Chapter 1
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Introduction and Literature Survey

1.1 Introduction

The ferrimagnetic oxides, ferrites are magnetic semiconductors, which cannot be replaced by any other magnetic materials because they are more stable, less expensive, easily produced and have wide field of technological applications due to their twin property of magnetic semiconductor and electrical insulator.

From the nineteen fifty, as radio and television spreads a ferrite, established a significant position in industry, and now ferrites are most essential materials in the electronic industry.

Ferrites have been recognized as one of the most important electro-ceramics in modern industry, and its processing and application technologies have been improved incessantly in the last two decades.

There are several types of ferrite materials being used in microwave components for obtaining non-reciprocal device action like isolation and phase shifting. The properties of the ferrites for use in devices at different frequency ranges are mostly designed by substituting diamagnetic metal ions for Fe$^{3+}$ in the chemical formula unit of the ferrite. The micro-level grain structure of the resulting bulk material also plays an important role.
Porosity and extra phase if present prove very disastrous for some of the properties. The properties of prime importance are magnetization, Curie temperature, dielectric and magnetic losses, hysteresis loop parameters, ferrimagnetic resonance line-width and spin-wave line-width. Ultimately these properties can be controlled by the parameters like magneto-crystalline anisotropy magnetostriction constant and microwave spin lattice relaxation.

The ferrites are technological important materials. They are widely used in electronic and computer industries because of its high permeability, high electrical resistivity, low losses and chemical stability. Recently, surface mounting devices have been rapidly developed using multi-layer chip inductor. These chip inductors are produced by coating ferrites and electrical pastes alternately and then co-firing. Such useful properties can be achieved by careful control of composition and microstructure. The physical property of ferrite depends on the method of preparation and the amount of dopant [1].

For technological purpose, the ferrites are classified as soft and hard ferrites. The soft ferrites are those, which allows the changes in magnetization to occur in weak fields, while the hard ferrite exhibit ferrimagnetic behaviour even in the absence of external field. All the magnetic elements in the pure forms are soft whereas magnetic solid solution and compounds can be either soft
or hard depending on the nature of the constituent materials and synthesis parameters.

The magnetic and electrical properties of the ferrites are strongly dependent on their physical structure. The dielectric properties of ferrites are dependent upon the several factors including the method of preparation, chemical composition and grain structure or size.

Ferro-spinels are usually synthesized by standard ceramic method. Solid-state reaction between component oxides or carbonates yields the required ferrite [2,3]. However, the method has some inherent drawbacks such as i) poor compositional control ii) chemical inhomogeneity iii) coarse particle size and iv) introduction of impurity during grinding process. Soft chemistry approaches are used for synthesizing fine particle ferrites. This method has overcome these drawbacks and produced homogeneous, fine and reproducible ferrite powder.

The ferrite (spinel, garnet and hexaferrite) can accommodate a variety of cations at different sites by virtue of their structure and exhibit a variety of electrical and magnetic properties. The method of preparation plays an important role in governing the structural, electrical and magnetic properties of ferrites [4].

The ferrites are grouped into three crystal types depending on the crystal structure; they adopt i) Cubic ferrite of spinel ii) Cubic ferrite of garnet type iii) hexagonal ferrite. [5,6,7].
The site preference of cations depends on the different factors like ionic radii, electronic configuration, electrostatic energies and polarization effects etc. [8, 9, 10]. The electrical and magnetic properties of spinel ferrites are governed by the distribution of cations amongst tetrahedral (A) and octahedral [B] sites. The relative strengths of the inter sub-lattice $J_{AB}$ and intra sub-lattice $J_{BB}$ and $J_{AA}$ interaction are thus influenced by cation distribution. The $J_{AB}$ inter sub-lattice interactions are much stronger than the $J_{BB}$ and $J_{AA}$ intra sub-lattice interactions. When $J_{AB} >> J_{BB} >> J_{AA}$ the spin exhibit the collinear structure. A non-collinear spin structure is possible when one of the intra sub-lattice [$J_{AA}$ or $J_{BB}$] interactions become comparable with inter sub-lattice interaction $J_{AB}$ [11, 12].

