CHAPTER 2

REVIEW OF LITERATURE

2.1 Introduction

This chapter includes overview of ferrites; the ferrites have been widely used in electronic applications such as transformer cores, choke coils, noise filters, recording heads etc. William Gilbert was the first who assumed earth as a giant magnet and observed that magnetic needle was attracted by the magnetic poles of the earth coinciding with geographical poles of the earth. He also realized that attraction of amber was not a cause of magnetism but because of “electricity” name derived from Greek name “electron”. He observed that the attraction between the substances was not a property of individual substance but it was a “fluid” produced by rubbing the two bodies. Ferrites are ferrimagnetic materials possessing good electrical and magnetic properties while maintaining dielectric properties. Electrical properties means ferrite can exhibits properties like conductivity and resistivity. Magnetic properties means a piece of ferrite can attract other magnetic materials. Dielectric properties mean electromagnetic waves can pass through ferrites without conducting electricity. Ferromagnetic materials such as transition metals iron, cobalt, nickel etc. exhibit ferromagnetic properties and readily conduct electricity as all the spin exhibit parallel alignment. But on the other hand ferrimagnetic material exhibit antiparallel alignment with different magnitude of magnetic moments. As the magnetic character of ferrites depends on the alignment of magnetic moments, so they lose their magnetism when subjected to high temperature or mechanical stress. The most important application of ferrites is used as medium for transmitting microwaves.

In 1909 William Hilpert was the first who successfully prepared manganese, copper, cobalt, magnesium and zinc doped spinel ferrite and use these magnetic materials for high frequency applications (Hilpert, 1909). In 1932 Dr. Takashi Takei and Dr. Yogoro Kato of Japan commercialize ferrite as electronic material. They reported that a solid solution of magnetite and cobalt ferrite strongly magnetized at approximately 100 °C and this was commercialized as “OP magnet” in 1935. Initially ferrites were used as a permanent magnet in order to oppose electromagnet. Other
types of applications in which ferrites were used such as electric motors and generators, inductor and transformer cores, up to 1990s cassettes and video tapes were used as recording media in which brownish ferrite material is coated on a plastic tape so as to recording purpose. In computers ferrites were used as magnetic core memories. There is also a discovery of commercial ferrite core when they reported that permeability of mixed ferrite is very large. Neel in 1948 explained three magnetic ordering of ferrites and explain the mechanism behind the enhancement in magnetization of zinc ferrite (Sugimoto, 1999). J.L. Snoek, (1936) studied the magnetic and electrical properties of the binary systems MO\(\cdot\)Fe\(_2\)O\(_3\). He reported that a single phase ferromagnetic system can be obtained and the manganese ferrite exhibit saturation along with a resistivity of \(10^5\) at room temperature.

The spinel ferrites which are commercial used from last 4 -5 decades for example: Cu-Zn, Ni-Cu-Zn, Mn-Zn, Ni-Zn ferrites are used in transformers as ferrite core magnetic recording; Mn-Zn ferrite are used as read write heads; Yttrium Iron Garnet (YIG), Ni-Zn and Mn-Zn ferrites are operating at microwave frequency; CoFe\(_2\)O\(_4\), Ba-ferrite and Sr-ferrite as permanent magnet. Microwave magnetic materials have been used in different radio frequency (RF) devices such as inductors, filters, circulators, isolators and phase shifters. The increasing demand of integrated circuit and miniaturization of electronic devices used in telecommunication radar systems stimulated the research in improving the properties of the magnetic material. The application of ferrites can be used in electromagnetic devices operating at the microwave frequency. There are two categories of electromagnetic devices; the first class of devices makes use of nonreciprocal behavior obtainable with ferrites and the second class is based on the fact that the microwave behavior can be substantially modified by the applications of a biasing field. The first class comprises primarily of isolators and circulators and second class comprises primarily switches phase shifters and tunable fillers. The good microwave material depends upon; the operating frequency which largely determines the saturation magnetization, low dielectric and magnetic loss, insensitivity to temperature variation, high ratio of remanent magnetization to saturation magnetization., sensitivity to strain (Schlömann, 1971). Magnetic material earlier which dominated the microwave devices technology were Mg-Mn and Ni ferrite. Ceramic magnetic materials have wide range of applications in our day to day life such as industry, technology, home appliances, electronic devices,
communication equipments, data processing devices etc. Ferrimagnetic materials are of three types; spinel, garnet and hexaferrites. Table 2.1 gives the bibliographical development of ferrites.

**Table 2.1 Development of ferrites**

<table>
<thead>
<tr>
<th>Year</th>
<th>Discoverer and Discovery</th>
<th>Phenomena</th>
</tr>
</thead>
<tbody>
<tr>
<td>600 B.C</td>
<td>Thales of Miletus</td>
<td>Rubbing amber and jet etc. attracts straw and leaves</td>
</tr>
<tr>
<td>800 B.C</td>
<td>Ancient Greeks</td>
<td>Ferrite (Fe_2O_3) an iron ore have ability to attract the iron nails</td>
</tr>
<tr>
<td>1600</td>
<td>William Gilbert</td>
<td>“De Magnete, Magneticisque Corporibus, et de Magno Tellure” described the magnetic properties of lodestone</td>
</tr>
<tr>
<td>1729</td>
<td>Stephen Gray</td>
<td>Electric force can be generated by rubbing glass and can transmit through a wire for long distance</td>
</tr>
<tr>
<td>1736</td>
<td>Charles Francois de Cisternay Du Fay</td>
<td>Rubbing glass and resin produce different kinds of charges</td>
</tr>
<tr>
<td>1746</td>
<td>William Watson</td>
<td>Rubbing a comb with wool transfer some electricity from comb to wool, hence wool get extra electricity which he called as positive (+) and comb left with less electricity (-)</td>
</tr>
<tr>
<td>1752</td>
<td>Benjamin Franklin</td>
<td>Discovered electricity proved that lightning was an electrical discharge when two clouds of opposite polarity come in contact with each other. The term “charge” introduced by him</td>
</tr>
<tr>
<td>1791</td>
<td>Charles Augustine de Coulomb</td>
<td>Coulomb’s Law of Electrostatic</td>
</tr>
<tr>
<td>1897</td>
<td>J.J Thomson</td>
<td>Discovered electron</td>
</tr>
</tbody>
</table>
| 1936, 1947 | J. L. Snoek         | “Magnetic and Electrical Properties of the Binary Systems MO·Fe_2O_3,” “New Developments in Ferromagnetic
2.2 Zinc ferrite

Zinc ferrite (ZnFe\(_2\)O\(_4\)) is normal spinel ferrite in which tetrahedral (A) site is occupied by Zn\(^{2+}\) ion and octahedral site is occupied by (B) site having a wide range of application such as catalytic activity and gas sensing. Gao et al., (2010) defined that ZnFe\(_2\)O\(_4\) is a normal with Zn\(^{2+}\) ions at the A sites and Fe\(^{3+}\) ions at the B sites and it exhibits antiferromagnetic ordering below 10 K. Nanocrystalline ZnFe\(_2\)O\(_4\) with a grain size of about 10-20 nm is magnetically ordered with a large magnetic moment even at high temperatures. The observed high temperature magnetic ordering is attributed to the change in the cation distribution from the normal to the mixed spinel type where Fe\(^{3+}\). Cost effectiveness, low eddy current losses, high frequency in core devices, compact size, and high saturation magnetization makes it important magnetic material. Core losses arise due to eddy current losses and hysteresis loss.

2.3 Cadmium ferrite

Cadmium ferrite (CdFe\(_2\)O\(_4\)) has normal spinel structure in which Cd\(^{2+}\) occupy A-site and Fe\(^{2+}\) occupy B-site. It exhibit anomalous antiferromagnetism which may be attributed to the small amount of occupancy of Fe\(^{3+}\) ion which couples with the Fe\(^{3+}\)
ions of B-site give rise to A-B interaction dominates the B-B interaction (Deraz et al., 2009).

### 2.4 Magnesium ferrite

Magnesium ferrite (MgFe$_2$O$_4$) is a partial inverse spinel ferrite and is a soft n-type soft magnetic semiconducting material and have application in catalysis, gas sensors and cores of transformers ferrofluids and magnetic coils etc. These ferrites also used in tumors treatment using thermal coagulation therapy by applying alternating magnetic field (Hankare, 2009 and Ahmed, 2010). Other applications of these ferrites are used in switching devices due to their spontaneous rectangular-hysteresis-loop behavior with high rectangular ratio.

### 2.5 Nickel ferrite

Nickel ferrite (NiFe$_2$O$_4$) is an inverse spinel ferrite in which metal cations are located at two different crystallographic sites [(Fe$^{3+}$)$_{tet}$ (Ni$^{2+}$Fe$^{3+}$)$_{oct}$O$_4$] as in inverse ferrospinsels Fe$^{3+}$ is located at tetrahedral site and octahedral site is occupied by Fe$^{3+}$ and other metal cation. It is a p-type semiconductor in order to possess p-type conductivity the material contains cation vacancies and there should be introduction of Ni$^{3+}$ ion at the octahedral site besides the cations Ni$^{2+}$ and Fe$^{3+}$. According to Smit and Wijn, (1965), the net magnetic moment per molecule in the nickel ferrite is 2µ$_B$ and in the cobalt ferrite is 3µ$_B$ with high Curie temperature (T$_C$) of 858 K and 793 K respectively.

Reddy et al., (1999) reported that NiFe$_2$O$_4$ can be used as a sensor to detect low concentration of chlorine gas in air. They prepared nickel ferrite by coprecipitation as well as citrate precursor method because for sensing application low density and high surface area is required. It was found that the material prepared by coprecipitation method has lower crystallite size ~ 175 Å and that prepared by citrate precursor method is ~ 275 Å therefore they concluded that the value of sensitivity for the sensor using nickel ferrite prepared by coprecipitation method is more. Amarendra et al., (2002) studied the magnetic properties of Mn-substituted Ni-Zn ferrite because of the reason that although Ni-Zn ferrites are good magnetic materials for high frequency applications due to their high resistivity and high saturation magnetization.
but Mn-Zn ferrite possesses more favorable magnetic properties. Bharathi and Markandeyulu, (2008) studied the ferroelectric and ferromagnetic properties of Gd substituted nickel ferrite. They reported that larger ionic size of Gd$^{3+}$ than that of Fe$^{3+}$ disturb the centrosymmetric nature which results in net polarization. The value of transition temperature for ferroelectric was found to be 512 K and for NiO · Fe$_{1.925}$Gd$_{0.075}$O$_3$ the polarization loop confirmed the existence of ferroelectricity. Also there is decrease in net magnetic moment at B site cause a decrease in the saturation magnetization.

