1.1 General Introduction:

Ferrites are superior magnetic materials widely used in microwave and electrical industries. In recent years, nanocrystalline ferrites have attracted much interest because of their unusual magnetic properties and their promising technological applications. It has high electrical resistivity, low eddy current and dielectric losses, high Curie temperature, moderate saturation magnetization, high permeability, permittivity etc. These properties make ferrite useful in variety of application. Ferrites cannot be replaced by any other magnetic material due to their combined property of electrical insulator and magnetic conductor, hence these materials are of great interest of academician and technologist. Ferrites are used in magnetic fluids, microwave device, computer memory chips, magnetic recording media, choke coils, recording heads and antenna rod etc [1].

They cover a vast area of applications ranging from satellite communications, memory devices and computer components to transformer cores [2, 3]. The basic important electrical and magnetic properties of ferrites depend on various factors such as method of preparation, preparative conditions, type, amount and nature of cations [4-6]. The distribution of cations over the available sites also plays important role in governing properties of ferrites.
Ferrites are ferrimagnetic material with iron oxide as their main component. Depending on the crystal structure, ferrites can be classified into three groups, namely spinel ferrites with cubic structure, garnet with cubic structure and hexaferrites with hexagonal structure (magneto-plumbite) (Table 1.1). The structure of a ferrite can be regarded as an interlocking network of positively charged metal ions and negatively charged divalent oxygen ions.

**Table 1.1**

**Crystal types of Ferrites**

<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>$\text{M}^{II}\text{Fe}_2\text{O}_4$</td>
<td>$\text{M}^{II}$ (Cd, Co, Cu, Mg, Mn, Ni, Zn etc.)</td>
</tr>
<tr>
<td>Garnet</td>
<td>Cubic</td>
<td>$\text{Ln}^{III}\text{Fe}<em>5\text{O}</em>{12}$</td>
<td>$\text{Ln}^{III}$ (Y, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Lu etc.)</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>Hexagonal</td>
<td>$\text{A}^{II}\text{Fe}<em>{12}\text{O}</em>{19}$</td>
<td>$\text{A}^{II}$ (Ba, Sr, Ca, Pb etc.)</td>
</tr>
</tbody>
</table>

The interesting and useful magnetic and electrical properties of spinel ferrites are governed by the choice of the cations along with $\text{Fe}^{2+}$, $\text{Fe}^{3+}$ ions and their distribution over the available tetrahedral (A) and octahedral (B) sites of the spinel lattice as well as preparative method, preparation conditions, chemical composition, sintering temperature, sintering time, doping, additives etc. It is very important in many applications to control the electrical and magnetic properties of the spinel ferrite.
Table 1.2 gives the information about the properties of the spinel ferrites such as, lattice constants (expressed in angstrom unit), Curie temperature (expressed in Kelvin) and theoretical and experimental values of saturation magnetic moment at 0 K (expressed in Bohr magneton $\mu_B$) of the spinel ferrite samples.

**Table 1.2**

Properties of the spinel Ferrites

<table>
<thead>
<tr>
<th>Ferrites</th>
<th>Cell dimension (Å)</th>
<th>Tc (K)</th>
<th>Magnetic moment per molecule ($\mu_B$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CoFe$_2$O$_4$</td>
<td>8.38</td>
<td>790</td>
<td>3</td>
</tr>
<tr>
<td>CuFe$_2$O$_4$</td>
<td>a=8.22</td>
<td>720</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>c=8.71</td>
<td></td>
<td>1.3</td>
</tr>
<tr>
<td>Fe$_3$O$_4$</td>
<td>8.394</td>
<td>858</td>
<td>4</td>
</tr>
<tr>
<td>MgFe$_2$O$_4$</td>
<td>8.36</td>
<td>710</td>
<td>1</td>
</tr>
<tr>
<td>MnFe$_2$O$_4$</td>
<td>8.507</td>
<td>585</td>
<td>5</td>
</tr>
<tr>
<td>NiFe$_2$O$_4$</td>
<td>8.325</td>
<td>858</td>
<td>2</td>
</tr>
<tr>
<td>ZnFe$_2$O$_4$</td>
<td>8.44</td>
<td>--</td>
<td>5</td>
</tr>
<tr>
<td>CdFe$_2$O$_4$</td>
<td>8.69</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

