1.11 to obtain the resultant paramagnetic susceptibility in terms of the parameters of the material. When \( \varepsilon = -1 \) (i.e. negative exchange interaction between the A and B sub lattice magnetic moments),

\[ \frac{1}{\chi} = \frac{H}{M} = \frac{T}{C} + \frac{1}{\chi_0} - \frac{\sigma}{T - \theta} \quad \text{(1.12)} \]

Where,

\[ \frac{1}{\chi_0} = n \left( 2\lambda\mu - \lambda^2\alpha - \mu^2\beta \right) \quad \text{(1.13)} \]

\[ \sigma = n^2C\lambda\mu[\lambda(1 + \alpha) - \mu(1 + \beta)]^2 \quad \text{(1.14)} \]

\[ \theta = nC\lambda\mu(2 + \alpha + \beta) \quad \text{(1.15)} \]

The last term in equation 1.12 causes a departure from classical linear Curie-Weiss law at the lower temperatures, and leads to a hyperbolic curvature concave towards the \( T \)-axis. As shown in the figure 1.9 [60], the curve meets the \( T \)-axis at the paramagnetic Curie temperature \( \theta_P \) given by

\[ \theta_P = \frac{1}{2}nC \left[ \lambda\alpha + \mu\beta + \left( \lambda\alpha - \mu\beta \right)^2 + 4\lambda\mu \right]^{\frac{1}{2}} \quad \text{(1.16)} \]

If \( \theta_P \) is positive, spontaneous magnetization is to be expected at temperatures below \( \theta_P \); otherwise the ferrite will remain paramagnetic at all temperatures. The case of positive \( \theta_P \) thus leads to ferrimagnetism.
Figure 1.9 Theoretical variation of reciprocal susceptibility with temperature for a ferromagnetic above Curie temperature.

Now consider the temperature range in which spontaneous magnetization occurs. The magnitudes of the spontaneous magnetizations $M_{AS}$ and $M_{BS}$ can be found by solving the following equations simultaneously

\begin{align*}
M_{AS} &= MB \left[ \frac{MH_A}{RT} \right] \\
M_{BS} &= MB \left[ \frac{MH_B}{RT} \right]
\end{align*}  \hspace{1cm} (1.17) \hspace{1cm} (1.18)

Where $M$ the absolute saturation magnetization of Fe ions, $R$ is the universal gas constant and $B_j$ is the Brillouin function, as employed in the modified Weiss theory of ferromagnetism. The overall resultant spontaneous magnetization becomes,

\[ M_S = \sqrt{2M_{AS} + \epsilon \mu M_{BS}} \]  \hspace{1cm} (1.19)

In Neel’s theory, when the A-B antiferromagnetic interaction dominates the A-A and B-B interactions, A and B sub lattice magnetizations will be aligned
antiparallel, resulting in ferrimagnetism in ferrites. When A-A or B-B interaction is
dominant, according to Neel, the substance remains paramagnetic down to the
lowest temperature. But this conclusion was not correct, as in the presence of strong
interactions some kind of ordering may occur at low temperature. Yaffet and Kittel
resolved this discrepancy by introducing triangular spin configuration due to angle
formation of spin moments in any one of the two sub lattices.

1.3.4 Electrical Properties of ferrites

General electrical properties of ferrites including the temperature
dependence of dc resistivity and the conduction mechanism are briefly described in
this section.

1.3.4.1 Dc Resistivity

Extensive investigations on the origin of the electrical conductivity of
spinels have been carried out by Verwey [64] and later on by Van Uitert [65] and
Jonker [66]. The room temperature resistivity of ferrite varies, depending on the
chemical composition between about $10^{-3}$ to $10^{11}$ Ω cm [57, 67]. The low value of
resistivity in some ferrites is due to the presence of ferrous and ferric ions on
equivalent lattice sites (octahedral sites) as proposed by Verwey [64, 67]. For
example in magnetite, Fe$_3$O$_4$, resistivity is of the order of $10^{-2}$ to $10^{-3}$ Ω cm, while in
Ni-Zn ferrite, Koops [68] found a resistivity of about $10^3$ Ω cm when the material
contained 0.42 weight percent of ferrous oxide and this increased approximately $10^3$
times when the specimen was completely oxidized.

