CHAPTER FOUR

MAGNETIC PROPERTIES

4.1. INTRODUCTION:

Magnetism is a force of attraction or repulsion that acts at a distance. It occurs due to the presence of magnetic field, which is caused by moving electrically charged particles or is inherent in magnetic objects such as a magnet. Many naturally occurring compounds are magnetic in nature. The first such substance to be studied was loadstone or magnetite (Fe₃O₄), a compound of iron [1]. It was extensively studied by many researchers for its magnetic properties. P. Weiss measured its saturation magnetization and Curie temperature [2]. Subsequently, magnetism and the behaviour of magnetic materials have been well studied by several researchers [3-6]. Magnetic materials have gained wide importance due to their applications in a variety of fields. The domain structure, magnetic interaction and the basic properties of these materials are of considerable importance in modern technology. Magnetic materials are important components of electromagnetic gadgets, memory or disc storage devices, high frequency transformers, power inductors, switches, broad band pulse transformers, actuators, sensors, electromagnetic interference (EMI) suppressors, telecommunications, microwave absorbers- for special applications in defence etc.
Materials exhibit one of these magnetic behaviours viz: diamagnetism, paramagnetism, ferromagnetism, antiferromagnetism and ferrimagnetism, when placed in an external magnetic field. It also depends on the temperature. However, the ferromagnetic, antiferromagnetic and ferrimagnetic materials are classified on the basis of ordered arrangement of spins over the space lattice.

4.1.1. DIAMAGNETISM:

Diamagnetism is exhibited by all common materials. In diamagnetic materials, the orbital magnetic moment and the spin magnetic moment cancel each other. Hence there is no permanent dipole moment. In diamagnetism, weak magnetic dipole moments are produced in the atoms of the material when the material is placed in an external magnetic field. The combination of all those induced dipole moments gives the material, as a whole, only a feeble net magnetic field. The dipole moments, with them, their net field, disappear when the external field is removed. Since the magnetic moments induced by the applied magnetic field always oppose the applied field there is repulsion. The diamagnetic material has a negative susceptibility which is independent of temperature.

4.1.2. PARAMAGNETISM:

Paramagnetism is exhibited by materials containing the transition elements, the rare earth elements and the actinide elements. Each atom of
such a material has a permanent magnetic dipole moment due to incompletely filled outermost orbits, but the moments are randomly oriented in the material and the material as a whole lacks a net magnetic field. However, an external magnetic field can partially align the atomic magnetic dipole moments to give the material a net magnetic field. The alignment and thereby its field disappear when external magnetic field is removed. These materials have small positive susceptibility, which depends on temperature.

4.1.3. FERROMAGNETISM:

Ferromagnetism is a property exhibited by iron, cobalt, nickel, and certain other elements (and also by compounds and alloys of these elements). Some of the electrons in these materials have their resultant magnetic dipole moments aligned, which produces regions with strong magnetic dipole moments. An external field can then align the magnetic moments of such regions, producing a strong magnetic field for a sample of the material; the field partially persists when external magnetic field is removed. In these materials, the contribution of spin magnetic moment to the total magnetic moment is large. Neighboring atoms, having magnetic moments aligned in the same direction as illustrated in the Fig.4.1. (a), form small regions called domains. This behavior is the result of strong exchange coupling between the atoms. This interaction arises due to coupling of spins on adjacent atoms. The exchange energy between the neighboring dipoles is positive, such that the lowest energy state is the one
in which all the dipoles are aligned with their magnetic moments parallel. A ferromagnet has spontaneous magnetic moment even in zero applied field.

The electron spins and magnetic moments are arranged in a regular manner. They are supposed to occur due to a field produced within the material, which is proportional to magnetization of the sample.

4.1.4. ANTIFERROMAGNETISM:

The material in which the atomic moments from two sublattices are such that the moment on one, equals in magnitude but is aligned antiparallel to that on the other. Thus the net magnetic moment is zero and the material is said to be antiferromagnetic (Fig.4.1. (b)). They do not produce any net magnetization at absolute zero temperature.

4.1.5. FERRIMAGNETISM:

Ferrimagnetism exists in those materials in which atomic moments are aligned antiparallel but magnetic moments are unequal as shown in Fig.4.1.(c). This is due to the fact that the opposing magnets have different moments or the number of atoms having one spin direction is different from that having opposite spin direction thus giving a magnetic moment.

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4.1.6. SOFT AND HARD FERRITES:

Ferrites are ferrimagnetic compounds with iron oxides as the main component. They are hard and brittle like most other ceramics. In terms of their magnetic properties, the different ferrites are often classified as "soft" or "hard" ferrites, which refer to their low or high magnetic coercivity.

4.2 CHARACTERISTICS OF SOFT FERRITES:

Ferrites used in transformer or electromagnetic cores contain nickel, zinc, and/or manganese compounds. They have a low coercivity and are called soft ferrites. The low coercivity means, in such material, magnetization can easily reverse direction without dissipating much energy (hysteresis losses), while the materials’ high resistivity prevents eddy currents in the core, another source of energy loss. Because of their comparatively low losses at high frequencies, they are extensively used in the cores of RF (radio frequency) transformers and inductors. Soft ferrites are also used in switched mode power supplies (SMPS). The most
common soft ferrites are manganese-zinc (with the general formula Mn\(_x\)Zn\(_{1-x}\)Fe\(_2\)O\(_4\)) and nickel-zinc (with the general formula Ni\(_x\)Zn\(_{1-x}\)Fe\(_2\)O\(_4\)). Ni-Zn ferrites exhibit higher resistivity than Mn-Zn ferrites, and are therefore more suitable for frequencies above 1 MHz. In comparison, the Mn-Zn ferrites have higher permeability and saturation induction.

