1.1: INTRODUCTION

The ferromagnetic materials, ferrites are magnetic ceramics consisting of iron oxide and metal oxides finds potential applications for making many devices such as permanent magnets, memory storage devices, micro-wave devices and for the telecommunication equipment purpose. The importance of ferrites lies in the fact that they possess wide range of electrical and magnetic properties. The high electrical resistivity, low eddy current and dielectric loss, high saturation magnetization, high permeability, high Curie temperature etc. are the remarkable electrical and magnetic features of ferrites \[^{1}\].

Ferrites with such combination of electrical insulator and magnetic conductor are important magnetic materials which are not be replaceable by any other magnetic materials. The advantage of ferrite is that they have higher efficiency and lower cost and are easier to manufacture than other materials. On account of their diverse and fascinating applications in wide technological and scientific fields, the synthesis and characterization of these materials become important.

The basic electrical and magnetic properties of ferrite are sensitive to method of preparation and associate parameters, type and amount of dopant, distribution of cations over the available sites. The selection of
dopant is also important criteria in governing the properties of ferrite materials [2, 3].

The ferrite materials history can be traced back to centuries ago with the discovery of stones that attracted iron. Ever since Neolithic man first used a piece of suspended lodestone to navigate, mankind has used magnetic materials of various kinds. However, it was not until the advent of electricity that the magnetic processes began to be understood. It is now known that lodestone is an iron ore, magnetite, which is one of a wide range of magnetic ceramics based on iron (III) oxide, called the ferrites. The stones were found in the district of Magnesia in Asia Minor, and hence the mineral’s name became Magnetite, Fe₃O₄, is in a structural class of compounds known as the spinels with the composition MeFe₂O₄ where Me is a divalent cation, Fe²⁺ in the case of magnetite. The naturally occurring ferrites such as magnetite are magnetically soft. The research efforts at that time for producing the analogue soft magnetic materials were not successful until in 1930’s when the first synthetic ferrites were developed independently in Japan and Netherlands [4, 5]. Ferrites were prepared as long as 1859, active research on the preparation of ferrite for radio frequency applications did not start until 1933. The main pioneering work performed by Late. Dr. Snoek [6] and his colleagues in 1948. The development of ferrite proceeded rapidly after the 2nd world war.

In the last 6 to 7 decades ferrites are extensively studied from academic and technological point of view by many researchers [7-9]. Since then, intensive efforts have been devoted to this research area, which led to the remarkable developments in both science and technologies of ferrite.
materials. Unique electric and magnetic properties of the ferrite materials have shown tremendous technological applications at room temperature such as data storage devices, magnetic sensors, transformer cores, actuators, targeted drug delivery, medical diagnosis, etc. [10-15].

Large number of methods available for the synthesis of ferrites, the most commonly used method is ceramic technique. The modifications in the properties for desired applications have been brought by substituting different type and amount of substituent’s [16,17]. The last two decades have witnessed a tremendous increase in the interest of the academics and the industry in materials that are aptly described by this new terminology—nano-structured materials. Naturally this in turn to the study ferrites at nano-scale a quite interesting subject both from the fundamental and application points of view. These ferrite nanoparticles have attracted much attention due to their surface and quantum confinement effects depending upon large surface-to volume ratio and size-dependent properties, respectively. These parameters resulted in different modifications in the physical and chemical properties of ferrites [18,19] and make them flexible to be used in different applications in the modern technology. Therefore, the chemical synthesis of ferrites has become the focus of diverse studies. Ferrite nanoparticles can be produced by different wet chemical methods, such as the co-precipitation [20], hydrothermal synthesis [21], micro-emulsion synthesis [22] spray pyrolysis [23], citrate precursor technique [24] and sol gel method [25] etc.
1.2: CLASSIFICATION OF FERRITE

Ferrites are a very well established group of magnetic semiconductor materials. Ferrites are classified by the following categories.

1.2.1: On the basis of Crystal structure

On the basis of their crystal structure ferrites are of three types namely Hexagonal ferrite, Garnet and Spinel ferrite. By virtue of their crystal structure they can accommodate variety of cations at available sites enabling wide variation in electrical and magnetic properties.

a) Hexagonal ferrite

Hexagonal ferrite was first identified by Went, Rathenau, Gorter & Van Ostershout 1952 and Jonker, Wijn & Braun 1956. The group of ferrites which possess hexagonal crystal structures is referred to hexagonal ferrites. There are four type of hexagonal ferrite and indicated as M, W, Y and Z.