Thakur et al., (2011) investigated porous and spinel structure nanoferrite with composition Ni$_{0.35}$Zn$_{0.35}$Co$_{0.2}$Mn$_{0.05}$Cu$_{0.05}$Fe$_{1.98}$O$_4$ possesses equal value of permeability and permittivity as a low loss magneto-dielectric material to miniaturize antenna operated at radiofrequency range. Coprecipitation method followed for the preparation of nanoferrite. It was concluded that Ni$_{0.35}$Zn$_{0.35}$Co$_{0.2}$Mn$_{0.05}$Cu$_{0.05}$Fe$_{1.98}$O$_4$ sintered at 900 °C with average crystallite size 38 nm. Prasad et al., (2011) studied the magnetic properties and DC electrical resistivity of cadmium substituted nickel-zinc ferrite. They reported the distinct effects of cadmium. Firstly, ionic radius of Cd$^{2+}$ is larger, substitution of Cd$^{2+}$ ions in the spinel lattice create a distortion, which affects the properties of material. Also, the outer shell electronic configuration of Cd$^{2+}$ ion is 5s5p which are sp$^3$ hybridized to form covalent bonds with oxygen ions. Secondly, volatilization of cadmium and zinc take place at elevated sintering temperature resulting in cation vacancies and formation of Fe$^{2+}$ ions affects the properties of the material. Substitution of Cd$^{2+}$ in place of Ni$^{2+}$ in Ni$_{0.65-x}$Cd$_x$Zn$_{0.33}$Fe$_2$O$_4$ (x = 0.00 to 0.20 in steps of 0.04) has been done. XRD pattern revealed the formation of single phase spinel structure, lattice parameter increase with cadmium substitution obeying Vegard’s Law. They found that there is decrease in room temperature specific saturation magnetization and curie temperature attributed to diminish of A-B exchange interaction and growth of B-B interaction due to the addition of cadmium concentration.

Šukta et al., (2015) synthesized p-type and n-type nickel ferrite and studied the influence of grain size on electrical resistivity with comparison in p-type or n-type nickel ferrites. They explained that in n-type spinel ferrite charge carrier concentration can be increased by introducing oxygen vacancies or cation interstitials. An oxygen vacancy carry two effective positive charges as the site will missing two electrons compared to O$^{2-}$ but cation interstitial carry positive charges due to additional positive
charges in interstitial sites. So in order to maintain the overall charge neutrality of the lattice these defects are neutralized by introduction of extra electrons, as these induced electrons are loosely bound to the lattice and hence contribute more to the conductivity. In p-type spinel ferrite charge carrier concentration can be increased by introducing cation vacancies or oxygen interstitials. As cation vacancies or oxygen interstitials both carries negative charges and hence neutralized by introduction of holes or by increasing oxidation state of doped metal cation at the octahedral site (Gimenes et al., 2012).

2.6 Manganese ferrite

High initial permeability, low losses, high resistivity, high saturation magnetization and high Curie temperature make manganese ferrites promising candidates than other spinel ferrites. Although Mn-Zn possess high initial permeability and magnetization but these are not found suitable for high frequency magnetic applications. On the other hand Ni-Zn ferrite possesses high resistivity, low dielectric loss and high Curie temperature but they have relatively low initial permeability at high frequencies. So the combination of Mn-Zn and Ni-Zn ferrite make them suitable for high frequency applications (Sattar et al., 2005). They reported the increment in the dc resistivity and Curie temperature of Mn-Ni-Zn ferrite with doping of non-magnetic Al$^{3+}$ ion. Manganese ferrite exhibit magnetization of different orders of magnitude even if having the similar size of particles due to inversion of Mn and Fe ions over sites (Farooq, 2012). Bulk manganese ferrite has low magnetic anisotropy at room temperature arising from the low magnetocrystalline anisotropy energy due to $^6$S ground state of manganous Mn$^{2+}$ and ferric Fe$^{3+}$ ions cubic crystalline symmetry (Zuo et al., 2005). Macklen, (1968) reported that MnFe$_2$O$_4$ was unstable in as Mn$^{2+}$ ions on the surface oxidize to form Mn$^{3+}$ ions resulting in dissociation of the ferrites.

Son et al., (2002) studied the structural and magnetic properties of thermally plasma synthesized Mn and Mn-Zn ferrite nanoparticles. XRD studies revealed the phase formation of Mn and Mn-Zn ferrite with all major peaks. Average particle size as calculated from Scherrer formula was found to be 15 nm and 21 nm for Mn-ferrite and Mn-Zn ferrite. They reported that saturation magnetization ($M_S$) and the
coercivity ($H_C$) of Mn ferrite are 23.6 emu/g and 20 Oe respectively. And the Neel temperature of as-prepared Mn ferrite is 200 °C. Hyeon et al., (2002) synthesized highly crystalline and monodisperse cobalt ferrite by the high temperature aging of a metal–surfactant complex followed by mild oxidation. The obtained magnetic nanocrystals are uniform supported by narrow energy distribution of magnetic anisotropy. In the co-precipitation method two metal salts are reduced to the hydroxide by the action of an alkali. The hydroxides then react to form the ferrite on mild heating (100 °C). It is this difference in temperature at which the ferrite forms that leads to the difference in crystallinity. Also the decomposition of a complex is a single nucleation process for each particle, whereas in the co-precipitation method multiple nucleations occur, leading to a wide particle distribution (Virden et. al., 2007). Mathur et al., 2007 reported that conduction mechanism in MnFe$_2$O$_4$ and Mn$_{0.8}$Zn$_{0.2}$Fe$_2$O$_4$ is n-type attributed to the hopping of electrons. Thakur et al., (2007) investigated the effect of substitution of Al$^{3+}$ and In$^{3+}$ ions on the electrical and magnetic properties of the system of ferrites Mn$_{0.4}$Zn$_{0.6}$M$_x$Fe$_{2-x}$O$_4$ (where M = Al$^{3+}$ and In$^{3+}$ and $x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5$). Substitution of Al$^{3+}$ on the basic Mn$_{0.4}$Zn$_{0.6}$Fe$_2$O$_4$ preferred B-sites and cause to displace the equal number of Fe$^{3+}$ ions from the B-site and hence increase in dc resistivity but for In$^{3+}$ ions it was observed that it occupied both A-site and B-site by displacing the Fe$^{3+}$ ions on both sites, therefore it was observed that there was increase in dc resistivity at very slow rate. Saturation magnetization (4π$M_S$) decrease with the introduction of Al$^{3+}$ on B-site while substitution In$^{3+}$ ion increase the magnetization for the composition (0 < $x$ < 0.3) and after $x = 0.3$ there was decrease. Initial increase in saturation magnetization was due to the fact that substitution of In$^{3+}$ ions at A-site lead to rise in magnetic moment of B-site while slight decrease in the magnetic moment at A-site, hence results in overall increase in net magnetic moment.

Mathur et al., 2007 studied the effect of temperature on structural, electrical and magnetic properties of Mn$_{0.4}$Zn$_{0.6}$Fe$_2$O$_4$ synthesized by co-precipitation method. They concluded that initial permeability ($\mu_i$) is a function of ambient temperature that is Curie temperature ($T_C$) because below just $T_C$ ($\mu_i$) increases to peak value with the temperature and decreases to ($\mu_0$) above the $T_C$. Also they found that coprecipitation method is an effective method to synthesize nanoparticles of Mn-Zn ferrite at low temperatures. The ferrite obtained at 500 °C sintering temperature has homogeneous
and fine grained microstructure. Mn-Zn ferrite sintered at low temperature possesses good electromagnetic properties. Magneto - dielectric materials are found to be promising candidates with high refractive index matching impedance to the free space possesses potential electromagnetic applications.

Tang et al., (2008) developed a heat inducible generation system in which thermal energy generated by Mn-Zn ferrite nanoparticles. They reported that it is a promising gene therapy approach which is applicable in treatment of cancer. Manganese zinc ferrite nanoparticles exhibit low Curie temperature which is advantageous in order to control in vivo hyperthermia temperature. Nalbandian et al., (2008) synthesized a series of $\text{Mn}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.1$ to $0.9$ in steps of $0.1$) by hydrothermal method by precipitating metal chloride solutions in aqueous ammonia. It was observed from thermo gravimetric analysis (TGA) that $200^\circ\text{C}$ to $400^\circ\text{C}$ a weight gain was observed attributed to the oxidation of $\text{Mn}^{2+}$ to $\text{Mn}^{3+}$ or $\text{Mn}^{4+}$. But for the temperature between $400^\circ\text{C}$ to $650^\circ\text{C}$ a weight loss was observed attributed to the reduction of $\text{Mn}^{4+}$ to $\text{Mn}^{3+}$. In the temperature range $650^\circ\text{C}$ to $750^\circ\text{C}$ a weight gain was observed attributed to the oxidation of $\text{Mn}^{2+}$ to $\text{Mn}^{3+}$ which was not completed at lower temperature. For the temperature above $750^\circ\text{C}$, a continuous weight loss occurs corresponding to the sintering of ferrite powder and formation of spinel structure. Saturation magnetization increased linearly as increment in manganese content attributed to the fact that manganese ion increase the magnetic moment of the sublattice consists of tetrahedrally coordinated ions. Mathur et al., (2008) reported that Mn-Zn ferrites possess high initial permeability but low resistivity whereas Ni-Zn ferrites possess high resistivity but low initial permeability. But for high frequency applications high permeability as well as high resistivity needed. So they synthesized $\text{Mn}_{0.4}\text{Ni}_x\text{Zn}_{0.6-x}\text{O}_4$ by citrate precursor and studied for low and high frequency applications. Lee et al., (2009) synthesized Ni-Mn-Co ferrite for gigahertz chip devices and studied the static, dynamic magnetic properties and thermal stability factor of Ni-Mn-Co ferrite. They reported that saturation magnetization increase with increase in Mn content, while coercivity increased with increase in Co content. Co-substituted Mn-Co content enhanced the thermal stability of the system as compare to the singly doped Mn or Co system. They found that the composite ferrites are good candidate for chip device application in megahertz and gigahertz. Bayrakdar and Esmer, (2010) investigated theoretically as well as
experimentally dielectric behavior of thin film of Ni$_{1-x}$Co$_{1-x}$Fe$_2$O$_4$ nanoparticles over a frequency ranges of (1 MHz – 3 GHz). XRD studies revealed the formation of high phase purity, crystallinity and inverse spinel ferrite. It was found that increase in Ni/Co ratio increase the real and imaginary part of permittivity shifts to higher frequency.

Lamani et al., (2011) studied the dielectric properties of polycrystalline Cu$_{1-x}$Zn$_x$Fe$_2$O$_4$ ferrites at microwave frequencies. It was reported that increase in Zn concentration enhances the dielectric properties. Batoo, (2011) studied the dielectric and impedance properties of Mn ferrites. He reported that variation of dielectric properties and ac conductivity with frequency revealed that the dispersion is due to Maxwell–Wagner type of interfacial polarization in general and hopping of charge between Fe$^{+2}$ and Fe$^{+3}$ as well as between Mn$^{+2}$ and Mn$^{+3}$ ions at octahedral sites. Hankre et al., (2011) studied the effect of Cr$^{3+}$ substitution in nanocrystalline characterizing the gel decomposition; only one TG step accompanies the decomposition of the as-prepared precursor. For the gel precursor, the first step up to 150 °C can be attributed to the gel dehydration process. The second step is the main decomposition step and exhibits a steep weight loss, amounting to 73 % at 188 °C which is attributed to the violent decomposition of the NH$_4$NO$_3$ contents of the gel. The precursor is observed to be thermally stable up to 275 °C, then its citrate contents starts to decompose in the third step, exhibiting a weight loss of 3.5%. Beyond 310 °C, no further weight loss can be detected.