4.2.1. MAGNETIC DOMAINS:

Weiss proposed that a magnetic material consists of physically distinct regions called domains. In a ferromagnetic domain, there is parallel alignment of the atomic moments. In a ferrite domain, the net moments of the antiferromagnetic interactions are spontaneously oriented parallel to each other (even without an applied magnetic field). The term, spontaneous magnetization or polarization is often used to describe this property. Each domain becomes a magnet composed of smaller magnets (ferromagnetic moments). Domains contain about 10\(^{12}\) to 10\(^{15}\) atoms and their dimensions are of the order of microns (l\(10^{-4}\) cm.). Their size and geometry are governed by certain considerations and is dependent on the intrinsic properties of the material [7]. Domains are formed basically to reduce the magnetostatic energy which is the magnetic potential energy contained in the field lines (or flux lines as they are commonly called) connecting north and south poles outside of the material.
4.2.2. MAGNETOSTRICTION:

Ferrites change their length when they are magnetized. This small change in length is called longitudinal magnetostriction which plays an important role in domain geometry and is important in practical use of transformer materials. The incremental change may be positive or negative for different materials at saturation. Most ferrites exhibit negative incremental change except for few cases like Fe$_3$O$_4$.

4.2.3. ANISOTROPY:

Apart from the exchange interaction between neighboring atoms, the spins have interaction with lattice atoms. The spin–lattice interaction is seen when all the spins are completely aligned and the direction of alignment is rotated relative to the crystal axis. Preferred directions of magnetic moments are then observed.

The excess work done in magnetizing a magnetic material or ferrite to saturation, in a direction which is different from the easy direction, is called crystal anisotropy and it plays an important role in determining the properties like permeability, hysteresis and magnetostriction [8].

4.2.4. HYSTERESIS:

If a demagnetized ferromagnetic or ferrimagnetic material is subjected to an external field, it gets magnetized due to the spins, as each
domain rotates parallel to the direction of the applied magnetic field until all the dipoles are aligned. And it will reach a saturation value at a certain critical field. The OABC curve is called magnetization curve as shown in Fig.4.2. The plateau region of the magnetization curve is the saturation magnetization ($M_s$), and it ($M_s$) is a measure of the magnetization ($M$) per gram. Its value is given by

$$M_s = \frac{M}{\rho} \text{ (emu/g)}$$  \hspace{1cm} (4.1)

where, ‘$\rho$’ is the density of the material. If the magnetizing field is reduced to zero and an increasing reverse field is applied, then, the original magnetization curve OABC is not followed but a lag (hysteresis) of the magnetization to the magnetic field occurs.

![Magnetization Curve](image)

Fig.4.2. Plot of magnetization ($M$) versus magnetic field strength ($H$). ‘$M_s$’ is the saturation magnetization, ‘$M_r$’ is the remanence magnetization, and ‘$H_c$’ is the coercivity in the figure.

Increasing the reverse field leads to saturation in the reverse direction, and if the field is again returned to the original direction, a complete cyclic loop CDEFGC is obtained as seen in the same Fig.4.2. The irreversibility and hysteresis in ferromagnetic material are due to the
impediments to the motion of domain walls. These impediments are the inclusions, grain boundaries, dislocations and heterogeneities which are due to other phases. The magnetization increases slowly by reversible wall motion at low fields and by irreversible wall motion above critical field and by irreversible rotation at very high field. The rotation of domains has been observed by Barkhahusen [9]. The wall energy is maximum at very high field leading to irreversible increase in magneto-elastic and magneto-static energies under the action of external magnetic field. When the magnetic field is reduced to zero, the residual magnetization is retained and the opposite field is used for the reversal of domains to their original state of zero magnetization. The area inside the loop is indicative of the losses occurring due to traversal of the loop. The slope of tangent to the magnetization curve at the origin (OX) gives the magnitude of initial susceptibility $\chi_0$. The maximum susceptibility occurs at the knee of magnetization curve determined by the slope of OY. The smooth curve depicts the rotation of the vector moment in the domain wall as the magnetic field strength (H) is varied.

When the applied field is decreased, magnetization decreases. In multi-domain bulk materials, demagnetization occurs primarily via spin rotation through the domain walls [10, 11]. The residual magnetization ($M_R$) at zero applied field is remanance or retentivity. The magnetic field required to demagnetize the material completely from retentivity to zero is called [12] the coercive force ($H_C$). The coercive force is found to vary from $10^{-1}$ to $10^{+3}$ oersted [13].
4.2.5. A. C. SUSCEPTIBILITY:

Curie temperature is one of the most important parameters of ferrites. It is intrinsic property of the spinel ferrites, and depends on method of preparation, sintering temperature, as also on the doping by additives [14]. Rezlescu et al. [15] investigated the influence of preparation technique and cation distribution of copper manganese mixed ferrites. They observed that the migration of tetrahedral site shifts the Curie temperature to lower values. The dependence of Curie temperature on the distribution of metallic ions was suggested also by Gorter [16] and Neel [17]. Apart from the method of preparation, sintering temperature and doping by additives, the microstructure, porosity and grain size also play a dominant role in deciding the a.c. susceptibility. With respect to their magnetic properties, the ferrimagnetic materials show similarities with those of ferromagnetic. These materials show hysteresis and susceptibility below Curie temperature. A.C. susceptibility studies explore the existence of multidomain (MD), single domain (SD) and super paramagnetic (SP) particles in the material. From the susceptibility curves [18-20], the Curie temperature and the domain structure can be determined.