When ferrites are diluted by substituting nonmagnetic ions, a variety of magnetic structures viz. ferrimagnetic order, antiferromagnetic order, uniform canting, local spin or non-uniform canting, cluster spin glass are possible [13, 14].

1.2 Historical background

The story of ferrites began with the search for ferromagnetic materials of unusually high resistivity to obtain reasonable eddy current losses. When a ferrimagnetic material immersed in an alternating magnetic field, eddy current is generated in it, which dissipates energy. Since eddy current losses in ferromagnetic
material are inversely proportional to the resistivity, it can be
minimized by use of magnetic materials of high resistivity.

Besides its engineering significance, the study of ferrites
comprises a very extensive activity in the field of magnetism.
Ferrites being mixed metallic oxides of high resistivity are
members of the semiconductor family.

Although the iron ferrites (Fe$_3$O$_4$) or magnetite was but
lodestone to the ancients, the first usable modern ferrite was made
only in 1946. This may be attributed in part to the demand for
magnetic material with low core losses in carriers, radio and
television applications in recent years.

The ferrites were first developed commercially by Snoek [15]
at Philips laboratory. The crystal structure of mineral spinel
(MgAl$_2$O$_4$) is studied for the first time by Bragg in 1925 [5] and
Nishikawa in 1915 [7] independently and found it to be face
centred cubic (fcc) with larger unit cell. Activities in microwave
ferrite commenced at a still later date. Polder [16] in 1949 first
derived the ferrite permeability tensor, which laid the groundwork
for the understanding of ferrite behaviour at microwave
frequencies.

It was not until 1952 that Hogan [17], preceded by
tellegen's analysis of gyrator network [18], constructed the first
workable ferrite microwave gyrator. At the end of 1953, the first
commercially available ferrite device, the unline, a ferrite loaded
wave-guide which has different attenuation in the two opposite directions of propagation, appeared on the market. Since then the study of ferrites has been the subject of many symposia and of large number of articles.

The structure of ferrite was established to be that of spinel type. X-ray analysis of ferrite was carried out by Barth and Posnjak in 1932 [19]. According to them, it is necessary to assume that divalent metal ion and trivalent metal ion interchanges position in crystal structure. Thus, they discovered inverted spinel structure.

1.3 Crystal structure

Ferrites generally have the chemical formula $M^{2+}Fe^{3+}O_4^{2-}$ or $MO-Fe_2O_3$ (where M is a divalent metal ion) and the crystal structure is that possessed by the mineral spinel $MgAl_2O_4$. Spinel crystallizes in the cubic system, and the structure was determined first by Bragg and Nishikawa [6,7]. It is found that it has face centred cubic packing with large unit cell.

Many oxide minerals viz. Gahnite ($ZnAl_2O_4$), Magneso ferrite ($MgFe_2O_4$), Hercynite ($FeAl_2O_4$), Ulvo- spinel ($FeTiO_4$) etc. also have the spinel structure. Non-oxidic compounds can have cubic or distorted spinel structure such as $CuCr_2Se_4$, $CuCr_2Te_4$, $CuCr_2S_4$ etc., which are referred to as chalcogenides and thiospinels respectively.
Though, the most of the oxides with chemical formula MFe₂O₄ are found to have spinel structure, there are some exceptions like Olivine (Zn₂SiO₄), Crysoberyl (BaAl₂O₄) which does not have spinel structure. Thus the chemical formula alone cannot decide the structure but the cationic radii decides the structure. For oxide spinels cation of radii \(0.45\text{Å}\) to \(0.95\text{Å}\) are suitable for the formation of spinels. There are few compounds with slightly different chemical formula such as \(\gamma\)-Fe₂O₃ and \(\gamma\)-Mn₂O₃ also has spinel structure. Thus compounds with slightly different chemical formula but with proper cationic radii can also have spinel structure.

In the ferrites with spinel structure the metallic ions are distributed over two crystallographically different sites namely octahedral [B] and tetrahedral (A) site. The unit cell contains eight molecules and may thus be written as \(\text{M}_8\text{Fe}_{16}\text{O}_{32}\). The oxygen anions are physically the greatest and they form, ideally a face centred cubic lattice [Fig.1.1]. Within this lattice two types of interstitial position occurs, tetrahedral (A) and octahedral [B], and these are occupied by the metallic cations.