Praveena et al., (2012) synthesized Mn-Zn ferrite by Microwave-Hydrothermal (M-H) method and investigated the electrical properties over a frequency range of 10 Hz-1.3 GHz and concluded that transformer constructed with nanocrystalline ferrite show high efficiency and show low temperature rise at the driving frequency of 1 MHz. Mn-Zn (manganese zinc) and Ni-Zn (nickel zinc) ferrites are used in various devices such as inductor cores, converters, magnetic heads, electromagnetic wave absorbers etc. Mostafa et al., (2013) synthesized MnFe$_2$O$_4$ and Cd-substituted MnFe$_2$O$_4$ via hydrothermal route and studied the effect of Cd doping on the structural and magnetic properties of Mn$_{1-x}$Cd$_x$Fe$_2$O$_4$ varying from 0.1 to 0.3. For x = 0.1 the Cd$^{2+}$ ions occupy the tetrahedral A – sites which results in increase in lattice parameter and saturation magnetization. With further increase in doping upto x
= 0.3, the Cd$^{2+}$ ions substitute Mn$^{2+}$ and Fe$^{3+}$ ions at A-site and B-site whereas saturation magnetization increased due to dilution of Fe$^{3+}$ in B-sublattice. Gabal et al., (2013) studied the influence of Al-substitution on structural, electrical and magnetic properties of Mn-Zn ferrites nanopowders prepared via the sol-gel auto-combustion method. They reported that thermogravimetric studies of the as-prepared manganese zinc ferrite showed a weight loss up to 320 °C assigned to the decomposition of citrate content and concluded that reaction is not completed during auto-combustion reaction but calcinations is required at 300 °C. Thakur et al., (2014) followed citrate precursor method because of its economic, effective and low cost production for the preparation of Mn$_{0.4}$Zn$_{0.6}$In$_{0.2}$Fe$_{1.8}$O$_{4}$ and studied structural, magnetic and electromagnetic properties. Substitution of In$^{3+}$ ion found to be useful for application at very high frequency (30-300 MHz). Superparamagnetic nanoparticles were obtained with saturation magnetization of 73.5 emu/g with negligible coercivity of 15 Oe.

2.7 Cobalt ferrite

Cobalt ferrite (CoFe$_{2}$O$_{4}$) is an inverse spinel ferrite, it consists of face centered cubic (fcc) lattice composed of oxygen atoms in which Fe$^{3+}$ occupy both the octahedral and tetrahedral site and Co$^{2+}$ occupy the octahedral site. The properties exhibited by cobalt ferrite and large magnetocrystalline anisotropy, moderate saturation magnetization, large magnetostrictive coefficient, coercivity, chemical stability and mechanical hardness. CoFe$_{2}$O$_{4}$ categorize in the hard magnetic material though it has spinel structure because of its high value of coercivity (5400 Oe) and moderate saturation magnetization (80 emu/g) and chemical stability. It has important biological application such as magnetic resonance imaging (MRI), magnetic fluid hyperthermia (MRH), magnetic separations, biosensors, targeted, controlled drug delivery and water purification (Mohamed et al., 2010). Melikhov, (2006) studied the temperature variation of magnetic anisotropy and coercive field of magnetoelastic manganese substituted cobalt ferrites. They reported that there is significant increase in anisotropy with decreasing temperature from 400 to 150 K while decrease with increase in Mn content. Substituting Fe$^{3+}$ ion by rare-earth metal ion in CoFe$_{2}$O$_{4}$ can improve their saturation magnetization magnetization and coercivity. Kambale et al., (2009) synthesized Mn substituted cobalt ferrite and studied the effect of Mn
substitution on the magnetic and dielectric properties of cobalt ferrites synthesized by an auto combustion route and reported that the dielectric permittivity increases with Mn concentration.

Sharifi et al., (2012) reported that magnetic nanoparticles are found to be very successful and effective in the removal of heavy metals from the water. They act as solid phase adsorbents and because of magnetic nature it is very easy to separate them from water. Culita et al., (2015) synthesized mesoporous and studied their capacity to absorb lead ions from aqueous solution. They synthesized CoFe$_2$O$_4$ by a surfactant-assisted method. Cobalt ferrites are well known magnetic compounds that have potential in electrical components, memory and microwave devices over a wide range of frequencies because of their high resistivity and low loss behavior. Its high negative magnetostriction, intrinsic robustness and ability to work at higher frequencies by minimizing the eddy current losses makes cobalt ferrite as suitable and low cost material for developing oxide based magnetostrictive materials. The Curie temperature and magnetostriction Co-ferrites are tunable by adjusting the suitable substitution level. Such substituted Co-ferrites with optimized material properties are used in magneto-mechanical stress sensors. The magneto elastic behavior of cobalt ferrite can be utilized in stress sensing applications for automobiles to improve the fuel efficiency. Efforts are continuously being made to enhance the mechanical robustness, to reduce the magneto-mechanical hysteresis at elevated temperatures and to improve the motor coefficient in order to enhance the stress sensitivity at lower magnetic field strengths by Mn substitution using metallic binders. Large magneto-mechanical effect and high sensitivity to stress make cobalt ferrites promising candidates for stress sensor (Paulsen et al., 2003). Nikumbh et al., 2014 studied the influence of rare-earth ions that is Nd$^{3+}$, Sm$^{3+}$ and Gd$^{3+}$ ions in CoRE$_x$Fe$_{2-x}$O$_4$ ($x =$ 0.1 and 0.2) on their structural, electrical, magnetic and dielectric properties. The crystallite size of rare-earth doped sample CoFe$_2$O$_4$ was found to be smaller than that of the pure CoFe$_2$O$_4$. Variation in electrical studies show breaks confirming transitions from ferrimagnetic to paramagnetic transitions which support metal-semiconducting behavior. Although Nd (Neodymium), Sm (Samarium), Gd (Gadolinium) are do not participate in conduction but on substitution in CoFe$_2$O$_4$ they showed p-type conduction, also the decrease in coercive force, saturation magnetization, the ratio of remanance to saturation magnetization and magnetic
moments found due to the dilution in magnetic interactions as dopants are non-magnetic in nature.

2.8 Lithium ferrite

Argentina et al., (1974) described the compositional formula: 
\[(\text{Fe}^{3+})[\text{Li}_{0.5}^{+}\text{Fe}_{1.5}^{4+3}]\text{O}_4\] where the parentheses ( ) and the brackets [ ] represent the ions distributed on tetrahedral and octahedral sites, respectively. As the magnetic spins on both the sites are anti-parallel, hence octahedral is the dominant site. Therefore for the reduction of magnetization a non-magnetic ion is to be introduced on the octahedral site in place of Fe$^{3+}$. But for the increment in magnetization a non-magnetic is to be introduced on the tetrahedral site. In both the cases the octahedral site plays dominant role. Baba et al., (1972) found that the cost and the better temperature stability of lithium ferrites are superior to rare earth garnets. The magnetic loss tangents of the S-band lithium ferrites are higher than that of garnets. Ravinder, (1999) assigned four types of absorption bands ($\nu_1$, $\nu_2$, $\nu_3$ and $\nu_4$) for Li$_{0.5-x/2}$Zn$_x$Fe$_{2.5}$O$_4$ prepared by double sintering method, where $\nu_1$ band correspond to tetrahedral complex , $\nu_2$ and $\nu_3$ correspond to the octahedral complexes, $\nu_4$ correspond to the lattice vibrations in the sample, also concluded that frequency bands $\nu_1$, $\nu_2$ and $\nu_3$ strongly depend on Fe$^{2+}$ concentration. Watawe et al., (2000) reported the inverse trends of dielectric constant and DC resistivity for Li$_{0.5-x/2}$Co$_x$Fe$_{2.5-x/2}$O$_4$ with increasing concentration of cobalt content, further with increase in temperature the dielectric constant increases and resistivity decreases. Venudhar et al., (2002) investigated the dielectric constant ($\varepsilon$) of Li-Co mixed ferrites in the frequency range $10^2 – 10^5$ Hz. At room temperature dielectric constant decreases continuously with increase in cobalt content. The frequency dependence of dielectric constant showed decrease. Ahniyaz et al., (2002) confirmed the formation of $\beta$-LiFe$_3$O$_8$ by hydrothermal ball milling method. Phase identification was carried out by calculation of lattice parameter. The lattice parameter for hydrothermal ball milled was found to be ($a = 8.3434$ Å) for $\beta$-LiFe$_3$O$_8$. Nakamura et al., (2003) prepared Li$_{0.5-x}$Zn$_{1.5}$Fe$_{2+0.5x}$O$_4$ by double sintering method. Low-frequency permeability increased while the natural resonance frequency shifted lower with increase in Zn concentration. Complex permeability was also numerically separated into spin rotation and domain wall motion. It was found that for the spin rotational component, the static spin susceptibility increased and the spin resonance
frequency shifted lower with an increase in the Zn concentration. Further the product values of static spin susceptibility and the spin resonance frequency, corresponding to the Snoek’s product value and proportional to the magnetization flux had useful application in high frequency devices such as single layered electromagnetic wave absorber.

Yusoff et al., (2004) studied the microwave absorption characteristics of polycrystalline (Li$_{0.5}$Fe$_{0.5}$)$_{0.7}$Zn$_{0.3}$Fe$_2$O$_4$ prepared by conventional sintering method. Addition of a small amount of CuO and MgO oxides into the matrix of LiZn ferrite reduced the dielectric constant and loss but increases the reflectivity and transmittivity of the ferrite. The absorption properties were analysed using a specular absorber method revealed two matching conditions of minimum reflection at low and high frequency regions. The first matching condition at low frequency was due to |$\mu_r^*$| = |$\varepsilon_r^*$| but this condition may be slightly affected by the propagation factor of the material. The second matching condition was observed only for LiZn/MgO due to the geometrical cancellation of the incidence and reflected waves at the surface of the absorber. The above condition satisfies when the thickness of the sample equals that of a quarter of the propagating wavelength in the material. Maisnam et al., (2004) studied the effect of V$^{5+}$ substitution on the microstructure, hysteresis parameters and initial permeability of Li$_{0.5+}$Zn$_{0.2}$Ti$_{0.2}$V$_{0.2}$Fe$_{2.1-2t}$O$_4$ prepared by conventional ceramic method. Porosity was found to be increase with the vanadium substitution. As the inverse variation of remanance with the porosity, the remanance ratio was found to be decrease with vanadium substitution. Also, there was deviation from B-H loop rectangularity with vanadium concentration. It was observed that initial permeability found to be increase with the increase of grain size. Gupta et al., (2005) reported the lower values of permittivity and permeability in the microwave frequency region for Li$_{0.5-x/2}$Co$_x$Fe$_{2.5-x/2}$O$_4$. The reduction in the losses was found to be suitable for high frequency application. Ahmed et al., (2005) studied the effect of replacement of divalent Zn$^{2+}$ on the electrical, magnetic, thermoelectric power and structural properties of Li-La ferrite. The dielectric constant ($\varepsilon'$) of Li-Zn-La ferrite decreases with increasing frequency and decreases with increasing Zn content. The doping of rare earth (La$^{3+}$) ions decreased the magnetic interaction between A and B-sites resulting in a decrease in the magnetic moment. Soibam et al., (2008) studied the dielectric behavior of Li$_{0.4+0.5x}$Zn$_{0.5}$Co$_x$Fe$_{2.4+0.5x}$O$_4$ as a function of Co concentration.
and also investigated the temperature dependence in the range 20-160 °C at different frequencies. It was found that the room temperature dielectric constant shows an initial increase till Co = 0.02, followed by decrease with cobalt concentration. Also the dielectric constant was observed to be increase with increasing temperature, but increase more pronounced at low frequency. A resonance peak was observed at low frequency. The dielectric loss was also observed to increase with increasing temperature at different frequencies.