4.2.6. PERMEABILITY:

Permeability is one of the most important parameters used in evaluating magnetic materials. Not only is it a function of the chemical composition and crystal structure, but it is also strongly dependent on microstructure, temperature, stress, time taken for complete
demagnetization and several other factors. The permeability of the magnetic material depends on microstructural conditions and is found to be true during excitation by alternating currents and becomes extremely important at high frequencies. This is because the a. c. excitations produce rapid a movement of the magnetic domain wall and the permeability is related to the ease of movement of these walls. The presence of any imperfections in the material structure will reduce the permeability. Fewer the grain boundaries, larger will be the grains and higher the permeability, as grain boundaries act as impediments to the domain wall motion. Tebble and Craik [21] pointed out that in very high permeability metallic materials, domain walls appear to move across grain boundaries easily. In ferrites as the grain boundaries are thicker, the same kind of unhindered movement does not occur as in the case of metals. Lack of purification, presence of pores and inclusions prevent the attainment of very high permeability, which extends upto 100,000 (in the case of metals).

4.2.6.1. MODELS OF PERMEABILITY:

Different research workers have developed models of permeability to explain the behaviour of the material as regards its permeability. Some of these models are discussed in short here.

(A) TWO PINNING MODEL:

This model [22-24] is based on the assumption that a component that varies with spatial co-ordinates along the grain boundary is
responsible for permeability. The disorientation of magnetic axes of the grains gives rise to micro stress and their sources are located on the grain boundary. This results in alternation of the region with best and worst coincidence on grain boundary and the magnetostrictional deformation creates the inhomogeneous stress along grain boundary. Thus domain wall is linked near grain boundary with the regions of increased anisotropy.

\[ \Delta K = (|K| - |K_1|) \] \[ ------- \quad 4.2. \]

(B) GLOBUS MODEL:

The model developed by Globus [25, 26] is based on the reversible motion of domain walls, under a very small magnetic field, giving rise to the initial permeability in the material and it considers the contribution of the spin rotation as rather negligible. In this model the domain wall is pinned at the grain boundaries and they bulge under the application of magnetic field until the critical field is reached, when the wall gets unpinned. Such a model can be extended to the cases where the domain walls are pinned at inter-granular pores. In such a model

\[ (\mu - 1) = \frac{3 M_s^2 D}{16 \gamma} \] \[ ------- \quad 4.3. \]

where \( M_s \) is saturation magnetization, \( D \) is grain diameter and \( \gamma \) is domain wall energy per unit area as \( \gamma \sim \sqrt{AK_1} \)

\[ \mu_i = \frac{M_s^2 D}{|K_1|} \] \[ ------- \quad 4.4. \]

Such a model can be extended to the case where the domain walls are pinned at intergranular pores i.e. span of domain wall.
Further, Globus and Co-workers [25, 27] felt that, in polycrystalline ferrites the magnetization mechanism may be different due to the granular structure of ferrites. They have developed a model in which bulging of domain wall by 180° is responsible for the initial permeability rather than the domain wall displacement.

(C) NON MAGNETIC GRAIN BOUNDARY MODEL:

Johnson [28] developed the non-magnetic grain boundary model, which can explain the entire grain size dependence of μi (initial permeability) at low anisotropy as the Globus model cannot account for grain size dependence of permeability when intergranular domain walls are absent. This model describes the grain size dependence of rotational permeability in polycrystalline materials [29]. According to this model there is almost a linear dependence of permeability on the grain size for fine grained polycrystals, where D<<μiδ.

It is given by the relation

\[ μ_e = \frac{μ_i D}{(μ_i δ + D)} \]  \hspace{1cm}  4.5.

where \( μ_e \) = effective permeability, \( μ_i \) = complex (initial) permeability, D = grain size, \( δ \) = grain boundary thickness.

For larger grain size where D>>μiδ, the model predicts constant rotational permeability equivalent to that in single crystal of the same material i.e. \( μ_e \approx μ_i \).
4.2.6.2. DEPENDENCE OF INITIAL PERMEABILITY:

(A) MICROSTRUCTURE DEPENDENCE:

Microstructure plays a very important role in deciding the magnetic properties of materials because of fine grains where there is reversal of magnetization by rotation, since the domain walls are energetically favorable in fine grains. The initial permeability is dependent on grain size, density and porosity. Porosity causes hindrance to domain wall motion and it decreases initial permeability [30]. Also the coercive force increases with porosity because of internal demagnetizing field where the decrease in permeability is caused by same reason. The larger grain size causes reduction in initial permeability due to the presence of voids that induce demagnetizing field and creates impediments for domain wall motion. Therefore the grain size is a very important parameter in the permeability. A duplex structure is undesirable because it lowers the permeability. It is often due to particle impurity, which produces rapid growth locally, while other impeded areas are unaffected [31, 32].

(B) TEMPERATURE DEPENDENCE:

Temperature dependence of initial permeability is one of the important parameter in a magnetic component. From the graph of variation of initial permeability with temperature, the slope at a specific temperature can be expressed as a material parameter called the temperature factor (T.F.) which is defined as

\[ \text{T.F.} = \frac{\Delta \mu}{\mu^2} \Delta T \]

-------- 4.6.
where, $\Delta \mu$ is the difference in permeability ($\mu_2 - \mu_1$) between the two temperatures, $T_2$ and $T_1$ respectively, while $\Delta T$ is the difference in temperature.

The temperature factor can be used to predict the variation in magnetic properties of a magnetic component. A thermal hysteresis is observed when temperature is cycled from higher temperature above $T_C$ to lower temperature. This is explained by taking into account the domain wall pinning component between the intrinsic parameter $M_S$ and $K_1$ around the transition point [33].