The crystal and magnetic structure of the different types of hexagonal ferrites are remarkably complex, as shown for the most important M-type \( \text{BaFe}_{12}\text{O}_{19} \) in Fig. 1.1. The elementary unit cell contains 10 oxygen layers, sequentially constructed from 4 blocks, S (spinel), R (hexagonal), S* and R*. S* and R* have equivalent atomic arrangements as S and R, but are rotated 180° about the c axis with respect to S and R. An S or S* block consists of two \( \text{O}^{2-} \)
layers; while an R or R* block contains three O\(^{2-}\) layers, with one oxygen site in the middle layer substituted by a Ba\(^{2+}\) ion \[^{28}\].

**b) Garnet**

The garnets have orthorhombic crystal structure (oxygen polyhedra, surrounding the cations) but with trivalent cations (including rare earth and Fe\(^{3+}\)) occupying tetrahedral (\(d\)), octahedral (\(a\)), or dodecahedral (\(c\)) sites. An octant of a garnet crystal structure composed of a combination of octahedral (trivalent cation surrounded by six oxygen ions), tetrahedral (trivalent cations surrounded by four oxygen ions), and 12-sided polyhedral- dodecahedral- (trivalent cations surrounded by 8 oxygen atoms) sites, the orientations of which are shown Fig. 1.2. The rare earth garnets have the general formula \(M_3^5Fe_2^6Fe_3^3O_{12}\), or \((3M_3O_8)c(2Fe_3O_4)a(3Fe_2O_3)d\), where M is a rare earth metal ion or an yttrium ion (such as nonmagnetic yttrium or a magnetic rare earth such as from lanthanum through ytterbium) and the superscripts c, a, d, refer to dodecahedron, octahedron and tetrahedron respectively.

**c) Spinel ferrite**

Spinel ferrite having the generic formula MeFe\(_2\)O\(_4\) in which Me and Fe display tetrahedral and octahedral cation sites, respectively, and O indicates the oxygen anion site. They are also called cubic ferrites. In spinel
ferrites, the relatively large oxygen anions form a cubic close packing with \(\frac{1}{2}\) of the octahedral and \(\frac{1}{8}\) of the tetrahedral interstitial sites occupied by metal ions. Spinel ferrites with the formula \(\text{MeOFe}_2\text{O}_3\) or \(\text{Me}^{\text{II}}\text{Fe}^{\text{III}}_2\text{O}_4\) where \(\text{Me}^{\text{II}}\) represents a divalent metal cation such as Mn, Fe, Co, Ni, Cu, Zn, Cd, Mg, and \(\text{Fe}^{\text{III}}\) is the trivalent iron cation, have the same crystallographic structure as the mineral spinel \((\text{MgAl}_2\text{O}_4)\), which was determined by Bragg \(^{[29,30]}\).

\[ \text{Figure 1.3:} \quad \text{(a) Spinel unit cell structure,} \]
\[ \text{(b) Octahedral interstice (B site: 32 per unit cell, 16 occupied), and} \]
\[ \text{(c) Tetrahedral interstice (A site: 64 per unit cell, 8 occupied).} \]
The unit cell of spinel ferrite belongs to the cubic structure (space group Oh\(^7\)F\(_3\)dm) and presents itself the cube formed by 8 MeOFe\(_2\)O\(_3\) molecules and consisting of 32 of O\(^2-\) anions. The oxygen anions form the close face-centered cube (fcc) packing consisting in 64 tetrahedral (A) and 32 octahedral (B) empty spaces partly populated by Fe\(^{3+}\) and Me\(^{2+}\) cations\(^{[21]}\). Fig 1.3 (a) represents Spinel unit cell structure, (b) represents octahedral interstice (B site: 32 per unit cell, 16 occupied), and (c) tetrahedral interstice (A site: 64 per unit cell, 8 occupied). Fig 1.3 (a) shows the crystal structure of spinel structure. In Fig. 1.3 (a) the ionic positions are the same in octants sharing only one edge and different in octants sharing a face. Each octant contains 4 Oxygen ions. In Figure 1.3 (a) ionic positions in only two adjacent octants are shown, where the octant on the left contains octahedral and the one on the right contains tetrahedral sites. According to the distribution of cations \(^{[31]}\), there are the following types of spinels:

i) **Random Spinel**

The divalent metal ions Me\(^{2+}\) and trivalent Fe\(^{3+}\) ions are distributed at both tetrahedral A site and octahedral B site then the ferrite is termed as random spinel ferrite. It can be represented by the formula Me\(_{1-x}\)Fe\(_{1-x}\)\_O\(_4\). It has an intermediate cation distribution, represented as [Fe\(_{0.67}\) Me\(_{0.33}\)]\(_{\text{tet}}\) [Me\(_{0.67}\)Fe\(_{1.33}\)]\(_{\text{oct}}\)\_O\(_4\). It has been established now that in the elementary unit cell of spinel structure eight tetrahedral and sixteen octahedral sites are occupied by metal ions and completely normal and inverse spinel represent the extreme cases. The distribution of ions between two types of sites is determined by a delicate balance of
contributions, such as the magnitude of ionic radii, their electronic configuration and the electrostatic energy of the lattice. The best known example of random spinel ferrite is copper ferrite.

**ii) Normal spinel**

A material with the normal spinel structure having general formula \( \text{Me}(\text{Fe}_2)\text{O}_4 \) has all the divalent metal (Me) cations on the tetrahedral (A) sites and the trivalent (Fe) cations on the octahedral [B] sites. This can be represented by the formula \([\text{Me}]_{\text{tet}} [\text{Fe}_2]_{\text{oct}} \text{O}_4\).

Examples of normal spinel are

- \( \text{MgO}.\text{Al}_2\text{O}_3 = \text{MgAl}_2\text{O}_4 \) (normal, parent mineral) (normal)
- \( \text{ZnO}.\text{Fe}_2\text{O}_3 = \text{ZnFe}_2\text{O}_4 \) (normal)
- \( \text{FeO}.\text{Al}_2\text{O}_3 = \text{FeAl}_2\text{O}_4 \) (normal)
- \( \text{CoO}.\text{Al}_2\text{O}_3 = \text{CoAl}_2\text{O}_4 \) (normal)
- \( \text{MnO}.\text{Al}_2\text{O}_3 = \text{MnAl}_2\text{O}_4 \) (normal)
- \( \text{NiO}.\text{Al}_2\text{O}_3 = \text{NiAl}_2\text{O}_4 \)

**iii) Inverse spinel**

In an inverse spinel structure, \( \text{Fe} (\text{Me Fe}) \text{O}_4 \), the divalent cations has stronger affinity for and octahedral [B] sites and the trivalent cations are equally divided among the (A) and remaining [B] sites. This can be represented by formula, \([\text{Fe}]_{\text{tet}} [\text{Me}, \text{Fe}]_{\text{oct}} \text{O}_4\). For example cobalt ferrite \( (\text{CoFe}_2\text{O}_4) \) is predominantly an inverse spinel with a formula; \( \text{Co}_x\text{Fe}_{1-x} (\text{Co}_{1-x} \times \text{Fe}_{1+x}) \text{O}_4 \) (with \( x = 0 \)) where, \( x \) is the cation distribution factor which describes the fraction of tetrahedral sites occupied by \( \text{Co}^{2+} \) cations.

- \( \text{CoO}.\text{Fe}_2\text{O}_3 = \text{FeCoFeO}_4 \) (inverse)
- \( \text{NiO}.\text{Fe}_2\text{O}_3 = \text{FeNiFeO}_4 \) (inverse)
- \( \text{MgO}.\text{Fe}_2\text{O}_3 = \text{FeMgFeO}_4 \) (inverse)
1.2.2: On The Basis of Magnetism

Due to the persistence of their magnetization, the ferrites are of two types i.e. hard and soft. This classification is based on their ability to be magnetized or demagnetized not their ability to withstand penetration or abrasion. Hard ferrites are difficult to magnetize or demagnetize whereas soft ferrites are easily magnetized or demagnetized. [32].

a) Hard ferrites

Hard ferrites are difficult to magnetize or demagnetize. They are used as permanent magnets. Hard ferrites has high coercivity and high remenance after magnetization, the high coercivity means the materials are very resistant to becoming demagnetized, an essential characteristic for a permanent magnet.