Verma and Joy, (2008) investigated the effect of chemical control for the formation of the α-phase of lithium ferrite, in single phase form, using citrate gels prepared from the precursor solution at two different pH values. Single phase lithium ferrite with relatively larger particle size was obtained from the kinetically controlled vigorous reaction. Superparamagnetic particles were obtained at pH ≈ 1 of precursor solution by the thermal decompostion of the lithium-iron-citrate gel. For the same metal to citric acid molar ratio, dried citrate gel formed from the precursor solution at pH ≈ 7 in the presence of ammonia leads to the formation of crystalline phase of ammonium nitrate. The heat released from the exothermic self-propagating combustion of citric acid and ammonium nitrate at a relatively lower temperature of 200 °C increases the flame temperature and results in the growth of the particle size. Gruskova et al., (2008) reported the measured permeability of Li_{0.5+0.5t-0.5x}Fe_{2.5-1.5t-0.5x}Ti_{t}Zn_{x}O_{4} exhibit characteristic frequency dispersion and the contributions of relaxation and resonance effects. The observed dispersion was the result from the contributions of probably the resonance-type of domain rotation superimposed over the relaxation-type or magnetization rotation. Naoe et al., (2008) developed a micro temperature sensor of Li-Zn-Cu ferrite by applying experiment of the lumped element LC resonance sensor and simulation of monolithic integrated LC resonance sensor using transmission-line structure assuming that the Li-Zn-Cu ferrite was used as a dielectric/magnetic substrate for transmission line. It was concluded that the lumped element has high temperature sensitivity. Numerical simulation, predicted the large temperature coefficient of resonance frequency. Fu, (2009) studied the effect of chromium (Cr) substitution on lattice parameter, theoretical density, cell volume, magnetic and electronic properties for Li_{0.5}Fe_{2.5-x}Cr_{x}O_{4}. It was revealed that the lattice parameter and cell volume decrease with the increase in chromium substitution. Li_{0.5}Fe_{2.5}O_{4} had the maximum value of permeability and decreased with the increase
in chromium concentration. Fu et al., (2009) studied the microwave properties of chromium substituted lithium ferrite. It was revealed that saturation magnetization decreases monotonically with increase in Cr-substitution content. The real and imaginary parts of both permittivity and permeability values decreased gradually with increasing frequency in microwave region.

Verma et al., (2009) compared the structural and magnetic properties of nanocrystalline \( \text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4 \) prepared by different methods such as flash combustion, sol-gel method, citrate precursor, solid state reaction method. It was found that single phase lithium ferrites can be achieved above the annealing temperature 700 °C. Sample prepared by citrate precursor method gave the minimum particle size and better magnetic properties. Soibam et al., (2009) studied the magnetic and Mössbauer properties of Ni-substituted Ni-Zn ferrite. The value of saturation magnetization and Curie temperature decreases with increase in Ni concentration. Hyperfine field at A-site show fall with Ni-substitution. Although observed magnetization decrease with increase in Ni substitution but the values were quite high. Verma et al., (2009) investigated the magnetic, electrical and microstructure properties of \( \text{Li}_{0.35}\text{Cd}_{0.3}\text{Mn}_x\text{Fe}_{2.35-x}\text{O}_4 \) (where, \( x = 0.0, 0.2, 0.4, 0.6, 0.8 \) and 1.0). Single phase and homogeneous ferrites were obtained. Permeability of manganese and cadmium co-substituted lithium ferrite showed quite high values. The value of resistivity first increases with Mn content and attains maximum value of \( 6.02 \times 10^7 \) Ω cm for Mn = 0.4 and further substitution of Mn it starts decrease. Akhter et al., (2010) studied the magnetic properties of \( \text{Li}_{0.5-x/2}\text{Cd}_x\text{Bi}_{0.02}\text{Fe}_{2.48-x/2}\text{O}_4 \) ( \( x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7 \) ) prepared by conventional ceramic technique. XRD revealed formation of single phase pure cubic spinel structure. Curie temperature decrease with increase in Cd content. The magnetic moment at room temperature and at 5 K increase upto \( x = 0.3 \) with increase in Cd content and for \( x > 0.3 \) whereas theoretically calculated magnetic moment increase linearly with Cd content. Fu and Hu, (2010) prepared magnesium substituted lithium ferrite by conventional ceramic method. Specimens were sintered at 1200 °C with heating rate of 5 °C per min. XRD studies revealed the formation of \( \alpha \)-phase and gradual increase in lattice constant indicate a small shift to a lower diffraction angle in the lithium ferrite peak. It was evident that net magnetization decreased gradually with an increase in Mg\(^{2+}\) ions. Also, permeability decreased gradually for \( \mu (f = 10 \text{ MHz}) = 34.0 \) for \( \text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4 \) to \( \mu (f = 10 \text{ MHz}) = 11.5 \) for
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Chapter-2

**Review of Literature**

Li$_{0.5}$Fe$_{1.5}$Mg$_{1.0}$O$_4$. Maximum value of electrical conductivity was found to be $\sigma_{700 \degree C} = 0.1274$ S/cm for Li$_{0.5}$Fe$_{2.5-x}$O$_4$. The electrical conductivity decreases with increase in Mg substitution in the temperature range of 250-700 °C. Soibam et al., (2010) reported dielectric properties of Ni substituted Li-Zn ferrites. The room temperature value of dielectric constant measured at 10 KHz is found to be decrease with the increase in Ni ion concentration. It was observed that the value of dielectric constant is high at low frequencies and decrease rapidly with increase in frequency. At higher frequency the dielectric constant is low and remains almost constant. Variation of dielectric constant with temperature at different frequencies show increase with increase in temperature. Similar behavior has been observed for variation of loss tangent (tan $\delta$) with temperature at different frequencies. It was concluded that the rise in dielectric loss with temperature indicates a higher conduction with increase in temperature.

Verma et al., (2010) synthesized Li$_{0.35}$Cd$_{0.3}$Fe$_{2.35}$O$_4$ by modified citrate precursor method in which combustion rate is controlled by the pH value of the solution at two different pH media pH1 and pH7. XRD studies revealed the formation of a small amount of $\alpha$-Fe$_2$O$_3$ at pH1 indicated from [104] peak in XRD pattern, whereas sample with pH7 showed pure phase formation. The crystallite size of the as-prepared sample with pH1 is smaller (10 nm) as compare to the crystallite size (30 nm) with pH7 due to the generation of high temperature during the last stage reaction whereas lattice constant $a = 8.365$ Å and 8.359 Å. FTIR spectra revealed the formation of ferrite phase with characteristic peak at 585 cm$^{-1}$. The value of Saturation magnetization for pH =1 ($M_s = 37.5$ emu g$^{-1}$) and coercivity ($H_c = 83.3$ Oe) at room temperature and ($M_s = 46.6$ emu g$^{-1}$), ($H_c = 186.6$ Oe) at 80 K while for pH = 7 ($M_s = 60.2$ emu g$^{-1}$) and coercivity ($H_c = 118.2$ Oe) at room temperature and ($M_s = 68$ emu g$^{-1}$), ($H_c = 151.7$ Oe) at 80 K. It was found that variation of magnetization with annealing temperature improves for pH 1 and reduces for pH 7 attributed to the loss of LiO$_2$. Hilli et al., (2011) prepared the Gd substituted lithium ferrite [(Li$_{0.5}$Fe$_{0.5}$)$_{0.5}$Ni$_{0.5}$Gd$_{0.5}$Fe$_{2.5}$O$_4$ where, $x = 0, 0.005, 0.01, 0.02, 0.03, 0.04, 0.05, 0.1$] by standard chemical solid reaction technique. It was reported that all the samples exhibits cubic spinel phase with small amount of secondary phases. But the XRD spectra of the composition (Li$_{0.5}$Fe$_{0.5}$)$_{0.5}$Ni$_{0.5}$Gd$_{0.0}$Fe$_{1.99}$O$_4$ at sintering temperature (1100 °C, 1200 °C, 1250 °C and 1300 °C) revealed the formation of pure phases. But
the secondary phases appeared at sintering temperature 1100 °C and 1350 °C. It was concluded that the secondary phase of GdFeO₃ at the grain boundaries reduces the grain growth and increase the resistivity. Obtained ferrites exhibit n-type behavior because of hopping of electrons between Fe²⁺ and Fe³⁺ ions on the A-site. It was found that there is decrease in electrical conductivity with sintering temperature which was supported by the fact that average grain size increases with sintering temperature because of decrease in porosity.

Shirsath et al., (2011) followed the sol-gel method for the preparation of ordered Li₀.₅Fe₂.₅O₄ nanocrystalline studied the magnetic and electrical properties as a function of sintering temperature and sintering time. XRD patterns of the lithium ferrite sintered at 875, 1075, 1275 and 1475 K showed formation of cubic spinel structure with a lattice constant (a = 8.331 Å). For the sintering temperature 1475 K the cubic spinel phase appeared with small amount of α-Fe₂O₃ (hematite) and γ-Fe₂O₃ (maghemite), but these phases were not appear for Li₀.₅Fe₂.₅-xO₄ sintered at low sintering temperature. Hence conclusion obtained that the sample sintered at 1475 K exhibits ordered structure with superstructure peaks, arised due to the 1 : 3 Li to Fe-ordered distributions on the octahedral sites. It was found that coercivity increases with particle size and after attaining a maximum value of ≈ 151 Oe at 24 nm (1075 K) it decreased with further increase in temperature and particle size. Also, value of saturation magnetization increases consistently with particle size while for smaller particle size the saturation magnetization is relatively lower than the bulk value. The dielectric constant increases with increase in sintering temperature. Dar et al., (2012) prepared the Li₀.₅AlₓFe₂.₅O₄ (x = 0.0, 0.1, 0.2, 0.3, 0.4) by citrate gel auto combustion method at pH of 6. Average crystallite size as calculated from XRD spectra range from 38 nm to 41 nm. Lattice parameter, crystallite size, density decreased with an increase in Al doping. It was reported that ac conductivity increases upto x = 0.1, then decrease with further doping of Al. Saturation magnetization decreases with Al³⁺ substitution in lithium ferrite. The complex impedance measurements showed that the resistive and the capacitive properties of the samples are associated with the grain and grain boundaries. Teixerira et al., (2012) reported the dielectric, morphological and structural properties of LiFe₅O₈ prepared by solid state reaction method. It was concluded that the LiFe₅O₈ crystal phase was obtained for the samples treated above 400 °C and below 1200 °C. The phase obtained was the disordered β-LiFe₅O₈ crystal.
phase. Raman spectroscopy revealed the formation of α-LiFe$_5$O$_8$ phase. It was observed that there was increase in the dc conductivity with the increase of the heat treatment temperature. Also the formation of the Li$_2$FeO$_3$ phase promotes an increase in the permittivity.