1.2 Types of ferrite:

Mixed metal oxides with iron (III) oxide as their main components are known as ferrites. Depending upon the crystal structure, ferrites are classified into three types namely Spinel ferrite, Garnet and Hexagonal ferrite.
1.2.1 Spinel Ferrite:

Complex oxides with the spinel structure often called “spinels” belong to the group of strategic materials which are used in the wide area of modern technologies. They exhibit excellent magnetic, semiconducting, catalytic and absorption properties. Spinel ferrites are soft magnetic materials represented by the formula MFe$_2$O$_4$ where M stands for divalent metal ions like Mn, Fe, Co, Ni, Cu, Zn, Mg, Cd etc. The crystal structure of spinel ferrite possess two interstitial sites namely tetrahedral (A) and octahedral [B]. A variety of cations can accommodate at tetrahedral (A) site and octahedral [B] site enabling wide variation in the properties of ferrites. M can be replaced by other divalent metal ions and we can have number of spinel ferrites. Fe$^{3+}$ ions can be replaced by other trivalent ions like Al$^{3+}$, Dy$^{3+}$, Nd$^{3+}$, Sm$^{3+}$, Ga$^{3+}$, Ho$^{3+}$, Cr$^{3+}$ etc. Fe$^{3+}$ ions can also be replaced by combination of divalent and tetravalent ions.

The oxygen atom position can be defined by crystallographic oxygen parameter ‘u’ which is in between 0.375 Å and 0.400 Å. The distribution of metal ions over the available tetrahedral (A) and octahedral [B] sites is governed by the relative site preference energies of the various cations present.

1.2.1.1 Classification of spinel ferrite:

Spinel ferrites are classified into three types on the basis of the distribution of metal cations among tetrahedral (A) site and octahedral [B] site [7].

a) Normal Spinel

Normal spinel has all the divalent (A) cations on the tetrahedral (A) sites and the trivalent cations on the octahedral [B] sites. This can
be represented by the formula $[A]^{\text{tet}}[B_2]^{\text{oct}}O_4$. Examples of normal spinel are

$$\begin{align*}
\text{ZnO.Fe}_2\text{O}_3 &= \text{ZnFe}_2\text{O}_4 \quad \text{(normal)} \\
\text{CdO.Fe}_2\text{O}_3 &= \text{CdFe}_2\text{O}_4 \quad \text{(normal)}
\end{align*}$$

b) Inverse Spinel

The inverse spinel, $B(AB)O_4$, has the divalent cations occupying the octahedral sites and the trivalent cations are equally divided among the (A) and remaining octahedral sites. This can be represented by formula, $[B]^{\text{tet}}[A B]^{\text{oct}}O_4$. Examples of inverse spinel are

$$\begin{align*}
\text{CoO.Fe}_2\text{O}_3 &= \text{FeCoFeO}_4 \quad \text{(inverse)} \\
\text{NiO.Fe}_2\text{O}_3 &= \text{FeNiFeO}_4 \quad \text{(inverse)} \\
\text{MgO.Fe}_2\text{O}_3 &= \text{FeMgFeO}_4 \quad \text{(inverse)}
\end{align*}$$

c) Random Spinel

It has an intermediate cation distribution, represented as $[B_{0.67}A_{0.33}]^{\text{tet}}[A_{0.67}B_{1.33}]^{\text{oct}}O_4$. 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, so the general cation distribution random spinel can be represented as