The temperature dependence of resistivity of ferrites follows Arrhenius
relation [57]

$$\rho = \rho_0 \exp\left(\frac{\Delta E}{kT}\right)$$  \hspace{1cm} 1.20
Where $\rho$ is the resistivity and $\Delta E$ is the activation energy required for hopping of an electron from one lattice site to another. According to this relation, resistivity of ferrites decreases with increase in temperature. The relationship between $\log \rho$ and $\frac{1}{T}$ is found to be linear; however breaks occur in these curves at temperatures which correspond closely with the observed ferromagnetic Curie temperature [69]. Such linear relationship is not always observed and sometimes the graph may be slightly curved [67].

Thus, it is clear that high activation energy is associated with high resistivity at room temperature. Although the stoichiometry of the material determines the resistivity of ferrites [70], presence of impurities can influence resistivity [71].

### 1.3.4.2. Conduction Mechanism

Even though ferrites exhibit negative temperature coefficient of resistance, the conduction mechanism in them is quite different from that of semiconductors. In semiconductors band type conduction occurs where as in ferrites, the cations are surrounded by closely packed oxygen anions and they are assumed to be isolated. There will be a little direct overlap of the orbitals and hence a localized electron model is more appropriate, rather than a collective electron model. This accounts for the insulating nature of ferrites. The carrier concentration is almost temperature independent; however the temperature variation affects drift mobility of the charge carriers and this in turn influence conductivity.

Conductivity in ferrites is reported to be due to the presence of ions of the same element existing in different valence states on equivalent lattice sites. Many models have been suggested to account for the electrical conduction in ferrite; out of which two important models are presented below.
1.3.4.2.1. Hopping Model of Electrons

According to Jonker [66], in ferrites there is a possibility of exchange of electrons between ions of same metal with different valency existing at similar lattice sites. As we know, in ferrites, besides the majority of ferric ions a small amount of ferrous ions are present in the octahedral sites that may be formed during the sintering process. Thus hopping of electrons can happen between Fe$^{2+}$ and Fe$^{3+}$ ions on the octahedral sites and that is responsible for conduction in ferrites [57, 72]. In ferrites, electrons are localized and there is a little overlap between the wave functions of ions situated at adjacent sites. Due to the lattice vibrations the ions occasionally come close together and the probability of electron transfer increases. Thus temperature variation influences carrier drift mobility and hopping rate which in turn affect conductivity. For such a process of hopping of electrons and holes, general expression for conductivity is given by

$$\sigma = n_e e \mu_e + n_h e \mu_h$$  \hspace{1cm} (1.21)

Where $e$ is the charge of electron, $n_e, n_h, \mu_e, \mu_h$ are the carrier concentration and mobility of electrons and holes respectively. The temperature variation of conductivity arises due to the change in mobility of the carriers and the carrier concentration is unaffected by the change in temperature.

1.3.4.2.2. Small Polaron Model

A small polaron is assumed to be a quasi particle composed of an electron along with its accompanying polarization field. A slow moving electron in a dielectric crystal when interacts with lattice ions through long range forces, it will be permanently surrounded by a region of lattice polarization and deformation caused by the movement of electron. Moving through the crystal the electron carries the distortion with, which can be assumed to be a cloud of phonons accompanying the electron. The resulting lattice polarization acts as a
potential well that hinders the movement of the charge and thus decreasing its mobility [73]. If the spatial extension of a polaron is large compared to the lattice parameter of the solid, it can be considered as a large polaron. When the self induced polarization caused by an electron or hole becomes of the order of the lattice parameter, a small polaron can arise. As distinct from large polarons, small polarons are governed by short range interactions. Low value of mobility, temperature independent Seebeck co-efficient and thermally activated hopping are important characteristics of small polaron conduction.

Small polaron formation can take place in materials whose conduction electrons belong to incomplete inner (d or f) shells, which due to little orbital overlap tend to form extremely narrow bands [74, 75]. Migration of small polaron requires the hopping of both the electron and the polarized atomic configuration from one site to an adjacent site. The small polaron model can explain the low mobility of charge carriers and thermally activated hopping in ferrites.