**C) FREQUENCY DEPENDENCE:**

At low frequencies, permeability is almost independent of frequency, as the domain wall motion is dominant mechanism. Also at low frequencies, the applied field causes domain wall shift and this motion results in change in net magnetization. The domain structure is responsible for high frequency permeability. At high frequencies, the domain wall inertia precludes any appreciable wall motion but the mechanism can rotate within each domain. This mechanism is same as ferromagnetic resonance. Smit and Wijn [34] have explained the extension of the loss over a relatively broad frequency region in terms of additional effects upon the resonance condition due to demagnetizing field in the domain structure.
Various magnetic properties viz saturation magnetization, a. c. susceptibility and initial permeability of Mn-Zn ferrite samples, prepared by the mechano-chemical method and the wet chemical method, were studied.

4.3. EXPERIMENTAL MEASUREMENT:

Saturation magnetization, AC susceptibility and permeability measurements of the samples prepared by both the methods, namely, the mechano-chemical method and the wet chemical method were done by the instruments described in Chapter Two. Experimental procedures employed in the measurements are discussed below.

4.3.1. SATURATION MAGNETIZATION:

Sample preparation:

Powdered samples of Mn$_x$Zn$_{(1-x)}$Fe$_2$O$_4$ synthesized by mechano-chemical and wet chemical methods were pressed into pellets of the size 1.0 cm in diameter and of thickness ranging between 2mm-3mm under a pressure of 75KN applied for about 5 minutes. Four sets of pellets were sintered in nitrogen atmosphere at temperatures; 1000$^0$C, 1100$^0$C, 1200$^0$C and 1300$^0$C, respectively, for 4 hours separately in a programmable Carbolite furnace model STF 15/180, with a heating and cooling rate of 5$^0$C min$^{-1}$. 
Measurement:

The saturation magnetization measurements of the samples were carried out using a high field hysteresis loop tracer supplied by Magneta India, Mumbai. This instrument works on the principle that high magnetic field is generated in a solenoid by passing a pulse current of sinusoidal shape. A pickup coil system is kept in the solenoid to detect field and the magnetization signal of a sample placed in the pickup coil. The signals produced are then processed by an electronic system. These transitory signals are digitized by a micro-controller and then sent to computer for plotting a hysteresis loop, which is observed on the monitor with calculated values of hysteresis parameters. The applied magnetic field was of 5 KOe. The magnetization sensitivity was of 10 EMU. The accuracy of measurement was in the range of 95-100%.

The calibration of the instrument was carried out using pure nickel as a standard having magnetization- 53.34 emu/g.

Magnetic measurements were also carried out by using vibrating sample magnetometer (VSM) OXFORD (Oxford Instruments) Mag LabVSM.
4.3.2. A. C. SUSCEPTIBILITY:

A.C. susceptibility measurements of the unsintered as well as sintered samples were made using computerized pulse field A. C. susceptibility apparatus described by Likhite et al. [35]. The apparatus consists of Helmholtz coil, two pick-up coils, furnace, sample holder, temperature measuring device, control unit, data acquisition system, power supply to run the furnace and PC with related software to execute the run cycle. The Helmholtz coil is powered to produce pulsating magnetic field. To avoid the over heating of coils, a glass jacket with water circulation was used. In a typical experiment, 0.5 g of the Mn-Zn ferrite powder was placed in the sample holder, a quartz tube fused at one end, which was then inserted in glass jacket and placed at the centre of the pick-up coil for uniform heating. The data, that is, magnetization (emu/g) as a function of temperature collected by the data acquisition system was directly saved in a file on the PC simultaneously showing the progress of the experiment by way of a graph on the PC monitor. The temperature of the furnace was maintained by a power supply and was measured by using platinum rhodium thermocouple. It is a regulated digital power supply whose voltage and current are varied automatically by the PID temperature controller output which can be programmed for a set temperature and a set heating rate. The magnetic moments were recorded at various temperatures, while the sample was heated to the preset heating rate. The heating was continued till the magnetization (emu/g) signal reduced to zero. This happens when the Curie temperature is attained.
4.3.3. INITIAL PERMEABILITY:

Sample preparation:

Magnetic permeability measurements were carried out on the torroids which had a winding of 100 turns of super enameled doubly insulated copper wire of 33 gauge. For this purpose, each powdered sample was pressed into a torroid with inner and outer diameter of 1 cm and 2 cm, respectively, with thickness ranging between 3-4 mm by applying a pressure of 75KN for about 5 minutes. The torroids were sintered at 1000°C, 1100°C, 1200°C and 1300°C in nitrogen atmosphere for 4 hours with a heating and cooling rate of 5°C min⁻¹.

Measurement:

The initial permeability and loss factor as a function of frequency and temperature were measured by recording the inductance and dissipation factor (tan δ) values starting from room temperature to 500°C and with frequency variation from 20Hz to 1MHz using LCRQ meter.

The initial permeability (μ₀) was calculated from the formula

\[ L = 0.0046 \mu_0 N^2 h \ln (OD/ID) \]

where 'L' is inductance in Henry, 'N' is the number of turns of copper wire on torroid, 'h' is the height of the core in meters, OD and ID are the outer and the inner diameters of torroid in meters, respectively.
4.4. RESULTS AND DISCUSSION:

The results obtained in the study of the magnetic properties of the Mn-Zn ferrite samples, prepared by two different methods as stated earlier, are tabulated and discussed in the following Sections. These ferrite samples are found to be nanomaterials having the particle sizes in the range 10-67 nm.