$$[M (2)^{q+}M (1)^{p+}]^{A_N} [M (1)^{p+}M (2)^{q+}]^{B_N} O_4$$

where $M(1)^{p+}$ and $M(2)^{q+}$ are the minority and majority cations respectively. The first quantity in brackets represents the average occupancy of A-sites (coordination number of four (IV)), where as the second quantity in brackets represents the average occupancy of B-sites (coordination number of six (VI)). The variable $\delta$ is the inversion parameter, which specifies the fraction of A-sites occupied by majority ions.
Normal  \[ A^{\text{tet}}[B^{\text{oct}} O_4] \delta = 0 \]
Inverse  \[ B^{\text{tet}}[A,B^{\text{oct}} O_4] \delta = 1 \]
Random  \[ B_{0.67}^{\text{tet}}A_{0.33}{^\text{oct}}[A_{0.67}B_{1.33}]^{\text{oct}} O_4 \delta = 0.67 \]

The inversion parameter is a measure of the degree of inversion and in some ferrites depends on the method of preparation.

### 1.2.2 Garnet:

Garnets are the ferrimagnetic oxides represented by the chemical formula \( R_3Fe_5O_{12} \), where \( R^{3+} \) is yttrium (Y\( ^{3+} \)) or a rare earth ion (\( R = \text{La}^{3+}, \text{Dy}^{3+}, \text{Gd}^{3+}, \text{Er}^{3+}, \text{Sm}^{3+} \) etc.). The crystal structure of garnet possesses three sites namely octahedral, dodecahedral, tetrahedral. Ferromagnetic garnets are assigned to cubic structure (space group I\( _{4}d \)), every cell contains eight \( R_3^{3+}Fe_5^{3+}O_{12} \) molecules. \( R^{3+} \) ion cannot occupy the octahedral and tetrahedral sites because of its large ion radius, so \( R^{3+} \) ion can only occupy dodecahedral (12-coordinated) sites which have larger space.

### 1.2.3 Hexagonal ferrite:

Hexagonal ferrites have the chemical formula \( MFe_{12}O_{19} \), where \( M \) is a divalent ion of a large ionic radius, such as barium (Ba\( ^{2+} \)), strontium (Sr\( ^{2+} \)) or lead (Pb\( ^{2+} \)). The crystal structure is complex, but it can be described as hexagonal with a unique c axis, or vertical axis. This is the easy axis of magnetization in the basic structure, because the direction of magnetization cannot be changed easily to another axis.

Barium hexaferrite (BaFe\( _{12}O_{19} \)) has a complex hexagonal unit cell and belonging to the magneto-plumbite structures. Magneto-plumbites are of the type \( A^{2+}O_{1.6}B_{2.3}^{3+}O_3 \). The arrangement of the 12 Fe\( ^{3+} \) ions in the unit cell is as follows: two ions in the tetrahedral sites
(four nearest $O^{2-}$ neighbours), nine ions in the octahedral sites (six nearest $O^{2-}$ neighbours) and one ion in the hexagonal site (five nearest $O^{2-}$ neighbors). Materials of this type have a strong uniaxial magnetic direction, making as permanent magnets. This type of ferrite is termed as hard ferrite due to their high coercive force, high saturation magnetization, high Curie temperature, chemically inert and mechanically resilient.

1.3 Literature review:

Literature survey reveals that spinel ferrites ($MFe_2O_4$) are the most important magnetic material and hence are widely used for electronic applications. The high electrical resistance and low eddy current and dielectric losses, moderate saturation magnetization and high Curie temperature, all these properties of spinel ferrites have attracted the researcher and technologists. Extensive studies have been carried out on the structural, magnetic, electrical and dielectric properties of spinel ferrites [8-11]. Though, the magnetic and electrical properties of spinel ferrites have been investigated by several workers, still large numbers of investigators are working on spinel ferrites to improve their properties for desired applications. Various factors like method of preparation, nature of dopant, and its amount etc. have been taken in to account to modify or tailor-made properties of spinel ferrites.