The most commonly used hard ferrites are:

- **Strontium ferrite**, SrFe$_{12}$O$_{19}$ (SrO·6Fe$_2$O$_3$), a common material for permanent magnet applications.

- **Barium ferrite**, BaFe$_{12}$O$_{19}$ (BaO·6Fe$_2$O$_3$), a common material for permanent magnet applications. perpendicular magnetic recording media materials, magnetic tapes, magnetic disks, magneto-optic materials, targeted drugs and microwave filters.

- **Cobalt ferrite**, CoFe$_2$O$_4$ (CoO·Fe$_2$O$_3$), used in magnetic recording applications such as audio and videotape and high-density digital recording disks, [33].
b) Soft ferrites

Soft Ferrites are those that can be easily magnetized or demagnetized. This shows that soft magnetic materials have low coercive field and high magnetization that is required in many applications.

<table>
<thead>
<tr>
<th>Frequency</th>
<th>Materials</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Static &lt; 1 Hz</strong></td>
<td>Soft iron, Fe–Co (permendur) Ni–Fe (permalloy)</td>
<td>Electromagnets, relays</td>
</tr>
<tr>
<td><strong>Low frequency</strong></td>
<td>Si steel, permalloy, finmet, magnetic glasses</td>
<td>Transformers, motors, generators</td>
</tr>
<tr>
<td>1 Hz–1 kHz</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Audio-frequency</strong></td>
<td>Permalloy foils, finmet, magnetic glasses, Fe–Si–Al powder (sendust) Mn–Zn ferrite</td>
<td>Inductors, transformers for switched mode power supplies, TV fly-back transformers</td>
</tr>
<tr>
<td>100 Hz–100 kHz</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Radio-frequency</strong></td>
<td>Mn–Zn ferrite, Ni–Zn ferrite</td>
<td>Microwave isolators, circulators, phase shifters, filters Inductors, antenna rods</td>
</tr>
<tr>
<td>0.1–1000 MHz</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Microwave &gt;1 GHz</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>YIG, Li ferrite</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The hysteresis loop for a soft ferrite should be thin and long, therefore the energy loss is very low in soft magnetic material. Examples are nickel, iron, cobalt, manganese etc. They are used in transformer cores, inductors, recording heads and microwave devices. Soft ferrites have certain advantages over other electromagnetic materials including high resistivity and low eddy current losses over wide range of frequencies. They have high permeability and are stable over a wide range of temperature. These advantages make soft ferrites paramount over all other magnetic materials. Table 1.1 gives the information of soft magnetic materials and its applications in microwave to radio frequency.
1.3: MAGNETIC BEHAVIOUR

An atom is said to be magnetic if it carries a permanent magnetic moment, usually represented by a vector of constant modulus. Every substance is formed from an assembly of atoms which can be either nonmagnetic or magnetic; in this later case, the direction, and sometime the modulus of the magnetic moment can depend on the particular environment of each atom (nature and position of the neighboring atoms, temperature, applied magnetic field). The genesis of magnetism has to do with the orbital and spin motions of electrons and how the electrons interact with one another as pertained to their spin.

The classification of magnetic materials is based on how they respond to magnetic fields. Although as surprising as it may sound, all matter is magnetic to varying degrees. The main delineating factor is that in some materials there is no collective long range interaction between atomic magnetic moments, whereas in other materials there is a very strong interaction. The main types of magnetism are the following:

Diamagnetism, paramagnetism, anti-ferromagnetism, ferromagnetism and ferrimagnetism.\[^{36}\]

1.3.1: Diamagnetism

Diamagnetism is a very weak form of magnetism, and it persists only while an external field is being applied to the material. Although the orbit and spin magnetic moments in such a materials cancel in the absence of external magnetic field, an applied field causes the spin moment to slightly exceed the orbital moment. The magnitude of the induced magnetic moment is extremely small, and in the opposite direction of the applied
magnetic field. The relative permeability is less than unity, and the magnetic susceptibility is negative; that is, the magnitude of flux density, B, within a diamagnetic solid is less than a vacuum.

1.3.2: Paramagnetism

For some other materials such as aluminium, and titanium, each atom possesses a permanent dipole moment due to incomplete cancellation of electron spin and/or orbital magnetic moments, resulting in a net magnetic moment for the atom even with no applied magnetic field. In the absence of the applied field, the orientation of these atomic magnetic moments is random, but when an external magnetic field is applied, they experience a torque which tends to align them with the direction of the field.