1.4 The Proposed Study

Nanocrystalline spinel ferrites are technologically important because of their wide applications, and it is believed that the production of ferrites will increase year by year as their applications become more and more diverse. Even though the saturation magnetization of ferrites is less than half that of ferromagnetic alloys, they have advantages like applicability at higher frequency, lower price, very high electrical resistivity, greater heat resistance and higher corrosion resistance. Unlike many other materials, they possess both high permeability and moderate permittivity at high frequencies. Due to their low eddy current losses, there exists no other material with such a wide range of applications in electronics in terms of power generation, conditioning and conversion. Besides the conventional applications such as transformer cores in high frequency power supplies, EMI shielding, microwave devices, high density magnetic recording etc, applications of
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nanoferites are diverging to new fields like medical diagnostics, site specific drug delivery, MRI contrast agents, magnetic refrigeration, ferrofluids and gas sensing.

The most important advantage of ferrites is their very high degree of compositional variability. Most of the original intrinsic properties on ferrites are made on the simple ferrites such as MnFe$_2$O$_4$, CoFe$_2$O$_4$ and NiFe$_2$O$_4$. However, most commercially important ferrites are of the mixed variety and actually consist of solid solutions of the various simple ferrites with infinite number of combinations possible. Depending on the requirements of the ultimate application, various combinations of different properties can be obtained by blending a judicious choice of the simple ferrites in a proper ratio [58].

Distribution of cations over A and B sites has a profound effect on the electrical and magnetic properties of spinel ferrites. Factors like ionic radius, electronic configuration, madelung energy, lattice energy and crystal field stabilization effects influence the metal ion distribution. Another factor which determines the occupation of cations is the site preference energy. For example nickel and cobalt have a strong preference to octahedral sites, while zinc and cadmium have strong tetrahedral site preference. Thus with knowledge of site preference energy and other factors affecting cation distribution, we can manipulate the synthesis of ferrites with optimum properties in the micro regime. The rules regarding cationic distribution are no longer valid in the nano regime. For instance, in zinc ferrite nanoparticles, a small percentage of Zn$^{2+}$ ions are found to occupy octahedral sites and in case of nickel ferrite nanoparticles, some of the Ni$^{2+}$ ions are occupying tetrahedral sites [76]. Owing to the changes in cationic distribution and surface effects like core-shell structure, broken exchange bonds and canting of spins on the surface etc, the properties of ferrite nanoparticles deviate from that of the bulk.

Nickel ferrite and nickel based mixed ferrite nanoparticles are of technical importance due to numerous applications in electronics [77]. These are promising
materials for use in telecommunication equipments, computer peripherals, and other electronic and microwave devices. Nickel ferrites have low eddy current losses and good magnetic properties, which make them suitable for the core material of power transformers [78, 79]. Nickel ferrite nanoparticles are widely used for improving the quality of magnetic resonance imaging, targeted drug delivery, ferrofluids and gas sensors. Nickel ferrite adopts an inverse spinel structure with Ni$^{2+}$ in octahedral sites and Fe$^{3+}$ equally distributed between octahedral and tetrahedral sites. However, as we have already seen, deviation in cation distribution is observed in nickel ferrite, when the particle size is in the nano range.

It is well known that the desired electrical and magnetic properties of soft ferrites can be tailored by the addition of suitable divalent, trivalent or tetravalent cations in to the spinel lattice. There are numerous reports on the structural and magnetic properties of divalent transition metal ion doped ferrites micro and nanoparticles. However there exist only a few systematic studies on the properties of trivalent rare earth metal ion substituted ferrites in the nanoregime. Incorporation of small amount of rare earth metal ions in to the spinel ferrites may lead to structural distortion due to their large ionic radius and to induce strain and significantly modify the microstructural, electrical and magnetic properties. Rare earth ions play an important role in determining the magnetocrystalline anisotropy in the 4f-3d intermetallic compounds [80]. Thus, from the application point of view, the properties of ferrite nanoparticles can be tuned by the inclusion of suitable rare earth ions.