Mane et al., (2012) reported the contribution of conduction mechanism in Nd:YAG laser irradiated Li-ferrite synthesized by ceramic technique. The infrared spectrum of irradiated sample showed formation of disordered structure as that of unirradiated samples. Debye temperature show change in conduction mechanism from n-type to p-type. DC electrical resistivity increases with the laser irradiation dose increase. Dielectric constant and dielectric loss tangent increases with increase in temperature. Sutradhar et al., (2012) prepared the nanoparticles of Zn-substituted lithium ferrite (Li$_{0.32}$Zn$_{0.36}$Fe$_{2.32}$O$_4$) by sono-chemical sol-gel route. XRD patterns confirmed the formation of single phase spinel structure with no impurity phase when the sample annealed at 500 °C. Linear dynamic magnetization curves of the sample confirmed that most of the particles are superparamagnetic in nature along with ferrimagnetic particles. The coercivity increases with the increase in particle size and frequency.

Safaan and Assar, (2012) studied the dielectric behavior of Li-Ni-Zn ferrite by the chemical co-precipitation method. It was found that there was general decrease in ac conductivity (σ) of the as-prepared nanosamples and their bulk counterparts versus NiZn ferrite samples was attributed to the incorporation of Li. The significance decrease in ac conductivity (σ) of the as-prepared nano samples versus their bulk counterparts was attributed to the increase of grain boundary volume and associated impedance to the flow of charge carriers. The value of dielectric constant and dielectric loss were lower than their bulk counterparts, where the small grain size of the nanosamples reduces the probability of electron hopping and hence of polarization grains among the grains. Maisam and Phanjoubam, (2012) synthesized Li$_{0.45-\chi/2}$Ni$_{0.1}$Mn$_{0.1}$Co$_{\chi}$Fe$_{2.35-\chi/2}$O$_4$ where $\chi$ ranging from 0 to 0.1 in steps of 0.02 by ceramic technique. XRD studies confirmed the formation of single phase spinel structure. It was observed that lattice constant and density increased with increase of $\chi$ attributed to the substitution of Co$^{2+}$ (0.82 Å) having larger ionic radii than average ionic radii of Fe$^{3+}$ and Li$^+$ (0.705 Å) which is relatively smaller in size resulting in unit cell
expansion. It was reported that Curie temperature decreased with increase in Co$^{2+}$ substitution supported by the fact that Curie temperature in ferrites is due to the strength of AB interaction, which is a function of the number of Fe$^{3+}_A$ — O$^{2+}$ — Fe$^{3+}_B$ linkages which depends on the number of Fe$^{3+}$ ions present in the composition. Substitution of Co$^{2+}$ in place of Fe$^{3+}$ results in decrease in number of Fe$^{3+}$ ions per formula unit. The frequency dependence of dielectric constant at room temperature measured in the range 100 Hz – 1 MHz show dispersive behavior where the value is high at low frequencies and decreased as the frequency increased, and become constant at 50 KHz. The frequency dependence of dielectric loss (tan $\delta$) for various compositions decreased initially with frequency followed by an increase and show resonance peak between 5 and 30 KHz. The position of the peak shifts towards the lower frequency as the Co$^{2+}$ substitution increases. Also Co$^{2+}$ substitution increased the initial permeability upto $x = 0.04$ and then decreased on further substitution showed a tendency for the onset frequency resonance around 1 MHz and permeability loss exhibit resonance at 2-5 MHz determining the operational limit.

Gurav et al., (2013) investigated the structural and magnetic properties of divalent Zn$^{2+}$ and tetravalent Zr$^{4+}$ co-substituted Li$_{0.5}$Fe$_{2.5}$O$_4$. Nanocrystalline powder of Li$_{0.5}$Zr$_x$Zn$_x$Fe$_{2.5-2x}$O$_4$ (where $x = 0.1, 0.2, 0.3, 0.4, 0.5$) were synthesized by sol-gel auto-combustion method. It was observed that the increase in the Zn$^{2+}$ and Zr$^{4+}$ content causes the change in the intensity of X-ray diffraction peaks of Li$_{0.5}$Fe$_{2.5}$O$_4$. XRD pattern revealed that the crystallinity of the ferrite phase disappears with the higher concentrations of Zn$^{2+}$ and Zr$^{4+}$ and amorphous phase appeared. The main reflection planes (220), (311), (400), (421), (422), (511) and (440) of the spinel structure is appeared in the XRD pattern and also the appearance of the superstructure peaks such as (210), (211), (310) and (320) confirmed formation of ordered phase. But at the higher concentration of Zr$^{4+}$ and Zn$^{2+}$ no superstructures lines were observed. Lattice parameter increased with increase in Zr$^{4+}$ and Zn$^{2+}$ substitution. The increase in lattice parameter was attributed to the larger ionic radii of Zr$^{4+}$ (0.80 Å) and Zn$^{2+}$ (0.83 Å) than Fe$^{3+}$ (0.67 Å). X-ray density increased with increase in concentration of Zr$^{4+}$ and Zn$^{2+}$, while crystallite size and bulk density decreased. The porosity of the sample increased with concentration. Cation distribution showed that Zr$^{4+}$ preferred octahedral B site, also it occupied tetrahedral A-site by small fraction. Zn$^{2+}$ preferred tetrahedral A-site, whereas Fe$^{3+}$ occupies both A and B site. Oxygen
positional parameter $u > 0.375$ due to anion displacement from the ideal situation so that it forms expanded tetrahedral interstices. The two prominent bands in the range $484 \text{ cm}^{-1} - 749 \text{ cm}^{-1}$ in FTIR spectra confirmed formation of spinel phase. Saturation magnetization of lithium ferrite increased with $\text{Zr}^{4+}$ and $\text{Zn}^{2+}$ up to $x = 0.2$ and then decreased for $x > 0.2$. The difference between observed and calculated magneton number for $x > 0.2$ indicate that canting exists at octahedral B site.

Arana et al., (2013) correlated the magnetic and structural properties of $\text{Li}_{0.5x}\text{Zn}_{0.3x}\text{Mn}_{0.4}\text{Fe}_{2+0.5x}\text{O}_4$ ($x = 0.0, 0.1, 0.2, 0.4$) and determine the cation distribution in the spinel structure that agreed with both structural and magnetic results. XRD pattern with reflection at (311), (440), (220) confirmed formation of ferrite phase. Lithium doping modified the saturation magnetization $M_s$, its value increases from $63.0 \text{ emu/g}$ for $x = 0.0$ to $101.5 \text{ emu/g}$ for $x = 0.4$. It was concluded that the inclusion of $\text{Li}^+$ and extra $\text{Fe}^{3+}$ in the lattice promotes a cation arrangement between tetrahedral and octahedral sites, increasing $M_s$ to the rather high observed values. Mössbauer spectra revealed presence of magnetic sextet due to superexchange interaction between the magnetic ions at tetrahedral (A) and octahedral (B) sublattices and the rise in the hyperfine fields ($B_{hf}$) of A and B sites indicate enhancement in magnetic coupling which support the increase of $M_s$. Also, lithium ion favors ion migration to the different crystalline sites was supported by formation of single phase material with no segregated phases. Sutradhar et al., (2013) prepared $\text{Li}_{0.32}\text{Zn}_{0.26}\text{Cu}_{0.1}\text{Fe}_{2.32}\text{O}_4$ (LZCF) by sol-gel method. In order to modulate the soft magnetic property and to enhance the quality of applications in the domain of microwave absorption, the prepared nanoparticles were encapsulated in the matrix of carbon nanotubes. A significant enhancement of reflection loss in the two bands ($X$ and $K_u$) of microwave frequencies in the nanocomposites sample of LZCF-CNT was found which make them suitable candidate for microwave absorption.

Iqbal et al., (2013), synthesized $\text{Li}_{1.2}\text{Mg}_{0.4}\text{Gd}_{x}\text{Fe}_{2-x}\text{O}_4$ ($x = 0.00, 0.02, 0.04, 0.06, 0.08, 0.10$) by sol-gel auto-combustion method. It was found by Differential Thermal Analysis (DTA) along with Thermo Gravimetric Analysis (TGA) that there was a constant and steady weight loss up to about 750 °C which reflect formation of ferrite phase along this range. XRD pattern revealed the formation of fcc single phase for ($x = 0.00, 0.02, 0.04$) with reflection at (220), (311), (400), (422), (511), (440) and
(533). But for $x \geq 0.06$, a second phase of GdFeO$_3$ obtained at (310) reflection revealed orthoferrite phase. It was extracted that small amount of Gd in Li$_{1.2}$Mg$_{0.4}$Fe$_{2-x}$O$_4$ distract the spinel phase. Lattice constant as calculated by using Nelson Relay function found to be increasing with increase in Gd substitution for ($x = 0.00$, 0.02, 0.04). Increase in lattice constant attributed to the larger ionic radii of Gd$^{3+}$ (0.938 Å) than Fe$^{3+}$ (0.645 Å). But for $x \geq 0.06$, lattice constant decreased due to the segregation of the Gd$^{3+}$ ions at the grain boundaries. Hence gadolinium substitution affect the phase and size of the spinel matrix. The X-ray density and bulk density found to be increasing, but X-ray density exhibit large value than bulk density attributed to the existence of pores. Due to the formation of secondary phase (GdFeO$_3$) inter-granular voids were filled and exhibit good densification, therefore a decrease in porosity was found. M-H loops were recorded at room temperature for magnetic field applied parallel to the sample surface and magnetic field applied perpendicular to the sample surface. For both cases saturation magnetization and remanent magnetization decreased with the increase of Gd$^{3+}$ concentration. This was supported by the fact that rare earth ion magnetic moments originate from the localized 4f electrons at room temperature their magnetic dipolar orientation is disordered. Thus due to the doping of non-magnetic Gd$^{3+}$ ion have no contribution to net magnetization. Overall effect was that replacement of Fe$^{3+}$ by Gd$^{3+}$ decrease the number of magnetic ion in the sample led to decrease in net magnetization. Squareness ratio indicated that the substitution of Gadolinium resulted in the cubic magneto crystalline anisotropy subsequently grain-grain interaction is enhanced. Coercivity increases with increase in Gadolinium substitution influenced by many factors like magnetic particle morphology, magnetocrystallinity, anisotropy and the magnetic domain size.