The cobalt ferrites has been studied for its basic, electrical, magnetic and dielectric properties by several workers [12-14]. It has been reported that the substitution of divalent zinc ions in $CoFe_2O_4$ gives rise, variety of magnetic structure [15].
The effect of rare earth ions in copper zinc ferrite was also reported in the literature [16-17]. Structural properties of polycrystalline Sm$^{3+}$ doped magnesium cadmium ferrite have been investigated by A. B. Gadkari [18]. The Young’s modulus and rigidity modulus of gadolinium substituted Mn-Zn ferrites with different composition was also been reported, [19] and magnetic properties of CoFe$_2$O$_4$ ferrite doped with Nd$^{3+}$ was also reported in the literature [20].

Nano-size powder of rare-earth ions added CdFe$_2$O$_4$ ferrites shows the influence of R ions (R= Sm$^{3+}$, Y$^{3+}$, and La$^{3+}$) on the microstructure and magnetic properties of CdFe$_2$O$_4$ ferrite was studied by Ashok Gadkari [21]. Composition dependence of elastic moduli of gadolinium and High-frequency dielectric behavior of erbium substituted Ni-Zn ferrites also reported in the literature [22, 23].

Recently, investigations of the structural and magnetic properties of nano-crystalline cobalt ferrite have been the subject of many researchers because of their unusual properties which are all together different than that of the bulk cobalt ferrite. The nanocrystalline cobalt ferrite can be obtained by soft chemical routes (chemical co-precipitation, Sol-gel, Hydrothermal etc.). Very few research articles have appeared on the effect of rare earth ions on the properties of ferrites [24-26]. No systematic investigations of the properties of Dy$^{3+}$ ions doped cobalt ferrite has been seen in the literature.

Therefore, it was decided to undertake a systematic study to understand effects of rare earth ions on the structural, electrical and magnetic properties of ferrite.
1.4 Motivation of the present work:

Among the several spinel ferrites cobalt ferrite is one of the important magnetic materials with excellent magnetic and electrical properties. The crystal structure of cobalt ferrite is inverse represented as \((\text{Fe})^{A} [\text{CoFe}]^{B} \text{O}_4\). Extensive work has been carried out on the structural, electrical and magnetic properties by substituting different cations \([27, 28]\). The literature survey revealed that the substitution of rare earth ions like Gd in cobalt ferrite \([29]\) and Ho in cobalt ferrite \([30]\) has modified the electrical as well as magnetic properties. Taking into consideration the importance of cobalt ferrite it has been decided to improve the structural, electrical, dielectrical and magnetic properties by substituting rare earth ion like Dy\(^{3+}\), Gd\(^{3+}\), Sm\(^{3+}\) and Nd\(^{3+}\) in small amount.

In the present work, Dy\(^{3+}\) doped cobalt ferrite having the general formula \(\text{CoFe}_{2-x}\text{Dy}_x\text{O}_4\) \((x = 0.00, 0.05, 0.06, 0.07, 0.08, 0.09 \text{ and } 0.10)\) have been studied for its structural, electrical and magnetic properties with a view to understand the effect of rare earth (Dy\(^{3+}\)) doping on the properties of cobalt ferrite. The attempts are also made to understand the effect of rare earth ions like Gd\(^{3+}\), Sm\(^{3+}\), Nd\(^{3+}\) and Dy\(^{3+}\) on the various properties of cobalt ferrites.

The spinel ferrite system \(\text{CoFe}_{2-x}\text{Dy}_x\text{O}_4\) with varying \(x\) under investigation has been prepared by standard ceramic technique using high purity oxides. The structural characterizations were carried out by X-ray diffraction and Infra-red spectroscopy measurements.

The magnetic properties were investigated using hysteresis loop technique at room temperature. Using M-H plots (hysteresis curve), the saturation magnetization, corecivity and remenence field were
obtained. The electrical properties like d. c. electrical resistivity of all the samples under investigations have been studied by two probe techniques in the temperature range 300 – 800 K.

The dielectric properties of all the samples were investigated using LCR meter as a function of frequency. The frequency was varied from 100 Hz to 1 MHz.
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