1.3.3: Ferromagnetism

In ferromagnetic substances, parallel arrangement of magnetic moments in neighboring atoms. They have high magnetic permeability, capable to become highly magnetic and have the ability to retain a permanent magnetic moment in the absence of an external field. Ferromagnetic materials such as iron, nickel, cobalt and some of the rare earth elements are considered to be the most important magnetic substances.

1.3.4: Ferrimagnetism

The word ferrimagnetism was first coined by Neel to describe the properties of those substances which below a certain temperature exhibit spontaneous magnetization arising from non-parallel alignment of atomic moments. In ferrimagnetic substances, the magnetic moments are not equal and aligned opposite to each other so that there is a net magnetic moment (not equal to zero) such a material is said to be ferrimagnetic.
Table 1.2: Different types of magnetic behaviors

<table>
<thead>
<tr>
<th>Types</th>
<th>Magnetic behavior</th>
<th>Magnetic susceptibility</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diamagnetic</td>
<td>No Magnetic</td>
<td>Small and negative</td>
<td>Copper, silver, gold and alumina</td>
</tr>
<tr>
<td></td>
<td>moment</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Paramagnetic</td>
<td>![paramagnetic]</td>
<td>Small and positive</td>
<td>Aluminium, titanium, and alloys of copper</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ferromagnetic</td>
<td>![ferromagnetic]</td>
<td>Very large and</td>
<td>Iron, nickel and cobalt</td>
</tr>
<tr>
<td></td>
<td></td>
<td>positive function of</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>applied field,</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>microstructure dependent</td>
<td></td>
</tr>
<tr>
<td>Antiferromagnetic</td>
<td>![antiferromagnetic]</td>
<td>Small and positive</td>
<td>Manganese, chromium, MnO and NiO</td>
</tr>
<tr>
<td>Ferrimagnetic</td>
<td>![ferrimagnetic]</td>
<td>Large and positive,</td>
<td>Ferrites</td>
</tr>
<tr>
<td></td>
<td></td>
<td>function of applied</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>field, microstructure</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>dependent</td>
<td></td>
</tr>
</tbody>
</table>

1.3.5: Anti-ferromagnetism

Materials that exhibit anti-ferromagnetism, the magnetic moments of atoms or molecules, usually related to the spins of electrons, align in a regular pattern with neighboring spins (on different sub-lattices) pointing in opposite directions. Anti-ferromagnetism, macroscopically similar to paramagnetism, is a weak form of magnetism. Generally, antiferromagnetic order may exist at sufficiently low temperatures, vanishing at and above a certain temperature, the Néel temperature (Neel temperature is the
temperature at which an antiferromagnetic material becomes paramagnetic; hence losing its magnetic properties). Above the Néel temperature, the material is typically paramagnetic.

1.4: LITERATURE REVIEW

Ferrite materials, which are magnetic and insulating oxides, have been received significant attention in recent years due to their wide range of applications in the current and emerging technological applications in fuel cells, high density magnetic recording and biological applications, including magnetic resonance imaging (MRI), magnetic fluid hyperthermia (MFH), magnetic separations, biosensors, targeted and controlled drug delivery [37-39].

In particular, nano-crystalline transition metal ferrites have been an important subject of research as they exhibit unique properties, different from those of bulk materials. For example, the magnetic properties are particularly affected at the nano-metric level, because when the particle size decreases down to the nano-metric range, each particle can behave as a single magnetic domain.

Among the spinel ferrites, the inverse type is more interesting due to its high magneto crystalline anisotropy and high saturation magnetization [40]. Nickel ferrite (NiFe$_2$O$_4$) is one of the most important materials in the inverse spinel family exhibiting ferri-magnetic properties combined with relatively low electrical properties and it displays low eddy current loss in alternating current applications [41]. The nickel ferrite NiFe$_2$O$_4$ (see Figure 1.4) adopts an inverse spinel structure with Ni$^{2+}$ in octahedral sites, labelled Ni (B), and
Fe$^{3+}$ equally distributed between octahedral (Fe(B)) and tetrahedral sites (Fe(A)) of the O$^{2-}$ fcc cell [42].