Cheruku et al., (2014) synthesized Li$_{0.5}$Fe$_{2.5}$O$_4$ (LFO), Li$_{0.5}$Fe$_{2.48}$Bi$_{0.02}$O$_4$ (LFBO), Li$_{0.5}$Fe$_{2.48}$Pb$_{0.02}$O$_4$ (LFPbO) combustion synthesis. Li$_{0.5}$Fe$_{2.5}$O$_4$ was sintered at different temperature 700 °C, 800 °C, 900 °C while LFBO and LFPbO sintered at 900 °C. XRD pattern revealed the formation of crystallite with cubic spinel structure of space group P4$_3$32. The crystallite of LFO sintered at different temperatures increase with increase in sintering temperature, also the crystallite size of LFBO and LFPbO are higher than LFO because of sintering aids. The liquid phase temperature of the Bi$_2$O$_3$ and PbO act as sintering aids to increase the proper grain growth of the nanocrystalline lithium ferrite. Thermal analysis determined the phase changes consist
of three regions. The first region was from room temperature to 250 °C, ascribed to decomposition of absorbed water. The second region extended from 250 °C to 600 °C, associated with redox reactions of organic matter involved in carbonaceous products. The third region start from 600 °C where weight loss of samples is almost constant which indicates the phase formation and the small weight loss observed above 720 °C for the samples. Fourier Transmission Infrared Microscopy revealed formation of first primary band (\(v_1\)) at 595 cm\(^{-1}\) which consists of three subsidiary bands \(v_1(1), v_1(2), v_1(3)\) at 710 cm\(^{-1}\), 673 cm\(^{-1}\) and 550 cm\(^{-1}\) respectively were present due to Fe\(^{3+}\)—O\(^{2-}\) complexes at the octahedral complexes. The second primary band (\(v_2\)) observed at 470 cm\(^{-1}\) was associated with band splitting at \(v_2(1)\) 470 cm\(^{-1}\) and weak band at 440 cm\(^{-1}\) attributed to Li—O vibrations. There was no band found above 750 cm\(^{-1}\) indicates no interference of Bi\(_2\)O\(_3\) and PbO substitution with formation of pure phase. Raman spectroscopy confirmed the formation of ordered phase with A\(_1\) band at 751 cm\(^{-1}\) involving in-phase vibrations of Fe — O bonds of Fe\(^{3+}\) — O\(_4^{2-}\) tetrahedral and the negligible intensity of the corresponding two-phonon scattering. It was concluded that the presence of Bi\(_2\)O\(_3\) and PbO do not affect the Raman modes and confirm that their presence did not alter the structure of lithium ferrite. Thin hysteresis loop indicated the soft-ferromagnetic nature of LFO, LFBO, LFPbO. It was found that saturation magnetization (\(M_S\)) and remanent magnetization of LFBO and LFPbO decreased because of the presence of non-magnetic elements Bi\(^{3+}\) and Pb\(^{2+}\) in the ferrite phase thus reduces magnetic properties. Also in the multi-domain region coercivity decreased as the particle diameter increases. From conductivity analysis, it was concluded that the behavior of conductivity at low temperature is superlinear and the activation energy of LFO is more as compare to LFBO and LFPO because of its density and is reflected in SEM morphology.

Srivastava et al., (2014) synthesize Li\(_{0.5}\)Cr\(_{0.1}\)Fe\(_{2.4}\)O\(_4\) and Li\(_{0.5}\)Co\(_{0.1}\)Fe\(_{2.4}\)O\(_4\) by sol-gel method, than a nanocomposites of Chitosan and ferrite samples in the form of film were prepared to study magnetic and dielectric properties. X-ray diffraction pattern of Cr and Co doped lithium ferrite revealed formation of cubic phase with space group P4132/(213) with peaks of maximum intensity (311), (400), (511), (440) and (620) with maximum intensity at (311). The lattice parameter for both the samples was found to be 8.33 Å. The average crystallite size was calculated to be ~ 45 nm. It was observed that intensity of XRD peaks of chromium doped lithium ferrite
Chitosan and cobalt doped lithium ferrite Chitosan decreased in comparison to pure lithium ferrite samples which occurred due to introduction of amorphous feature of Chitosan polymer in nanocomposites system. Also, shift in the intensity of XRD peaks was observed in case of Cr-LFCN as compared to Co-LFCN. This was attributed to bigger crystallite size in case of Cr-LFCN compared to that of Co-LFCN. FTIR spectra revealed two bands in the range 400 cm\(^{-1}\)-1000 cm\(^{-1}\) attributed to the presence of metal-oxygen bond at tetrahedral and octahedral sites. The FTIR spectra of LFCN exhibit similar feature to the FTIR spectrum of Chitosan with a small variation in the intensity band at ~1750 cm\(^{-1}\) attributed to the presence of functional group (C═O) of acetic acid. Energy band gap analysis from UV spectroscopy revealed semiconducting features of Li\(_{0.5}\)Cr\(_{0.1}\)Fe\(_{2.4}\)O\(_4\) and Li\(_{0.5}\)Co\(_{0.1}\)Fe\(_{2.4}\)O\(_4\) and also Chitosan ferrites showed semiconducting features. VSM studies revealed that value of saturation magnetization (\(M_S\)) for Li\(_{0.5}\)Cr\(_{0.1}\)Fe\(_{2.4}\)O\(_4\) nanoparticle was lower than that of Li\(_{0.5}\)Co\(_{0.1}\)Fe\(_{2.4}\)O\(_4\) because of lower magnetic moment of Cr as compared to the Co doped nanoparticle. Also the value of saturation magnetization (\(M_S\)) of LFCN was low as compared to values of Li\(_{0.5}\)Cr\(_{0.1}\)Fe\(_{2.4}\)O\(_4\) and Li\(_{0.5}\)Co\(_{0.1}\)Fe\(_{2.4}\)O\(_4\) attributed to the diamagnetic nature of Chitosan. TGA/DTA analysis shows that the rate of weight loss in case of pure Chitosan was much faster than weight loss in case of ferrite Chitosan. Hence revealed the interaction of Chitosan with lithium ferrite which leads to restrict the thermal motion of the Chitosan polymer chains and restrict the easy degradation of Chitosan in nanocomposites system. The dielectric constant for all the samples had high value at low frequency range and decreased with increase in frequency. Also it was found that dielectric constant of LFCN was lower than that of pure chromium and cobalt doped lithium ferrite nanoparticles. It was also observed that the tangent decreased with increase in frequency for all the samples becomes constant over the frequency 4 MHz attributed to space charge polarization. Sawant et al., (2014) synthesized Li\(_{0.5-(x/2)}\)Co\(_x\)Fe\(_{2.5-(x/2)}\)O\(_4\) (where \(x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5 \) and \(0.6\)) by solution combustion synthesis method and studied the influence cobalt substitution on IR properties. X-ray Diffractometer revealed the formation of single phase cubic spinels. Lattice parameter depend linearly on cobalt substitution was attributed to ionic volume differences of Co\(^{2+}\) (0.82 Å), Fe\(^{3+}\) (0.67 Å) and Li\(^+\) (0.69 Å). It was observed that IR spectra consist of two significant absorption band, first at 600 cm\(^{-1}\) and second at 450 cm\(^{-1}\), evident the formation of single phase spinel structure having
two sublattices, tetrahedral (A) and octahedral (B) site. It was reported the IR bands at tetrahedral complexes slightly shift towards high frequency side with composition upto x = 0.4 while at octahedral complexes shift towards lower frequency side with x. The cation distribution was given by magnetization data as follows (Fe$^{3+}$0.95 - x/2Co$^{2+}$0.35x)_A[Fe$^{3+}$1.55Co$^{2+}$0.65xLi$^{1+}$0.5-x/2]O$_4$ in which Co$^{2+}$ occupies both tetrahedral and octahedral sites along with Fe$^{3+}$, Li$^+$ being on octahedral site. It was concluded that bond length increases linearly with cobalt concentration. Assar et al., (2014) reported the effect of incorporation of Li ions on Co-Ni ferrite and studied their dielectric behavior. Nanoparticles of Co$_{0.5}$Ni$_{0.5-x}$Li$_x$Fe$_{2+x}$O$_4$ had been prepared by citrate precursor method (where, x ranges from 0.00 to 0.05 in steps of 0.05). It was found that frequency dependent conductivity $\sigma(\omega)$ increases while $\varepsilon'$ and $\tan\delta$ decrease as the frequency increases at the selected temperatures. Also, $\sigma_{ac}$, $\varepsilon'$ and $\tan\delta$ increase with increasing temperature explaining the semiconductor behavior of ferrites. The activation energy of the samples increases with the increase of Li content upto x = 0.15 and then decreases again on contrary to the ac conductivity and the dielectric loss, indicating that high activation energy is associated with high resistivity and low dielectric losses. It was concluded that adding Li ions to the Co-Ni nanoferrites improve their dielectric properties and make them promising candidates for microwave applications. It was obtained from dielectric measurements that non-Debye type of relaxation prevails in the prepared nanosamples. From the Cole-Cole diagrams of M vs M' indicate that the property dominating in the studied ferrite is called the effective stiffness.

Chaudhari et al., (2014) studied Co$^{2+}$ substituted lithium chromium ferrite in order to improve their structural homogeneity, magnetic properties, resistivity and low dielectric loss for the possible application in microwave devices. Li$_{0.5-x/2}$Co$_x$Cr$_{0.5}$Fe$_{2-x/2}$O$_4$ (where x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5) were prepared by sol-gel auto-combustion method. X-ray diffraction pattern revealed superstructure peaks such as (210), (211), (310), and (421) which indicate formation of ordered spinel type structure for low concentration of cobalt. For higher concentration of Co$^{2+}$ it was observed that the lithium atoms got disordered with a statistical distribution over the octahedral sites, as a result of which superstructure peaks were not observed. The ordering parameter was calculated using two most sensitive peaks of the ordered and disordered phase. It was observed that the ordering parameter decreased with increase in Co$^{2+}$ substitution.
shift towards lower 2θ diffraction angle found which was attributed to the increase in lattice constant with increase in Co$^{2+}$ substitution because it replaced Li$^{+}$ and Fe$^{3+}$ their respective ionic radii are less. It was found that crystallite diameter increased with increase in Co$^{2+}$ substitution which resulted in increase in bulk density which further decreased porosity. From FTIR spectra it was concluded that well-defined sharp absorptions in the IR spectrum revealed presence of the ordered lithium ferrite in the sample. The first primary band $\nu_1$ appeared at 640 cm$^{-1}$ — 600 cm$^{-1}$ was attributed to the vibrations of Fe — O — Fe$^{3+}$ bond in the tetrahedral site. The second primary band $\nu_2$ appeared at 376 cm$^{-1}$ — 397 cm$^{-1}$ was attributed to the vibrations of Fe — O — Fe$^{3+}$ bond at the octahedral site. It was observed that there was splitting of second primary band attributed to the presence of Fe$^{2+}$ causes Jahn-Teller distortion. The difference between $\nu_1$ and $\nu_2$ decreased with Co$^{2+}$ substitution. The decreased value of ($\nu_1 - \nu_2$) indicates increasing separation between A and B sites. Such increasing separation of A and B sites weaken the A-B super exchange interaction.