4.4.1. SATURATION MAGNETIZATION:

Ferrite samples prepared by mechano-chemical method:

The variation of the saturation magnetization with Mn contents for the Mn-Zn ferrite samples of various compositions, prepared by the mechano-chemical method, is given in Table 4.1. It can be observed that the maximum value for saturation magnetization (Ms) was 50.91emu/g for the unsintered $\text{Mn}_{0.625}\text{Zn}_{0.375}\text{Fe}_2\text{O}_4$ sample. The value of Ms decreases for all the samples when sintered at 1000°C. Saturation magnetization of $\text{Mn}_{0.7}\text{Zn}_{0.3}\text{Fe}_2\text{O}_4$ was found to be 22.53emu/g, which was the highest as compared to all the samples sintered at this temperature. On further sintering of the samples, at 1100°C and beyond, the saturation magnetization values showed an increasing trend with the highest value shown by $\text{Mn}_{0.675}\text{Zn}_{0.325}\text{Fe}_2\text{O}_4$ sample being 44.57emu/g. However, the maximum value of Ms at 1200°C was 63.39emu/g for $\text{Mn}_{0.675}\text{Zn}_{0.325}\text{Fe}_2\text{O}_4$ whereas at 1300°C it was 68.59emu/g for $\text{Mn}_{0.65}\text{Zn}_{0.35}\text{Fe}_2\text{O}_4$. Fig.4.3 and Fig.4.4 (a), (b) and (c) illustrate the variation of saturation magnetization.
of Mn-Zn ferrite samples with the amount of Mn for different sintering temperatures.

Table 4.1. Saturation magnetization values of unsintered and sintered Mn-Zn ferrite samples, of various compositions, obtained by the mechano-chemical method.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Saturation magnetization values (emu/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Unsintered</td>
</tr>
<tr>
<td>Mn₀.₄Zn₀.₆Fe₂O₄</td>
<td>16.68</td>
</tr>
<tr>
<td>Mn₀.₅Zn₀.₅Fe₂O₄</td>
<td>28.20</td>
</tr>
<tr>
<td>Mn₀.₆Zn₀.₄Fe₂O₄</td>
<td>39.47</td>
</tr>
<tr>
<td>Mn₀.₆₂₅Zn₀.₃₇₅Fe₂O₄</td>
<td>50.91</td>
</tr>
<tr>
<td>Mn₀.₆₅Zn₀.₃₅Fe₂O₄</td>
<td>45.46</td>
</tr>
<tr>
<td>Mn₀.₆₇₅Zn₀.₃₂₅Fe₂O₄</td>
<td>43.90</td>
</tr>
<tr>
<td>Mn₀.₇Zn₀.₃Fe₂O₄</td>
<td>32.35</td>
</tr>
</tbody>
</table>

Fig. 4.3. Variation of saturation magnetization value of Mn-Zn ferrite unsintered samples with Mn contents, prepared by the mechano-chemical method.
Fig. 4.4. Variation of saturation magnetization of Mn-Zn ferrite samples, with Mn contents sintered at (a) 1100°C (b) 1200°C and (c) 1300°C.
Ferrite samples prepared by wet chemical method:

For the samples synthesized by the wet chemical method, the variation of the saturation magnetization with Mn contents is given in Table 4.2. The saturation magnetization values for unsintered samples were found to be lower when compared with the samples prepared by the mechano-chemical method. The highest value of $M_s$ being 43.66 emu/g, for the $\text{Mn}_0.7\text{Zn}_0.3\text{Fe}_2\text{O}_4$ sample. When sintered at $1000^\circ\text{C}$, the Mn-Zn ferrite samples prepared by the wet chemical method were found to show a similar trend as observed in the case of samples from the mechano-chemical method. Initially, there was a decrease in the saturation magnetization value for all the samples. The maximum $M_s$ value of 22.37 emu/g was observed in the case of $\text{Mn}_0.675\text{Zn}_0.325\text{Fe}_2\text{O}_4$ sample. When the samples were further sintered at temperatures $1100^\circ\text{C}$, $1200^\circ\text{C}$ and $1300^\circ\text{C}$, increase in the saturation magnetization at each higher temperature was observed. And the maximum value of $M_s$ was found to shift from $\text{Mn}_0.65\text{Zn}_0.35\text{Fe}_2\text{O}_4$ to $\text{Mn}_0.625\text{Zn}_0.375\text{Fe}_2\text{O}_4$ and to $\text{Mn}_0.675\text{Zn}_0.325\text{Fe}_2\text{O}_4$ with values being 42.86 emu/g, 61.63 emu/g and 68.36 emu/g, respectively, at three sintering temperatures. Fig.4.5. and Fig.4.6. (a) and (b) show variation of saturation magnetization of Mn-Zn ferrite samples with amount of Mn for different sintering temperatures.
Table 4.2. Saturation magnetization values of unsintered and sintered Mn-Zn ferrite samples, of various compositions, obtained by the wet chemical method.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Saturation Magnetization (emu/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Unsintered 1000°C</td>
</tr>
<tr>
<td>Mn0.4Zn0.6Fe2O4</td>
<td>14.93</td>
</tr>
<tr>
<td>Mn0.5Zn0.5Fe2O4</td>
<td>17.40</td>
</tr>
<tr>
<td>Mn0.6Zn0.4Fe2O4</td>
<td>21.06</td>
</tr>
<tr>
<td>Mn0.625Zn0.375Fe2O4</td>
<td>34.08</td>
</tr>
<tr>
<td>Mn0.65Zn0.35Fe2O4</td>
<td>27.41</td>
</tr>
<tr>
<td>Mn0.675Zn0.325Fe2O4</td>
<td>39.99</td>
</tr>
<tr>
<td>Mn0.7Zn0.3Fe2O4</td>
<td>43.66</td>
</tr>
</tbody>
</table>