The properties of nanoferrites are influenced by the composition and microstructure, which are sensitive to the preparation methodology used in the synthesis and to the sintering conditions. Ferrite nanoparticles are usually prepared by various physical and chemical methods like high energy milling, plasma deposition, inert gas condensation, citrate precursor technique, reverse micelle technique, micro emulsion, hydrothermal reaction, polymer pyrolysis, sol-gel
technique, chemical co-precipitation etc [81-86]. Among the available chemical methods, sol-gel and co-precipitation are two simple techniques without much complicated procedure and give ferrite nanoparticles of high purity at low cost. Sol-gel technique is a combination of combustion and chemical gelation process and has the advantage of good stoichiometric control and the production of ultra fine particles with a narrow size distribution. Advantages of co-precipitation are the high production rate, very small particle size, low synthesis temperature etc.

In the proposed study, \( \text{NiFe}_2\text{O}_4 \) nanoparticles are to be prepared by sol-gel and co-precipitation techniques. By appropriate heat treatment, variation of grain size with temperature will be studied. The structural evaluation will be carried out using X-Ray Diffraction (XRD) technique. Magnetic parameters and electrical properties like dielectric permittivity, ac conductivity, and dc resistivity of the samples prepared by the two methods will be compared.

In sol-gel derived \( \text{NiFe}_2\text{O}_4 \) nanoparticles, \( \text{Fe}^{3+} \) ions will be partially replaced by small amount of rare earth ions \( \text{Gd}^{3+}, \text{Tb}^{3+} \) and \( \text{Sm}^{3+} \) and the influence of doping on structural parameters like lattice constant, X-Ray density, porosity, crystallite size etc will be evaluated. Modifications in the magnetic parameters such as saturation magnetization (\( M_s \)), remanence (\( M_r \)) and coercivity (\( H_c \)) will be studied. Electrical properties like dielectric permittivity and ac conductivity will be investigated as a function of frequency, temperature and rare earth ion concentration.

Zinc substituted \( \text{NiFe}_2\text{O}_4 \) nanoarticles are one of the best soft magnetic materials suitable for high frequency applications, due to their low magnetic coercivity, high electrical resistivity, low loss, fairly high mechanical hardness and chemical stability. Ni-Zn mixed ferrites are widely investigated and it is well known that their properties can be tuned by varying Ni or Zn content [87-89]. In order to improve the properties, \( \text{Fe}^{3+} \) ions in Ni-Zn mixed ferrites will be partially replaced
by Tb$^{3+}$ ions and the changes in electrical and magnetic properties will be thoroughly examined.

We have seen that zinc and cadmium ions have a strong preference to tetrahedral sites in the spinel ferrite lattice. Hence the substitution of magnetic ions in ferrite by nonmagnetic zinc or cadmium ions can lead to an improvement in magnetic properties. In order to optimise magnetic as well as electrical properties, Ni-Cd mixed ferrites will be synthesized by sol-gel technique and structural, magnetic as well as electrical properties will be investigated. A small amount of Gd$^{3+}$ ions will be incorporated into these mixed Ni-Cd ferrites and the resulting improvement in properties will be evaluated.

Thus, the objectives of the present work can be summarized as follows,

- Preparation of NiFe$_2$O$_4$ nanoparticles by sol-gel and coprecipitation techniques.
- Structural characterization of the samples using XRD.
- Magnetic and electrical characterization of the samples and the comparison of properties of nano ferrites obtained by the two methods.
- Partial replacement of Fe$^{3+}$ ions in sol-gel derived nanocrystalline NiFe$_2$O$_4$ by rare earth ions Gd$^{3+}$, Tb$^{3+}$ and Sm$^{3+}$ and to study the modifications in structural, magnetic and electrical properties in each case.
- Preparation of Tb$^{3+}$ doped mixed Ni-Zn ferrite nanoparticles and the structural, magnetic and electrical characterization.
- Synthesis of Ni-Cd mixed ferrite nanoparticles by sol-gel technique and to investigate its properties.
- Substitution of Fe$^{3+}$ ions in Ni-Cd mixed ferrite by Gd$^{3+}$ ions and to evaluate the effect of doping on its structural, magnetic and electrical properties.
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