The site occupancy in spinel ferrite was obtained from X-ray diffraction pattern using Bertaut method. It was found that Cr$^{3+}$, Co$^{2+}$ and Li$^{+}$ ions had a strong preference towards the octahedral B-site, whereas Fe$^{3+}$ showed preference over both A and B sites. The variation of saturation magnetization ($M_S$), coercivity ($H_C$) and magneton number ($n_B$) obtained from hysteresis. It is observed that the saturation magnetization and observed magneton number increase as Co$^{2+}$ ions increase which was attributed to the substitution of Co$^{2+}$ ions, which generally preferred B-site occupancy, result in increase in the exchange interaction between A and B-site. The calculated and observed values of the magneton number reflected the collinear structure. Also, the coercive force ($H_C$) tends to rise with increasing Co$^{2+}$ substitution, in which the values of coercive force varied in the range of 183 – 285 Oe. The strong magnetocrystalline anisotropy of the octahedral Co$^{2+}$ ions contributed to the strengthening of the coercive force. The DC electrical resistivity decreased with increase of Co$^{2+}$ content x attributed to the electron hopping between cations with two different valence states distributed randomly on equivalent lattice sites. The variation of DC resistivity show a decrease with increase of temperature, indicate the semiconducting nature of the ferrite system. The variation of dielectric constant ($\varepsilon'$) and dielectric loss tangent (tan$\delta$) with temperature is taken at a constant frequency 1 KHz. It was observed that interfacial polarizations increases with increase in temperature, this was attributed to
the creation of crystal defects. Also, there was decrease in the dielectric constant for the increase in Co$^{2+}$ substitution.

Teixeira et al., (2014) studied the influence of thermal treatment on the magnetic properties of lithium ferrite (LiFe$_2$O$_4$) prepared by wet ball-milling using nitrates as raw materials. XRD spectra of the powder treated at 200 °C revealed the presence of lithium nitrate crystal phase, which disappeared with increase of the heat-treatment temperature. At 400 °C the α-Fe$_2$O$_3$ crystal phase was obtained as major phase. But as the annealed temperature increased diffraction pattern showed major LiFe$_5$O$_8$ phase at 1000 °C, further increase in annealing temperature show major lithium ferrate phase at 1400 °C along with some weak diffraction peaks associated with lithium ferrite. FTIR spectra of the samples annealed at 400 °C show vibrations bands in the range of 468 cm$^{-1}$ – 484 cm$^{-1}$ and 574 cm$^{-1}$ – 575 cm$^{-1}$, confirmed the presence of the α-Fe$_2$O$_3$ phase. For the samples annealed above 400 °C reveals vibration band at 711 cm$^{-1}$, 676 cm$^{-1}$ and 399 cm$^{-1}$ confirmed formation of lithium ferrite phase. The magnetic susceptibility as function of the temperature has a maximum value of nearly 1750 emu (gT)$^{-1}$ for the sample treated at 1200 °C. Arjunwadkar and Patil, (2014) synthesized Al$^{3+}$ substituted lithium ferrite (Li$_{0.5}$Fe$_{2.5-x}$Al$_x$O$_4$, where x = 0, 0.5, 1.0, 1.5, 2.0) by combustion method. X-ray diffraction and IR analysis confirmed formation of spinel structure with space group (Fd3m). It was observed that substitution of smaller ionic radii Al$^{3+}$, there was decrease in lattice parameter was observed which was almost linear. Reduction in bond length was confirmed with Al$^{3+}$ substitution attributed to the shift in peak position of octahedral absorption band towards higher frequency side. The low loss of Li$^+$ ions during synthesis by combustion method was responsible for low observed conductivity owing to the fewer amounts of Fe$^{2+}$ ions formed while synthesizing nanoparticles. It was found that inert nature of Al$^{3+}$ ions led to increase in resistivity and decrease in $T_C$ with increase in substitution. It was concluded from thermoelectric emf studies that n-type of conduction is asserted for x < 0 and p-type for x = 2.0 supported by the fact that for x < 2.0 exchange of electron, in the process Fe$^{2+}$ ↔ Fe$^{3+}$ was responsible for conduction while for x = 2.0 lithium ions are responsible for conduction. Low field hysteresis study revealed that saturation magnetization and the retentivity decreased with increase in Al$^{3+}$ content. Smaller values of observed coercivity was attributed to the single domain behavior, suggesting that particle sizes less than a
critical size, which is usually about hundred angstroms. The samples with x < 0 were found to be ferrimagnetic at room temperature and for x = 2.0 paramagnetic nature of the sample was found at room temperature attributed to the relatively larger amount of non-magnetic Al$^{3+}$ in the compound which replaced Fe$^{3+}$ cations from the octahedral site result of A-B interaction. It was concluded that further decrease in particle size can be obtained by controlling the various parameters such as sintering temperature during synthesis of compound by combustion method.

Kadam et al., (2014) studied structural, magnetic and electrical properties of Li$^+$ substituted CoFe$_2$O$_4$ by sol-gel auto-combustion method. X-ray diffraction analysis of Li$_{3x}$CoFe$_{2-x}$O$_4$ (where x = 0.0, 0.1, 0.2 and 0.3) revealed the cubic spinel phase for CoFe$_2$O$_4$ up to x = 0.0, no additional phase was obtained but for lithium doping x ≥ 0.2 second phase corresponding to the superstructure lines arise because of ordering of lithium sub lattice was obtained. It was observed that diffraction peaks shifted towards lower diffraction angle (2θ) with increase in Li$^+$ substitution. The lattice constant (a) was found to increase with increase in Li$^+$ content attributed to the larger ionic radii of Li$^+$ (0.78 Å) than Fe$^{3+}$ (0.67 Å). Li$^+$ enter into the octahedral-site (B – site) which swells lattice and result in enlargement of lattice parameter. Crystallite size decreased from 25 nm to 16 nm with increase in Li$^+$ substitution. FTIR spectroscopy confirmed the transition from spinel to ordered lithium ferrite phase with Li$^+$ doped cobalt ferrite. IR spectra revealed three types of band first primary band ($\nu_1$) attributed to Fe$^{3+}$—O$^2$ vibrations at tetrahedral site, second primary band ($\nu_2$) attributed to Fe$^{3+}$—O$^2$ vibrations at octahedral site and third primary band ($\nu_3$) attribute to Li — O vibrations. Saturation magnetization decreased with increase in Li$^+$ substitution attributed because of two reasons; firstly the overall magnetic nature is reduced with increase in Li$^+$ substitution, secondly exchange interactions are weakened due to Li$^+$ ions. Coercivity increased as Li$^+$ substitution increases. DC resistivity shows a linear decrease with increase in temperature, also resistivity decreased with increase in Li$^+$ substitution was attributed to hopping mechanism. The increase in Li$^+$ ions at the B sites replaces Fe$^{3+}$ ions, decreased the number of ferrous ions formed, thereby causing a decrease of BB hopping between Fe$^{3+}$ and Fe$^{2+}$ ions at B site. The substitution of Li$^+$ replaces Fe$^{3+}$ ions at the octahedral site, reducing the distance between two metal ions in B-sublattice, which increased the hopping probability and hence overall decrease in resistivity with increase in Li$^+$ substitution.
The dielectric constant increase with increase in temperature attributed to increase in polarization of electrical charge carriers.

Srivastava et al., 2014, synthesized chromium (Cr) doped lithium ferrite (Li$_{0.5}$Cr$_{0.1}$Fe$_{2.4}$O$_4$) at different pH levels by sol-gel method. X-ray diffraction revealed the formation of inverse spinel with the cubic type structure with maximum orientation of crystallites in (311) direction. The average crystallite size was calculated from three most intense peaks and found to be steady increase by increase in pH. A shift and broadening of peak towards higher 20 value with decrease in pH. Lattice parameter was found to be decrease with increment in pH attributed to the cation distribution and size effect. Mössbauer spectroscopy revealed the two magnetic sextets corresponding to the two Fe sites (A and B). The values of hyperfine field in Cr-doped Li-ferrite were smaller than those in undoped Li-ferrite. The magnetization of the sample synthesized at higher pH was higher than that of the sample synthesized at lower pH, magnetization first increases abruptly with increase in field up to 0.1 T and then increases slowly and saturates at nearly 0.25 T of applied magnetic field. A change in magnetic anisotropy constant was found attributed to the shape effect of the samples synthesized at different pH which was supported by TEM analysis. There was large increase in the value of saturation magnetization with increase in pH value, however there was small variation in crystallite size attributed to the fact that at higher pH the presence of Fe$^{3+}$ ions was at the B-site. Iqbal et al., (2013) synthesized Li$_{1.2}$Mg$_{0.4}$Eu$_x$Fe$_{2-x}$O$_4$ (x = 0.00, 0.02, 0.04, 0.06, 0.08, 0.10) by sol-gel auto combustion method. X-ray diffraction pattern of the prepared sample reveals formation of fcc single phase with reflections at 220, 311, 400, 422, 511, 440 and 533. Further doping of (Europium) Eu$^{3+}$ in Li$_{1.2}$Mg$_{0.4}$Eu$_x$Fe$_{2-x}$O$_4$ show the formation of orthoferrite (EuFeO$_3$) phase with 310 reflection. It was found that lattice constant first increased and then decreased with further increase in Eu$^{3+}$ substitution attributed to the segregation of the Eu$^{3+}$ at the grain boundaries. Moreover it was concluded that at x > 0.02 indicate the solubility of Eu$^{3+}$ at the spinel lattice. Dielectric measurements revealed that dielectric constant ($\varepsilon'$) and complex dielectric constant ($\varepsilon''$) decrease with the increase of Europium concentration attributed to the electronic exchange between Fe$^{2+} \leftrightarrow$ Fe$^{3+}$ resulted in local displacement and responsible for polarization of charges in these ferrites. Variation of $\varepsilon'$ and $\varepsilon''$ with frequency indicated that both of them were high at low frequency and then decreased rapidly with increase in
frequency attributed to the fact that polarization decreased with increase in frequency and reached a constant value due to fact beyond a certain frequency of external field. The higher values of dielectric constant observed at lower frequencies was attributed to the interfacial dislocations piles-up oxygen vacancies and grain boundary defects. Dielectric loss (\(\tan \delta\)) was high and decreased rapidly at high frequency supported by Koops phenomenological theory. It was concluded that energy loss was high at low frequency region while it was low at high frequency region.