There are ninety-six interstitial sites in the unit cell, sixty-four tetrahedral and thirty-two octahedral, out of which only eight and sixteen respectively are occupied by cations.
Wyckoff [20] gives the spinel space group as $O_h^7$ (Fd3m) and the ionic positions as:

**anion 32 b**

\[ u, u, u; \frac{1}{4} - u; \frac{1}{4} - u; \frac{1}{4} - u; \]

\[ -u, u \uparrow; u \uparrow; \]

**cation 16c**

\[ \frac{5}{8}, \frac{5}{8}, \frac{5}{8}, \frac{5}{8}, \frac{7}{8}, \frac{7}{8}, \frac{7}{8}, \frac{7}{8}, \frac{7}{8}, \frac{7}{8}, \frac{7}{8}, \frac{7}{8}, \frac{7}{8} \]

**cation 8f**

\[ 0, 0, 0; \frac{1}{4}, \frac{1}{4}, \frac{1}{4} \]

with the translations, for a face centred lattice,

\[ +0, 0, 0; 0, \frac{1}{2}, \frac{1}{2}, 0, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}, 0 \]

packing of the ions within the lattice is perfect when the oxygen parameter, $u = 3/8$.

The crystal structure is best described by subdividing their unit cell into eight octants, with edge $1/2$ a ['a' is edge of the unit cell] as shown in Fig.1.2. The location of oxygen ion and metal ion in every octant can easily be described. The oxygen ions are arranged in identical manner in all these octants. Each octant
contains four oxygen ions in the body diagonals and they lie at the tetrahedron [Fig.1.2]. Each oxygen ion is located at a distance equal to 1/4 of the body diagonals at the alternate corners of the octant. The array of oxygen ions as a whole in the crystal constitutes a fcc lattice with edge = a/2 and thus there are four such interpenetrating fcc oxygen lattices. The positions of metal ions are different in the two octant of a unit cell as can be seen from the Fig.1.2. Each cation on a so-called A-site has four neighbouring oxygen ions, tetrahedrally distributed. Each cation on B-site has six neighbouring oxygen ions, in the form of regular octahedron.

Each oxygen ion is surrounded by one tetrahedral ion (A ion) and three octahedral ions (B ion) as shown in Fig.1.3. This unit can be regarded as basic component of the spinel lattice. Each A ion belongs to such four unit and each B ion to six. In many cases the close packing of oxygen ions is defined due to presence of metal ions of different sizes in these interstices. The oxygen ion then moves along the body diagonal. The direction of OA is that of the body diagonal of a cube and the direction OB are along the cube edge.

If the distance between the oxygen ion and given cube edge is u-A, u-gives a quantitative measure of displacement of an oxygen ion from its ideal position and is called oxygen ion parameter. It is 0.375 in an ideal spinel structure corresponding to perfect close
packing of cations. The structural coordinates of all cation in the cubic spinel are specific and those of anions are general in terms of ‘u’.

1.4 Classification of spinels

The ferrites with spinel structure, takes its name from mineral spinel MgAl$_2$O$_4$, which crystallizes in cubic system [6,7]. The ferrites are semiconductors having the general chemical formula MFe$_2$O$_4$, the M cation usually being divalent and Fe$_2$ cation trivalent. The spinel structure consists of a closed packed face-centred cubic arrangement of the oxygen ions. The cations are distributed in the interstitial sites between them. The unit cell contains thirty-two anions and twenty-four cations of both kinds. Eight cations on A-site are surrounded tetrahedrally by four oxygen ions and remaining sixteen cations on the B-sites are surrounded octahedrally by six oxygen ions.

If all M$^{2+}$ ions in MFe$_2$O$_4$ are in tetrahedral A-site and all Fe$^{3+}$ in octahedral B-site positions, the spinel ferrite is then called "Normal". The typical examples of normal ferrites are ZnFe$_2$O$_4$ and CdFe$_2$O$_4$ [8,21]. If one half of the cations Fe$^{3+}$ are in A-positions and the rest together with the M-ions are distributed among the B-positions, the spinel ferrite is called an “Inverse”. The typical examples of inverse ferrites are NiFe$_2$O$_4$ and CoFe$_2$O$_4$ [22,23]. There are several examples of intermediate cases
between a normal and an inverse spinel (mixed spinel). Therefore, in order to characterize fully the spinel structure, a further parameter is needed describing the degree of inversion. The chemical formula may be written as,

\[(M_{1-x}Fe_x)^A [M_xFe_{2-x}]^B O_4 \]  \hspace{1cm} (1.1)

when \( x = 0 \), Normal spinel
\( x = 1 \), Inverse spinel
\( 0 < x < 1 \), Partially inverse spinel.