Fig. 4.5. Variation of saturation magnetization of Mn-Zn ferrite unsintered samples, with Mn contents, prepared by the wet chemical method.
Zinc ferrite, ZnFe$_2$O$_4$, is a normal spinel, and the unit cell has no net magnetic moment ($\text{ZnFe}_2\text{O}_4/\text{Zn}^{2+}[\text{Fe}^{3+}\text{Fe}^{3+}]\text{O}_4/d^0[d^5d^4]$). In contrast, the manganese ferrite is an inverse spinel and, consequently, the two magnetic sublattices are antiferromagnetically aligned ($\text{MnFe}_2\text{O}_4/\text{Fe}^{3+}[\text{Mn}^{2+}\text{Fe}^{3+}]\text{O}_4/d^5[d^5d^5]$). When the nonmagnetic zinc...
ion (d^10) is substituted into the manganese ferrite lattice, it has a stronger preference for the tetrahedral site than does the ferric ion and thereby reducing the amount of Fe^{3+} on the A site. Because of the antiferromagnetic coupling, the net result is an increase in magnetic moment on the B lattice and an increase in saturation magnetization. Therefore the addition of nonmagnetic zinc ferrite to the inverse spinel manganese ferrite raises the saturation magnetization in Mn–Zn ferrite. However, the change in the magnetic properties of Mn–Zn ferrites depends on the solubility of cations (Mn^{2+} or Zn^{2+}) in the ferrite lattice and the occupying positions of tetrahedral or octahedral sites.

On the other hand, magnetic properties of the ferrites depend on the microstructure [36, 37]. The microstructure of the ferrite is determined by a variety of factors such as: raw material quality, sintering temperature, sintering time and material composition. This fact is very important because the microstructures developed during sintering are determined, to a large extent, by the powder's characteristics namely crystallite size, shape, size distribution, porosity, state of agglomeration, chemical and phase composition, which are closely associated with the preparation method.

Various investigators [38, 39] have studied the saturation magnetization values for Mn–Zn ferrites and have observed that the saturation magnetization is the highest for the samples when the Mn content is around 0.8 in the Mn–Zn ferrites. The changes in the magnetic
properties, due to sintering of the nano sized Mn–Zn ferrites at various temperatures, are because of the influence of cationic stoichiometry and their occupancy in the specific sites. In addition, it is also due to the formation of dead layers on the surfaces, existence of random canting of particle surface spins, non-saturation effects caused by a random distribution of particle size and deviations from the normal cation distribution [40].

A decrease in the coercivity value $H_C$ was observed for higher sintering temperatures of the samples as well as for increased Mn value. This decrease can be attributed to an increase in grain size and the decrease in porosity of the samples.

For most of the unsintered samples, the values of retentivity ($M_R$) and the coercivity ($H_C$) were found to be higher indicating single domain (SD) behavior of the samples, whereas on sintering the samples beyond $1200^\circ C$ the values of retentivity $M_R$ and the coercivity $H_C$ were found to be lower pointing towards multi domain (MD) behavior of the samples. The hysteresis losses were found to be low for the unsintered as well as for the sintered samples and were found to depend on the amount of Mn and the sintering temperature.

In the present investigation, from among all the samples prepared by mechano-chemical method as well as wet chemical method, sintered (at higher temperature) at $1100^\circ C$, $1200^\circ C$ and $1300^\circ C$, the maximum value of
M_s was found for the samples with Mn contents ('x' value) around 0.65. Saturation magnetization and hysteresis study was also carried out on VSM and the results obtained confirm of the low loss in the magnetic behaviour. The VSM results are illustrated in Fig. 4.7., and Fig.4.8.

Fig. 4.7. Magnetic hysteresis curves obtained by VSM at room temperature for unsintered samples (a) Mn_{0.5}Zn_{0.5}Fe_2O_4 and (b) Mn_{0.6}Zn_{0.4}Fe_2O_4, for the mechano-chemical method.
Fig. 4.8. Magnetic hysteresis curves obtained by VSM at room temperature for (c) Mn$_{0.625}$Zn$_{0.375}$Fe$_2$O$_4$ sintered at 1200°C and (d) Mn$_{0.675}$Zn$_{0.325}$Fe$_2$O$_4$ sintered at 1300°C for the wet chemical method.
4.4.2. A.C. SUSCEPTIBILITY:

Ferrite samples prepared by mechano-chemical method:

The variation of the Curie temperature with increasing Mn content in unsintered Mn-Zn ferrite samples prepared by the mechano-chemical method is given in Table 4.3. It can be seen that, there was a systematic increase in the value of the Curie temperature \( (T_C) \) from 447K for \( \text{Mn}_{0.4}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4 \) to 603K for \( \text{Mn}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4 \) as the manganese amount increases in these ferrites [41]. This is due to the substitution of non-magnetic \( \text{Zn}^{2+} \) ions by the magnetic \( \text{Mn}^{2+} \) ions in the samples. The value of \( T_C \) was found to be higher in the case of the ultrafine powder than that in bulk ferrites. This is due to the deviation of cation distribution in a nanosized particle as in comparison with its bulk counterparts [42].

In general, magnetic properties are controlled by exchange interaction of the metallic ions on the two interactive sub-lattices \( \text{A and B} \). The change in \( T_C \) may be positive or negative depending on the boundaries, the geometry, and the interaction. It is also possible that \( T_C \) decreases due to some unknown surface effect. For small particles a significant fraction of atoms are on the surface, and it is reasonable to expect their magnetic interactions to be different. As such, a different average Curie temperature [43] is observed. The graph of the variation of the magnetization with temperature for each sample with different Mn content is shown in Fig. 4.9 and Fig. 4.10. Chandana Rath et al.. in 2002 [42] and others [44, 45] observed a cusp (i.e. the magnetization increased beyond a
point instead of approaching zero) in some specific compositions among many samples of Mn-Zn ferrite.