Oxygen atoms have been added in order to complete the Ni (Oh) and Fe (Oh) first coordination shell. In Fig 1.4, Ni atoms are shown in blue, Fe ones in green and O atoms in red. The complete structure crystallizes in a cubic system O$_h^1$ space group 227; oxygen atoms occupy the 32e positions, Fe (A) atoms occupy the 8a ones and the Ni (B) and Fe (B) atoms are distributed on the 16d positions, using Wyckoff notations [43]. The cubic unit cell thus contains 56 atoms, of which 24 are magnetic transition metals. In this structure, oxygen atoms are surrounded by four metallic cations in a pseudo-tetrahedral environment. Two oxygen species are present in the volume: the first one, denoted O$_{Fe}$, is surrounded by three Fe atoms (two in B sites and one in a A site) and one Ni atom; the second one, denoted O$_{Ni}$, is surrounded by two Fe atoms (one in an octahedral B site and one in a tetrahedral A-site) and two Ni ones. All oxygen atoms are thus linked to three metallic cations in B sites and one in an A-site. Nickel ferrite (NiFe$_2$O$_4$) is one of the most important materials in the inverse spinel family exhibiting ferri-magnetic properties combined with relatively low electrical properties and it displays low eddy current loss in alternating current applications. Thus the compound can be represented by the formula (Fe$^{3+}$)$_A$[Ni$^{2+}$Fe$^{3+}$]$_B$O$^{2-}_4$. The inverse spinel structure of nickel ferrite structure is shown Fig. 1.4.

Figure 1.4: NiFe$_2$O$_4$ inverse spinel unit cell.
Nickel ferrite and substituted nickel ferrite has been widely studied because of their typical ferromagnetic properties, low conductivity and thus lower eddy current losses, high electrochemical stability, high mechanical hardness, high electrical resistivity and low cost \([44-48]\) etc. making it a good contender for the application as soft magnets and low loss materials at high frequencies. Many investigators have been studied magnetic properties of the nickel ferrite nanoparticles \([49-51]\).

Mahmoud Goodarz Naseriet.al\([52]\) have studied structural, morphological properties of nickel ferrite nanoparticles prepared by a thermal treatment method utilizing only nickel nitrate and iron nitrate as precursors, deionized water as a solvent and PVP as a capping agent.

Chandan Upadhyayet. et. al.\([53]\) have studied cation distribution in nanosize Ni-Zn ferrite synthesized by chemical precipitation method. He showed that the growth of particles is obstructed by the presence of zinc so that the average particle size decreases and he concluded that the cation preferences are not satisfied when Zn is introduced in the Ni–Zn ferrite.

Babita Baruwati et.al.\([54]\) have studied the conductivity behavior of nanocrystalline NiFe\(_2\)O\(_4\) prepared by hydrothermal route. She showed that the desired properties of ferrite materials can be controlled by employing the suitable preparative method, preparation condition.

T.K. Kundu et. al\([55]\) have reported the structural, electrical and magnetic properties of nanosize structured nickel ferrites (NiFe\(_2\)O\(_4\)) prepared by doping with Ti\(^{4+}\) ions using solid-state reaction route. He achieved the grain size of 55 nm of the specimens with 20 mole\% TiO\(_2\) doping.
Zhigang Zhang et. al. \cite{56} were prepared the nickel ferrite nanoparticles by solid state reaction route using NaCl as a dispersant. He studied the effects of synthesis parameters on the morphology and magnetic properties of nickel ferrite nanoparticles.

Mohammad Javad Nasr Isfahani et. al. \cite{57} have reported the structural and magnetic properties of bismuth substituted nickel ferrite nanoparticles prepared by sol-gel method. Mossbauer and SAED measurements revealed the preservation of both the valence state of iron cations and the spinel structure of NiFe$_{2-x}$Bi$_x$O$_4$ series with increasing bismuth content x.

M.A. Gabal et. al. \cite{58} has investigated the structural and magnetic properties of Cu$^{2+}$ substituted nickel ferrite have been prepared by thermal decomposition technique. He was suggested the proper cations distribution on the basis of magnetic measurement data.

M. A Airimioaei et. al. \cite{59} have prepared Mn substituted Ni ferrite by sol-gel combustion technique and its electrical, dielectric and magnetic properties as function of Mn content.