The electro-neutrality considerations lead to three basic spinel types, according to the cation valency combinations in MFe₂O₄:

\[ M^{2+}Fe^{3+}O_4^{2-} \hspace{1cm} (2 - 3 \text{ spinel}) \]
\[ M^{4+}Fe^{2+}O_4^{2-} \hspace{1cm} (2 - 4 \text{ spinel}) \]
\[ M^{6+}Fe^{1+}O_4^{2-} \hspace{1cm} (6 - 1 \text{ spinel}). \]

Completely normal or completely inverse ferrites represent extreme cases. The general cation distribution can be written as

\[(M_{1-x}^{2+}Fe_x^{3+})^A [M_x^{2+}Fe_{2-x}^{3+}]^B O_4^{2-}\]  \hspace{1cm} (1.2)

where, the degree of inversion, \( x \), depends on the preparation conditions, particularly the heat treatment. For example, the compounds MgFe₂O₄ and CoFe₂O₄ are partially inverse spinels and the cation distribution in them is strongly dependent on the
heat treatment of the material. The site preference of cations depends upon factors like i) ionic radius ii) electrostatic energy [8] iii) covalent bonding and hybridization etc. [9].

1.5 Literature survey and aim of the present work

Ferrites have been the subject of extensive study because of their wide range of applications from microwave to radio frequency and of their importance in understanding the theories of magnetism. They exhibit relatively high resistivity at carrier frequency, sufficiently low losses for microwave applications and a wide range of other electrical properties. These materials are extensively used in microwave devices, computer memory chips, magnetic recording media etc. Ferrites belonging to magnesium ferrite family having inherent rectangular hysteresis loop characteristics were first to be identified for use in memory cores. The spinel ferrites with divalent nonmagnetic substitution like Zn\(^{2+}\) and Cd\(^{2+}\) have been the subject of many investigations [24,25,26] because of their magnetic properties resulting from a particular configuration of cations in the lattice. It is well known that the Zn\(^{2+}\) and Cd\(^{2+}\) ions preferably occupies tetrahedral A–sites, thereby perturbing collinear Neel structure due to A–site dilution and give rise to canted spin structure.

The interesting physical and chemical properties of ferrospinels arise from their ability to distribute the cations
among the available tetrahedral A and octahedral B-sites. The knowledge of cation distribution and spin alignment is essential to understand the magnetic properties of spinel ferrite. The magnetic structure of the spinel ferrites depends upon the types of magnetic ions residing on the tetrahedral A and octahedral B-sites and the relative strength of the inter [J_{AB}] and intra sub-lattice interaction [J_{AA}, J_{BB}].

Magnesium ferrite belongs to a class of compounds having the general formula \( \text{M}^{2+}\text{Fe}^{3+}_2\text{O}_4^{2-} \) crystallizing with spinel structure. Magnesium ferrite [MgFe\(_2\)O\(_4\)] is a typical spinel in which the cation distribution in the crystal lattice site is very much sensitive to heat treatment due to high diffusibility of Mg\(^{2+}\) ions [27]. According to literature survey the magnesium ferrite belongs to the partially inverse spinel and it can be considered as a collinear ferri-magnet whose degree of inversion depends on the thermal history of the samples [28]. In the literature, studies on the substitution of nonmagnetic Zn\(^{2+}\) and Cd\(^{2+}\) ion in MgFe\(_2\)O\(_4\) are available [29,30,31,32]. Recently some work has been reported on Al\(^{3+}\) substituted MgFe\(_2\)O\(_4\) [33,34] and Cr\(^{3+}\) substituted Mg-ferrite [35,36]. The addition of tetravalent ions in spinel ferrites influences the structural, electrical and magnetic properties of the MgFe\(_2\)O\(_4\) system. The substitutions of tetravalent ions like Ti\(^{4+}\) are reported in the literature. Brand et al [37] have found in the case of Mg\(_{1-x}\)Ti\(_x\)Fe\(_{2-2x}\)O\(_4\) that on increasing dilution x the
collinear ferrimagnetic phase breaks down before reaching the ferrimagnetic percolation threshold and for higher concentration of Ti$^{4+}$ system approaches towards spin glass.