In our present study of variation of Curie temperature of Mn-Zn ferrite, a small cusp was observed for the samples as can be seen from Fig. 4.9. The nature of the Ms versus T plots of the samples indicates near single domain behavior.

When the samples were sintered at 1100°C and 1300°C, the Curie temperature was found to decrease for all the samples. The decrease in this value of $T_C$ was due to the increase in the grain size from initial nano-size, on sintering, changing to the bulk, which allows redistribution of cations to occupy their preferential site. $T_C$ values were found to be in the range 413K to 588K for the samples sintered at 1100°C. For the samples sintered at 1300°C, the $T_C$ further decrease, and the values were in the range 354K to 549K. The samples thus show a multidomain behavior as can be seen from the Fig. 4.10.

<table>
<thead>
<tr>
<th>Table 4.3. Curie temperature of unsintered and sintered Mn-Zn ferrite samples obtained by the mechano-chemical method.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Composition</strong></td>
</tr>
<tr>
<td>Mn$<em>{0.4}$Zn$</em>{0.6}$Fe$_2$O$_4$</td>
</tr>
<tr>
<td>Mn$<em>{0.5}$Zn$</em>{0.5}$Fe$_2$O$_4$</td>
</tr>
<tr>
<td>Mn$<em>{0.6}$Zn$</em>{0.4}$Fe$_2$O$_4$</td>
</tr>
<tr>
<td>Mn$<em>{0.7}$Zn$</em>{0.3}$Fe$_2$O$_4$</td>
</tr>
<tr>
<td>Mn$<em>{0.8}$Zn$</em>{0.2}$Fe$_2$O$_4$</td>
</tr>
</tbody>
</table>
Fig. 4.9. Curie temperature for various unsintered Mn-Zn ferrites samples with different Mn content, prepared by the mechano-chemical method.
Fig. 4.10. Curie temperature for various Mn-Zn ferrite samples with different Mn content sintered at 1300°C, prepared by the mechano-chemical method.
Ferrite samples prepared by wet chemical method:

Similarly, the Curie temperature for Mn-Zn ferrite samples prepared by the wet chemical method varies with increasing Mn content as can be seen in Table 4.4. For the same composition, the Curie temperature was marginally higher than that for the samples prepared by mechano-chemical method in the range from 481K for Mn0.4Zn0.6Fe2O4 to 628K for Mn0.8Zn0.2Fe2O4.

The graph of variation of the magnetization with temperature for Mn-Zn ferrite samples for different compositions of Mn is shown in Fig. 4.11. Cusp for the samples with Mn proportion of 0.7 and 0.8 is pronounced in the figure. When the samples are sintered at 1100°C and 1300°C, invariably, the Curie temperature is found to decrease for all the samples. The decrease in the $T_c$ can again be attributed to the increase in the grain size, on sintering, to form the bulk material. This allows stable cation, redistribution of Mn$^{2+}$, Zn$^{2+}$ and Fe$^{3+}$ in their preferential site. $T_c$ was found to be in the range of 446K to 609K for the samples sintered at 1100°C, whereas for the samples sintered at 1300°C, the $T_c$ further decrease to the range 378K - 563K.
Table 4.4. Curie temperature of Mn-Zn ferrite sample of various composition, obtained by the wet chemical method.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Unsintered</td>
</tr>
<tr>
<td>Mn₀.₄ Zn₀.₆ Fe₂ O₄</td>
<td>481</td>
</tr>
<tr>
<td>Mn₀.₅ Zn₀.₅ Fe₂ O₄</td>
<td>509</td>
</tr>
<tr>
<td>Mn₀.₆ Zn₀.₄ Fe₂ O₄</td>
<td>578</td>
</tr>
<tr>
<td>Mn₀.₇ Zn₀.₃ Fe₂ O₄</td>
<td>613</td>
</tr>
<tr>
<td>Mn₀.₈ Zn₀.₂ Fe₂ O₄</td>
<td>628</td>
</tr>
</tbody>
</table>

Fig. 4.11. Curie temperature for various unsintered Mn-Zn ferrite samples with different Mn content, prepared by the wet chemical method.

4.4.3. PERMEABILITY:

The variation of permeability with temperature at frequency 20 Hz for the samples prepared by the mechano-chemical method sintered at 1000°C, 1100°C, 1200°C and 1300°C is shown in Fig. 4.12 (a), (b), (c) and (d). It is observed that the initial permeability slowly increases, reaches a certain peak value at a specific temperature and drops gradually to zero at
Curie temperature. The increase in permeability with temperature is due to the fact that the anisotropy decreases faster with temperature than the saturation magnetization. However, most of the samples sintered at 1000°C show two peaks. The peak at the far right drops to zero at the Curie point when ferrimagnetism is lost. The peak to the left is called the secondary maximum of permeability (SMP). This peak most often occurs close to the temperature at which the magnetostriction goes through zero.

In 1957, Guillaud has shown [46] the existence of secondary maxima of permeability for Mn-Zn ferrite. Lescroel and Pierrot (1960) have reported that many manganese ferrites containing ferrous ions have a secondary permeability maxima [47].

For the samples sintered at this temperature (1000°C), the initial permeability (μ₁) of Mn₀.₅Zn₀.₅Fe₂O₄ is 1791 at 120°C and secondary maximum of permeability is at 60°C. However, the highest value of μ, equal to 2433 at SMP of 170°C and curie peak of 210°C was observed in the case of Mn₀.₆₇₅Zn₀.₃₂₅Fe₂O₄, among all the samples sintered at this temperature. The Curie temperature values for various Mn-Zn ferrite samples were found to be in the range 240°C to 380°C.