Khot et al., (2015) studied the effect of Zn substitution and the chemical reaction temperature on the magnetic properties of Li-Cu ferrites synthesized by microwave sintering method. \(\text{Li}_x\text{Zn}_{(0.6-2x)}\text{Cu}_{0.4}\text{Fe}_2\text{O}_4\) (\(x = 0.05, 0.1, 0.15, 0.2, 0.25, 0.3\)) had been prepared by combination of lower chemical reaction temperature 150 °C and sintered using non-conventional microwave sintering method. XRD analysis confirmed formation of spinel phase. The lattice parameter was found to be in the range 8.3690 Å to 8.4653 Å. The bond length linearly increased with Zn\(^{2+}\) content attributed to the increase in lattice parameter ‘a’ with Zn content. Reported value of Saturation Magnetization and magnetic moment ranging from 13.71 emu/gm to 36.19 emu/gm and 0.6 μB to 1.5 μB. It was concluded that Saturation Magnetization (\(M_S\)) and magnetic moment increase with the increase in Zn\(^{2+}\) for \(x \geq 0.2\) obeying Neel’s model for magnetization and decreased for \(x = 0.15\) and 0.1 due to the existence of non-collinear spin interaction. For higher concentration of Zn (\(x = 0.05\)), the sample showed increase in saturation magnetization and magnetic moment, attributed to the dilution of magnetization of A-sub lattice by non-magnetic Zn\(^{2+}\) ion explained on the basis of Neel’s two sub lattice model. It was found that coercivity \(H_C\) decreased with increase in Zn\(^{2+}\) concentration and at higher values of Zn\(^{2+}\) concentration coercivity decreased. Moreover Curie temperature decreased with increase in Zn\(^{2+}\) content supported by the fact that Curie temperature mainly related to strength of A-B interaction. Therefore substitution of Zn\(^{2+}\) decreased the strength of A-B interaction as a consequence less thermal less thermal energy to offset the spin alignment and Curie temperature decreased. Rashad et al., (2015) synthesized lithium ferrite (LiFe\(_5\)O\(_8\)) at different annealing temperatures via a sol-gel auto-combustion method urea had been used as chelating agent and a fuel. Thermal Gravimetric Analysis (TGA) of un-annealed lithium ferrite illustrated that the lithium iron precursor decomposed thermally in two endothermic steps. The first endothermic step...
started at 57.8 – 228.2 °C due to loss of physically and chemically bonded water and decomposition of urea to evolve CO₂, H₂O and NO₂ gases, after dehydration reaction, the anhydrous ferrite precursor was decomposed into Li₂O and Fe₂O₃. The second endothermic step started at 384.5 °C and step related to the solid-solid interaction of Li₂O and Fe₂O₃ decomposed to form lithium ferrite phase. It was concluded that there was no significant weight loss was observed 400 °C indicated the formation of stable phase. XRD analysis showed formation of single phase cubic spinel structure at different annealing temperatures from 400 to 800 °C for 2 h. The lattice parameter was found to decrease on increasing the temperature. Electrical mobility was calculated and found in the range from 0.05 to 0.29 eV, which clearly indicated the lithium ferrite sample had semiconductor like behavior. The saturation magnetization was increased steadily on increasing the annealing temperature from 400 °C to 800 °C. The lithium ferrite powder annealed at 800 °C for 2h exhibit the highest saturation magnetization 51.9 emu/g attributed to increased value of crystallite size.

Ramesh et al., (2015) studied the cation distribution of Ni-Cu substituted lithium ferrite (Li₀.₅₋ₓNiₓCuₓFe₂.₅₋ₓO₄, x = 0.00, 0.05, 0.10, 0.15, 0.20, 0.25) were prepared by double sintered ceramic method. XRD diffraction patterns of the sample with maximum peak of intensity at (220, 311, 400, 422, 511 and 440) indicated formation of spinel cubic crystal structure with space group of Fd₃m. The basic lithium ferrite (Li₀.₅Fe₂.₅O₄) showed extra peak with hkl indices at (210, 211, 310, 321) indicated formation of Fd₃m space group to a P4132 space group with the presence of hematite (antiferromagnetic Fe₂O₃). Lattice parameter was found to be increase with increase in nickel/copper concentration. The introduction of Ni²⁺ and Cu²⁺ ions in the Li₀.₅Fe₂.₅O₄ cause shift in 2θ in the lithium ferrite peaks. The increment in lattice parameter was explained on the basis of net increase in the ionic radii, where the radius of Ni²⁺ ion (0.069 nm) is smaller than that of Li⁺ ion (0.073 nm) and the radius of Cu²⁺ ion (0.073 nm) is larger than of the Fe³⁺ (0.0645 nm) ions. The introduction of larger sized Cu²⁺ ions with increased concentration induced uniform strain in the lattice. As a result unit cell expands to accumulate the larger ion and expected to increase the lattice parameter.
Chapter-2
Review of Literature

2.9 Barium Ferrite

Xu et al., (2010) studied the influence of Nd$^{3+}$ substitution on the microstructure and electromagnetic properties of barium W-type hexaferrite. They reported the values of the lattice (a) of the samples were nearly same but there was slight decrease in the value of c with the increase of the amount of doped Nd$^{3+}$. With the doping of Nd$^{3+}$ ion the lattice distortion suppressed the abnormality of grains growth availability. The grain was found to be smaller and more homogeneous for the hexaferrite doped with Nd$^{3+}$ than the pure ferrite. Partial substitution of Nd$^{3+}$ ions in place of Ba$^{2+}$ result in the change of Fe$^{3+}$ to Fe$^{2+}$ which ultimately increase the permittivity. Microwave absorption characteristics increased with more addition of Nd$^{3+}$ ions when $x \leq 0.20$, while it slightly decreased with more addition of Nd$^{3+}$ ions that is $x = 0.025$ for the frequency range of $0.5 – 14.0$ GHz. Stergiou et al., (2010) studied the dielectric and magnetic properties of Dy (Dysprosium) and Gd (Gadolinium) substituted Ba-hexaferrites synthesized by chemical co-precipitation method. Real part of permeability of the samples lies close to 1.1 while magnetic losses appear less than 0.08. Low-level permeability attributed to the strong uniaxial anisotropy of M-type hexaferrites and the low filling factor. The value of permittivity for Gd-series is found to be increased while for Dy-series found to be increased. Deng et al., (2011) studied the electromagnetic properties and microwave absorption of W-type hexagonal ferrites doped with La$^{3+}$ synthesized by sol-gel method. They reported that the magnetic loss of the material enhanced by partial substitution of La$^{3+}$ at Ba$^{2+}$ sites and the super exchange interaction of the magnetic moment AA in Fe$^{3+}$—O—Fe$^{2+}$ got strong. Enhancement in the dielectric loss was also found with La$^{3+}$ doping attributed to the fact that La$^{3+}$ increased the chance of electron hopping between Fe$^{3+}$ and Fe$^{2+}$ resulting in higher dielectric loss in the material. It was concluded that microwave absorption performance of hexaferrite is enhanced by partial substitution of La$^{3+}$ for Ba$^{2+}$.

Rai et al., (2011) investigated the effect of strontium substitution for Cd$^{2+}$ in barium based BaCd$_{2-x}$Sr$_x$Fe$_{16}$O$_{27}$ W-type hexagonal ferrite. They reported that the substitution of Sr$^{2+}$ for Cd$^{2+}$ ions in BaCd$_{2-x}$Sr$_x$Fe$_{16}$O$_{27}$ sintered at 1400 °C ferrite showed improvement in phase formation. Significant decrease in coercivity $H_C$ up to few hundreds Oersted with substitution of Sr$^{2+}$ was found. Decrease in the real and
imaginary part of complex permittivity and tangent loss lead them suitable for high frequency application. Iqbal et al., (2011) synthesized Zirconium and cadmium doped W-type hexaferrite by co-precipitation method and annealed at 1153 K temperature. XRD analysis confirmed the formation of single phase W-type hexaferrite. SEM images showed rice shape pattern which is a useful geometry for application in catalysis, photonics, plasmonics, information storage, surface enhance Raman scattering, biological labeling, imaging and sensing. It was concluded from Mössbauer analysis that Zr and Cd were substituted at tetrahedral 4e and 4fiv site with some Zr ions substituted on bi-pyramidal 2d site as well. But for the high substitution level Mn ions preferred 6g and 4f octahedral sites. Higher values of $M_S$, $M_R$ and $H_C$ supported the application of the material for perpendicular recording media.

Aen et al., (2011) studied the effect of holomium (Ho) substitution on the magnetic and electrical properties of barium based W-type hexagonal ferrites. It was concluded from the XRD studies that homogeneous single phase of Ho doped hexaferrites were obtained. The lattice constant ‘a’ and ‘c’ increased with the increase of Ho concentration due to large ionic radius of Ho. Coercivity of the samples follow $H_C \propto 1/r$ behavior. DC electrical resistivity increased due to large density of grain boundaries which obstruct the Verwey mechanism. Substitution of La$^{3+}$ for large divalent Ba$^{2+}$ ions, that is in BaZn$_{0.5}$Mg$_{0.5}$Fe$_{16}$O$_{27}$ enhanced the electrical resistivity and dielectric constant of the product. The Curie temperature has been previously reported to decrease with the increment of the dopant contents. Doping with Nd$^{3+}$ ions varied the microstructure and improved the microwave absorption characteristics of BaCo$_2$Fe$_{16}$O$_{27}$ hexaferrites. Different oxides such as antimony doped tin oxide (ATO) and vanadium pentoxide (V$_2$O$_5$) considerably improved electromagnetic properties of ferrites. Doping of BaZn$_2$Fe$_{16}$O$_{27}$ with Co$^{2+}$ on divalent ionic site of Zn$^{2+}$ is known to reduce the saturation magnetization and Mg$^{2+}$ ions incorporated at divalent ionic sites in BaCoZnFe$_{16}$O$_{27}$ showed an increased magnetic susceptibility. Iqbal et al., (2012) synthesized Mn$^{2+}$, Zr$^{4+}$ and Ni$^{2+}$ doped W-type barium ferrite in which Mn$^{2+}$ ion is substituted on Co$^{2+}$ ionic site and a binary mixture of Zr$^{4+}$ + Ni$^{2+}$ is doped partially to replace Fe$^{3+}$ ions. It was concluded from the Mössbauer studies that Zr$^{4+}$ ions occupy 2d site at lower concentration and f$_{IV}$ ions for higher doping concentration. Mn$^{2+}$ and Ni$^{2+}$ ions prefer 12k, 2b and 4f$_{VI}$ sub-lattices. They reported that 90% absorption ability make these materials suitable for self attenuating electromagnetic radiations for
high frequency devices. Wu et al., (2012) synthesized the Pr$^{3+}$ substituted W-type barium ferrite and studied the electromagnetic and microwave absorption of the hexaferrites. They concluded that saturation magnetization ($M_S$) increased with Pr$^{3+}$ content. Doping of Pr$^{3+}$ in place of Fe$^{3+}$ decrease real part of permittivity while increase imaginary part of permittivity. It was reported that microwave absorbency gave good results for $x = 0.10$ in the frequency range of $4 – 14.0$ GHz.

Guo et al., (2012) synthesized W-type barium hexaferrite doped with rare earth ions La$^{3+}$, Nd$^{3+}$ and Sm$^{3+}$ by solid state reaction method and investigated the microwave absorbing properties. They concluded that microwave absorbing property of rare earth substituted ferrite is enhanced in the superhigh frequency range. While La-substituted ferrite exhibit the maximum dielectric loss angle tangent of 0.75 in frequency of 16 GHz. Hooda et al., (2014) synthesized Cd/Pb doped W-type hexaferrites by solid-state reaction method and studied the structural, electrical and magnetic properties. It was concluded from Nyquist plots that decrease in resistance offered by grains and grain boundaries for cadmium (Cd) doped W-type barium ferrite (BZCFO) than lead (Pb) doped W-type barium ferrite (BZPFO) for conduction vice-versa. High resistivity and low values of conductivity, real part of permittivity and dielectric loss of BZPFO than BZCFO make this material suitable for high frequency application.