M.A. Ahmed et.al. \cite{60} have reported the silver doping effect on the magnetic properties of Ni ferrite prepared by citrate method. His results showed the normal ferrimagnetic behavior as the general trend for all ferrite. Many efforts have taken to investigate the magnetic properties of nickel ferrite substituted by Zn \cite{61,62}, Cd \cite{63}, Al \cite{64}, Cr \cite{65}, etc. However, as per our best search, we have not found any detailed report in the literature on the electric, dielectric and transport properties of Al$^{3+}$ and Cr$^{3+}$ substituted nickel ferrite nanoparticles prepared by sol-gel auto-combustion.
method. Therefore, keeping in view the high demand in technological applications, we decided to study the effect of substitution of $\text{Al}^{3+}$ and $\text{Cr}^{3+}$ on the structural, electrical, dielectric and transport properties of nano-crystalline nickel ferrites. Dielectric properties were studied as function of frequency as well as a function of temperature also.

1.5: AIM OF THE PRESENT WORK

Advanced novel materials are essential for the various applications whereas nano-structured materials have become essential for the advancement of science and technology in the recent years. Therefore, preparation of nano-sized spinel ferrite particle has become an important component of modern ceramic research. Various physical properties of ferrites are greatly influenced by the distribution of cations among the sub-lattices, nature of grain, grain boundaries, voids, inhomogeneities, surface layers and contacts, etc.

The important properties of the ferrite materials such as their high value of resistivity and low eddy current and dielectric losses are conducive to the high frequency applications \[^{66}\]. Owing to dielectric behavior; they are sometimes called multi-ferroics. Spinel ferrites with small dimensions, lightweight and modified structures are important components for many electronic products. The size reduction and compact arrangement of electronic devices in a smaller area have a welcoming feature in nanotechnology. Scientific interest on nano-sized nickel ferrites is on the rising because of its promising interesting applications in magnetic refrigerators, microwave devices, colour imaging and high density recording devices \[^{67}\].
According to literature survey, the synthesis, structural and magnetic properties of nano-size spinel ferrites have been intensively studied by number of workers. Nanoparticles of spinel ferrites exhibit super-paramagnetism and hence they show enhanced and interesting magnetic properties which are helpful in the recent applications like magnetically guided drug delivery, hyperthermia, gas sensors and catalyst. In the light of their applications in the current technology, magnetic nanoparticles of spinel ferrites have been the subject of focus for the scientist and technologist. However, the electrical and transport properties of nano-size spinel ferrites are also important from the point of view of their high frequency applications, magnetic recording materials etc. It is observed that the porosity of nanoparticles of spinel ferrite is large as compared to bulk spinel ferrite. Large porosity values of nano-size spinel ferrites leads to increasing electrical resistivity and decrease in dielectric losses. Thus, the high electrical resistivity, low eddy current and dielectric losses of nano-size spinel ferrites as compared to the bulk ferrite is the added advantage over the magnetic properties. Hence, it is important to study the electrical and transport behaviour of magnetic nanoparticles of spinel ferrite.

In the family of spinel ferrites, nickel ferrite and substituted nickel ferrite finds a special class on account of their high electrical resistivity, low eddy current and dielectric losses, inverse spinel structure, moderate magnetic properties. Though, in the literature the magnetic properties of nickel ferrite were reported by many workers, the electrical, dielectric, thermoelectric properties were not much been studied. It is thought that electrical conduction in ferrites results from thermal activation of electrons or positive
holes along chains of neighboring cations in the ionic lattice and that the activation energy of transport is greatly reduced if the crystal lattice intrinsically contains cations of one element in more than one valence state.

In view of the immense importance of nickel ferrites and fact that their properties undergo significant changes on substitution with trivalent metal cations, it is decided to synthesize aluminium and chromium substituted nickel ferrite \( \text{NiAl}_x\text{Fe}_{2-x}\text{O}_4 \) and \( \text{NiCr}_x\text{Fe}_{2-x}\text{O}_4 \) for \( x = 0.0, 0.2, 0.4, 0.6, 0.8 \) and \( 1.0 \) in nano-size form by using sol-gel auto-combustion technique and to investigate their electrical, dielectric and thermoelectric behaviour in systematic way, with a view to improve their structural, electrical, dielectric and transport properties. The trivalent cations \( (\text{Al}^{3+} \text{ and Cr}^{3+}) \) chosen for the substitution studies are non-magnetic and magnetic in nature respectively.
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