In order to understand the influence of magnetic ions Mn$^{4+}$ in place of nonmagnetic Ti$^{4+}$, we have carried out the studies of Mg$_{1+x}$Mn$_x$Fe$_{2-2x}$O$_4$ by replacing non-magnetic Mg$^{2+}$ by magnetic Mn$^{4+}$. With a view to understand the structural, electrical and magnetic properties of Mg$_{1+x}$Mn$_x$Fe$_{2-2x}$O$_4$ for $x \leq 0.9$.

Cobalt ferrite possesses an incomplete inverse inverse spinel structure and the degree of inversion depends on the heat treatment [38]. The addition of tetravalent ions like Ti$^{4+}$, Ge$^{4+}$ and Si$^{4+}$ influence electrical and magnetic properties of the systems [39,40,41]. The addition of Cr$^{3+}$ ions in the ferrite systems is likely to increase the resistivity and decrease the saturation magnetization [42]. In the literature the studies on the substitution of divalent cations like Zn$^{2+}$ and Cd$^{2+}$ [43,44] and trivalent cations like Al$^{3+}$ and Cr$^{3+}$[45,46] have been appeared. Many workers have studied the substitution of Sn$^{4+}$ ions in nickel ferrite [47,48,42,50]. It has been reported that a smaller substitution of Sn$^{4+}$ ions in nickel ferrite increases the resistivity by segregating at grain boundaries and hence acts to decrease the electrical losses. A larger substitution of Sn$^{4+}$ ions however causes discontinuous grain growth, which decreases the initial permeability and increases the magnetic loss factor. The presence
of Mn\textsuperscript{3+}, Fe\textsuperscript{2+} or Co\textsuperscript{2+} in the ferrite system introduces an additional factor (i.e. uniaxial anisotropy [50]) which increases the possible magnetic structure and may changes the phase diagram of the system.

The system under investigations Co\textsubscript{1+y}Sn\textsubscript{y}Fe\textsubscript{2-2y-x}Cr\textsubscript{x}O\textsubscript{4} (y = 0.05 x = 0.0 to 0.5) contains the anisotropic magnetic ions Co\textsuperscript{2+}, small amount of Sn\textsuperscript{4+} and Cr\textsuperscript{3+}, which may lead to affect the magnetic and electrical properties of the system. In view of this the structural, electrical and magnetic properties of the Co\textsubscript{1+y}Sn\textsubscript{y}Fe\textsubscript{2-2y-x}Cr\textsubscript{x}O\textsubscript{4} system (y = 0.05, x = 0.0 to 0.5) are investigated by means of X-ray diffraction, infrared, a.c./d.c. resistivity, thermoelectric power measurements, dielectric properties, a.c. susceptibility and magnetization. No measurements have previously been reported in the literature.

Second chapter of thesis is devoted to experimental techniques used in the present investigation of the ferrite systems.

Third chapter of the thesis describe briefly the electrical and magnetic properties of the spinel ferrites. It also includes the Neel’s model and Yafet-Kittel model of ferrimagnetism.

Fourth and fifth chapters of the thesis are devoted to Results and Discussion of the Mg\textsubscript{1+x}Mn\textsubscript{x}Fe\textsubscript{2-2x}O\textsubscript{4} (x = 0.0 to 0.9) and Co\textsubscript{1+y}Sn\textsubscript{y}Fe\textsubscript{2-2y-x}Cr\textsubscript{x}O\textsubscript{4} (y = 0.05, x = 0.0 to 0.05) ferrite system respectively.
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Fig. 1.1  Details about the crystal structure of spinel
Fig. 1.2  The eight octants in the unit cell
Fig. 1.3 Basic component of a spinel lattice

○ — Octahedral Metal Ions
○ — Tetrahedral metal Ions
○ — Oxygen Ions

→— Indicates the direction in which the oxygen ion moves in the case $u > 3/8$