When the samples were sintered at 1100°C, Mn₀.₄Zn₀.₆Fe₂O₄ was found to show permeability value of 4522 at 100°C, while, within the series Mn₀.₆₅Zn₀.₃₅Fe₂O₄ has the highest value of permeability i.e. 9202 at 120°C. A few samples show the secondary maximum of permeability at this sintering temperature.
In the case of $\text{Mn}_0.625\text{Zn}_0.375\text{Fe}_2\text{O}_4$, when sintered at 1200°C, the samples showed highest value of initial permeability equal to 15234 at 100°C. Similarly, $\text{Mn}_0.6\text{Zn}_0.4\text{Fe}_2\text{O}_4$ was found to have the value of 16183 at 90°C for the samples sintered at 1300°C. The Curie temperature was found to decrease from about 180°C to about 150°C as the sintering temperature increased from 1200°C to 1300°C.

Chikazumi (1964) co-related permeability to saturation magnetization. He suggested [48] that both the permeabilities, due to the domain rotation and that in turn, the domain wall movement, are in one manner or another related to $(\text{Ms})^2$. It is not surprising therefore to find the higher permeabilities in ferrites in the higher saturation Mn-Zn ferrites as compared to the others. Of course, low anisotropy and magnetostriction, are also responsible for the same. Keluskar et al. [49] have found the initial permeability values for Mn-Zn ferrite samples to be more than 25000. Also manganese-zinc ferrites certainly have higher permeabilities at low or medium frequencies. When the frequencies involved are in the upper megahertz range, the permeability drops off due to the higher increase in the losses.

In 1966, Roess, Beer and Schwartz [50, 51] and later on Perduijn and Peloschek, [52] have confirmed the linear dependence of grain size to permeabilities. The relationship between grain size and permeability will generally be linear only if the grain growth is normal, that is if all the grains grow almost at the same rate and same time. This leads to a rather
narrow range of final grain sizes. If, indeed, some grains grew very rapidly, they would trap pores, which can limit the permeability by pinning domain walls. When conditions permit this type of grain growth to occur, with many intragranular pores included, it is called exaggerated or discontinuous grain growth.

Drofenik [53, 54] has reported results that indicate that the distances between the pores account for variations in permeability. Samples with giant grains and included porosity owing to exaggerated grain growth still had higher permeabilities than those with normally grown grains, provided the distances between pores were the same. Drofenik concludes that the large grained samples are less sensitive to grain boundary effects and thus the \( \mu \) versus \( T \) curve is more peaked.

SEM micrographs of two samples prepared by mechano-chemical method are given in Fig.4.13. and Fig.4.14. The morphology of Mn\(_{0.6}\)Zn\(_{0.4}\)Fe\(_2\)O\(_4\) sample (Fig. 4.13.) and that of Mn\(_{0.5}\)Zn\(_{0.5}\)Fe\(_2\)O\(_4\) (Fig. 4.14.) at various temperatures is clearly visible. These ferrite powders have particle size in the range 20-90nm before sintering. However, the particle size increases gradually, as the sample is subjected to heating from 1000\(^\circ\)C upwards. SEM data for samples heated at 1000, 1100 \(^\circ\)C, 1200 \(^\circ\)C and 1300 \(^\circ\)C show normal uniform crystalline growth for almost all the particles visible in the micrographs, with very little aberration. In the present studies, it is observed that the permeability of the samples
increases with the sintering temperature indicating that there is uniform compact growth of the particles.

Fig. 4.12.(a). Variation of magnetic permeability of Mn-Zn ferrite with temperature for sintered (1000°C) samples obtained by mechano-chemical method.

Fig. 4.12.(b). Variation of magnetic permeability of Mn-Zn ferrites with temperature for sintered (1100°C) sample obtained by mechano-chemical method.
Fig. 4.12.(c). Variation of magnetic permeability of Mn-Zn ferrites with temperature for sintered (1200°C) sample obtained by mechano-chemical method.

Fig. 4.12.(d). Variation of magnetic permeability of Mn-Zn ferrites with temperature for sintered (1300°C) sample obtained by mechano-chemical method.
Fig. 4.13. SEM micrographs of $\text{Mn}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$ ferrite (a) unsintered sample, and sintered at (b)1000°C, (c)1100°C, (d)1200°C, (e)1300°C.
Fig. 4.14. SEM micrographs of Mn$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ ferrite (a) unsintered sample, and sintered at (b) 1000°C, (c) 1100°C, (d) 1200°C, (e) 1300°C.
4.4.4. RELATIVE LOSS FACTOR:

Relative loss factor (rlf) is the ratio of tan δ (dissipation factor) to \( \mu_i \) (initial permeability). The relative loss factor versus frequency is graphically represented in Fig.4.15. For most of the samples, the value of relative loss factor rapidly decreases as the frequency is increased. At higher frequencies, the ‘rlf’ touches very low value for samples at different sintering temperatures. For a few samples, the ‘rlf’ value is low at lower frequencies. The ‘rlf’ is found to depend on the composition and the microstructure of the Mn-Zn ferrites which is dependent on the sintering profile of the samples. The ‘rlf’ values obtained in the present investigation were from \( 8 \times 10^2 \) to as low as \( 10^5 \), in the frequency range of 20Hz to 1MHz.
Fig. 4.15. Variation of relative loss factor with log f for various Mn-Zn ferrites sintered at (a) 1000°C and (b) 1200°C, obtained by the mechano-chemical method.
REFERENCES:


