CHAPTER FIVE

ELECTRICAL PROPERTIES

5.1. INTRODUCTION:

Mechanism of charge transport can be understood from the measurement of electrical conductivity, thermo-electric power, Hall coefficient and magneto-resistance. Density and mobility of charge carriers are the key quantities for obtaining inner details of the conductivity. The ferrites in general are semiconductors and have low conductivity as compared to the metals and thus greatly influence their various applications. The principle application of dielectric and the ac electrical properties is the capacitive element in the electronic circuits and as electrical insulators, therefore the knowledge of parameters such as dielectric constant, dielectric loss factor and dielectric strength is highly important for their use.

Most of the high frequency applications related to electric properties are concerned with dielectrics. The advantages of the ferrites, which are ceramic in nature, over the other available dielectric materials are elastic properties, and greater resistance to environmental changes, particularly at higher temperature.

Hall-effect and thermoelectric properties are widely used in interpretation of the conduction mechanism in semiconductors. The
interpretation of Hall-effect is straight forward and it gives precise results. However, in the case of low mobility materials, like the ferrites, it is sometimes difficult to measure the Hall-effect. In such cases, the thermo-electric power measurement is the only alternative. The sign of the thermo-emf gives vital information about the type of conduction in the semiconductors, whether it is p-type or n-type. Another important significance is that it enables one to calculate the value of carrier concentration.

The frequency dependent dielectric behaviour of ferrites created considerable interest among researchers [1-4] to understand many physical and chemical properties of ferrites. Verway [5] attributed high conductivity to the presence of Fe$^{2+}$ and Fe$^{3+}$ ions on equivalent sites (octahedral sites). However Koops [6] proposed that it is largely due to the preparation technique. According to Koops, iron deficiency results in high resistivity, while low resistivity is due to excess of iron.

The temperature dependence of conduction in ferrite is studied by Guillaud and Bertrand [7] and also by Bradburn and Rigby [8]. The effect of small concentrations of manganese on magnesium ferrite is investigated by Van Uitert [3]. Rosenberg et al. [9] have investigated variation of resistance and thermoelectric power with temperature for manganese ferrite and observed ferrimagnetic transition near the Curie temperature.
Maizen [10], amongst many investigators, studied the conduction mechanism on the basis of band picture and hopping model. Band picture takes into account the temperature dependence of conductivity to charge carrier concentration, whereas, hopping model considers that conductivity is because of changes in mobility of charge carriers with temperature.

The dependence of resistivity and activation energy of nickel-zinc ferrite on the sintering temperature and porosity has been studied by Naik and Powar [11]. It was found that there is more densification or less porosity at the higher sintering temperature. The electrical conductivity is also increased when the sintering temperature was high. The observed results were explained on the microstructural changes brought about by sintering conditions.

5.2. RESISTIVITY:

Ferrites are semi conductors in nature having a wide range of resistivity from $10^{-3}$ to $10^{11}$ ohm cm at room temperature [3]. These low and high resistivities of ferrites are explained on the basis of location of cations in the spinel structure and also the hopping mechanism. High conductivity in the ferrite is found to be due to the presence of ferrous and ferric ions in the crystallographically equivalent sites (octahedral sites). Both Fe$^{2+}$ and Fe$^{3+}$ ions are at B-site and conduction takes place when electrons move from Fe$^{2+}$ to Fe$^{3+}$ ions. The high resistivity in ferrites is attributed to the occupation of B-sites by other divalent metal ions and trivalent iron ions.
The resistivity of the ferrites is sensitive to temperature. The
diffusion of charge carriers from one state to the other state takes place
only when the charge carriers acquire the activation energy. The thermal
lattice vibrations consistently give rise to phonons, and electrons hop
between the pairs of states either by absorption or by emission of phonons.
In this way transport of charge carriers is achieved by the hopping process
through an interaction with phonons. On the basis of this, the temperature
dependence of resistivity of ferrites is given by the relation.
\[ \rho = \rho_0 \exp\left( -\frac{\Delta E}{kT} \right) \]
\[ \quad \text{5.1.} \]
Where, \( \rho_0 \) is temperature dependent constant, \( \Delta E \) is the activation
energy, \( k \) is Boltzmann constant and \( T \) is absolute temperature.

Unlike in the semiconductors, wherein the charge carriers occupy
states in wide energy band, the charge carriers in the ferrites, are localized
at the magnetic atoms. In the ferrites, the cations are surrounded by close
packed oxygen anions and can be treated as isolated from each other.
There will be little direct overlap of the anion charge clouds or orbitals.
Alternatively, the electrons associated with particular ion will largely
remain isolated and hence a localized electron model is more appropriate
in the case of ferrites rather than the collective electron (band) model.

These factors that differentiate the electrical behavior of ferrites
from that of the semiconductors, lead to the hopping model of electrons
[12, 13]. Conduction is due to exchange of the 3d electrons, localized at
the metal ions, from Fe\(^{3+} \) to Fe\(^{2+} \) [14]. Assuming that all the Fe\(^{2+} \) in the B
sites participates in the hopping transport, the number of charge carriers works out to be of the order of $10^{22}$ cm$^{-3}$. Since the mobility is very low, the conductivity is also low, even though the charge carriers may be high. Many models have been suggested to account for the electrical properties like the hopping electron model, the small polaron model and the phonon induced tunneling.

The mechanism of transport phenomena in ferrites mainly follows the two following routes for conductivity [15].

$$\begin{align*}
\text{Fe}^{2+} + \text{Fe}^{3+} & \leftrightarrow \text{Fe}^{3+} + \text{Fe}^{2+} + \Delta E \\
\text{Me}^{2+} + \text{Fe}^{3+} & \leftrightarrow \text{Me}^{3+} + \text{Fe}^{2+} + \Delta E
\end{align*}$$

where ‘$\Delta E$’ is the activation energy, required for transfer of electron from Fe$^{2+}$ to Fe$^{3+}$ or Me$^{2+}$ to Fe$^{3+}$ and vice versa. The valence states of two ions get interchanged. Under the influence of an electric field, these extra electrons are responsible for the generation of current by the jumping or the hopping process [16].

The free electron model cannot explain the electrical conductivity of ferrites because of the fact that the electrons in ferrites are not free and energy band model is not suitable to explain the electrical conductivity for the lack of Bloch type wave functions for electrons in ferrites. The conductivity of ferrites can be, however, explained in terms of electronic charge carriers, like electrons and holes, by the relation

$$\sigma = e \left[ n_e \mu_e + n_h \mu_h \right]$$

where $\sigma$ is the electrical conductivity, $n_e$ and $n_h$ are the concentrations of electrons and holes, respectively, and $\mu_e$ and $\mu_h$ are the mobilities of electrons and holes, respectively.
where, \( n \) and \( \mu \) are the concentration and mobility of electrons (e) and holes (h), respectively.

In ferrite lattice, the electrostatic interaction between electron and the neighboring ions results into the polarization field called polaron. When such an association is weak, it constitutes a large polaron. Such polarons are found in ionic crystals.

When electron plus lattice deformation have a linear dimension smaller than the lattice constant, they constitutes small polarons. Such polarons are found in covalent crystals.

Using mechanism of hopping of polarons, the electrical resistivity, the change in activation energy at Curie temperature and the relation of activation energies with composition have been successfully employed to explain the electrical properties of ferrites [17, 18]. These polarons have low activation energy in magnetic region, while high activation energy in non-magnetic regions.

In the electrostatic interaction between conduction electron or a hole and the nearby ions may result in a displacement of the latter and hence lead to the polarization of the surrounding region. So the carrier gets situated at the centre of the polarization potential well. If this well is deep enough, a carrier may be trapped at a lattice site and its transition to a neighboring site may be determined by thermal activation. If this
activation is sufficient, the conduction can take place by the hopping of electrons, from one lattice to another.

In ferrites, having spinel structure, the B-B distances are smaller than A-A and A-B distances. Even then, the B-B distance is much larger than the sum of the ionic radii of the cations involved, indicating a little or no overlap between d-d wave functions of the ions on adjacent octahedral sites. This gives rise to a situation in which electrons are not free to move through the crystal but remain fixed on B-sites, necessitating a hopping process. However, in the ferrite samples, conductivity is decided mainly by the availability of a pair of cations [19] that facilitate hopping.

5.2.1. MODELS FOR THE ELECTRICAL PROPERTIES:

Various models are proposed by many research workers after investigating the electrical properties of the ferrites under various conditions. Some of these models are discussed in brief in this section.

5.2.1.1. HOPPING ELECTRON MODEL:

Jonker [20] has observed that in cobalt ferrites the transport properties differ considerably from those of normal semiconductors, as the charge carriers are not free to move through the crystal lattice but jump from one ion to the other ion. It was further observed that in this type of materials the possibility of a change in the valency of a considerable fraction of metal ions and especially in that of Fe ions.
Assuming the number of electrons contributing to the conductance to be equal to the number of Fe$^{2+}$ ions and the number of electron holes to be equal to the number of Co$^{3+}$ ions, Jonker has calculated (from resistivity data) extremely low values of mobilities for electrons and holes, and showed a fairly strong exponential dependence of resistivity on temperature. The temperature dependence of conductivity arises only due to mobility and not due to the number of charge carriers in the sample.

5.2.1.2. SMALL POLARON MODEL:

A small polaron is a defect created when an electron carrier becomes trapped at a given site as a consequence of the displacement of adjacent atoms or ions. The entire defect (carrier as well as distortion) then migrates by an activated hopping mechanism. Small polaron formation can take place in materials whose conduction electrons belong to incomplete inner (d or f) shells, which due to small electron overlap tend to form extremely narrow bands. The possibility for the occurrence of hopping conductivity in certain low mobility semiconductors, especially oxides, has been widely recognized for some time, and extensive theoretical discussion which considers the small polaron model and its consequences has been reported [21-26].

The migration of small polaron requires the hopping of both the electron and the polarized atomic configuration from one site to its adjacent site [27]. The small polaron model also explains the low value of
mobility, temperature independent, Seebeck coefficient and thermally activated hopping. In addition to these properties, if the hopping electron becomes localized by virtue of its interaction with phonons, then a small polaron is formed and the electrical conduction occurs due to the hopping motion of small polarons.

5.2.1.3. PHONON INDUCED TUNNELING:

Srinivasan and Srivastava [27] have explained electrical properties of ferrites on the basis of tunneling of electrons amongst Fe$^{2+}$ and Fe$^{3+}$ atoms on B sites. It has been assumed that the electrons, which take part in the Fe$^{2+}$ $\leftrightarrow$ Fe$^{3+}$ + e$^{-}$ exchange process, are strongly coupled to the lattice and tunnel from one site to the other due to a phonon-induced transfer mechanism.

5.3. THERMO-ELECTRIC POWER:

In the case of low mobility semiconductor materials like ferrites, the thermo-electric power measurement is used to determine the type of conduction mechanism responsible for the conduction. It is the sign of the thermoe-mf which gives the information about whether it is p-type or n-type [28].

Zinc ferrite and lithium ferrite are found to be n-type semiconductors. Murthy et al. [29] have investigated the dc conductivity
and Seebeck coefficient of some nickel-zinc ferrite as a function of temperature from room temperature to 300\(^\circ\)C. The ferrites with excess iron show n-type semiconduction and those with iron deficiency show p-type semiconduction. Gabelle et al. [30] has measured the electrical conductivity and Seebeck effect of nickel ferrite as a function of temperature. Fayek et al. [31] have studied thermo-electric power of Zn substituted Cu-Ga ferrite and has shown that there are two types of conduction mechanism mainly due to Cu\(^{2+}\)-Cu\(^{2+}\) and Fe\(^{3+}\)-O\(^{-2}\)-Fe\(^{3+}\) interaction. At lower concentration of Zn it shows p-type behaviour as Cu\(^{2+}\)-Cu\(^{2+}\) interaction dominate, while at higher concentration of Zn it is n-type as Fe\(^{3+}\)-O\(^{-2}\)-Fe\(^{3+}\) interaction dominates. Sattar et al. [32] have shown that in Mn substituted Ni-Zn ferrite; it is n-type conductor with polaron hopping mechanism.

There are two known methods to measure the thermo-electric power [33]. They are as follows:

a) **Integral method:** In this method one end of the sample is kept at the fixed temperature ‘\(T_1\)’, while at the other end the temperature ‘\(T_2\)’ is made to vary through the desired temperature range. Thermo-electric voltage ‘\(V\)’, developed across the sample is measured as a function of the temperature.

\[
V(T) = \int_{T_1}^{T_2} QdT
\]  

b) **Differential method:** In this method, a small temperature difference ‘\(\Delta T\)’ is established across the sample to induce a small
thermoelectric voltage \( \Delta V \). The Seebeck Coefficient is then determined by an equation

\[
Q(T) = \lim_{\Delta T \to 0} \frac{\Delta V(T)}{\Delta T}
\]

5.6.

The accuracy of this method depends on \( \Delta T \) being sufficiently small at which \( Q(T) \) changes in the temperature interval \( \Delta T \). On the other hand \( \Delta T \) should be large enough to generate a voltage that can be detected to the desired precision.

5.4. DIELECTRIC CONSTANT:

Ferrites have wide range of applications from microwave to radio frequencies. With rapid expansion in the field of solid-state electronics it is important to study their behaviour at different frequencies [6, 34]. Ferrites show high dielectric constant and the dispersion of dielectric constant in the frequency range from 20Hz to 1GHz. Ferrites have low conductivity, which is one of the important considerations for microwave applications. The order of the magnitude of conductivity greatly influences the dielectric and magnetic behaviour of ferrites this has aroused considerable interest in the electrical conductivity and the frequency dependent dielectric behaviour of ferrites [35, 36].

The dielectric properties of ferrites are sensitive to method of preparation [36], chemical composition and the substitution [37], porosity and grain size [38]. Krammer [39] has explained the relation between grain size and dielectric constant. The polycrystalline ferrites have very high
dielectric constants of the order of several thousands at low frequencies, falling to very low values at microwave frequencies. The very low conductivity of these materials makes them useful for microwave applications. Several research workers have studied the frequency dependence of the dielectric behaviour of ferrite [40, 41].

Koops [6] suggested a theory in which relatively good conducting grains and insulating grain boundary layers of ferrite material can be understood as given by inhomogeneous dielectric structure, as discussed by Maxwell [42] and Wagner [43]. Since an assembly of space requires finite time to line up their axes parallel to an alternating electric field, the dielectric constant naturally decreases, if the frequency of the field reversal increases. Iwachi [44, 45] studied the low frequency dielectric behaviour of Fe$_3$O$_4$, Mn and Mn-Zn ferrites in powder form and attributed this behaviour to Maxwell Wagner polarization arising from the heterogeneity in oxidation. He pointed out that the powder samples of oxides prepared by calcination at high temperature may have conducting and nonconducting layers similar to the sintered oxides, because a considerable amount of sintering takes place in these samples.

The dielectric material reacts to an electric field differently from free space because it contains charge carriers that can be displaced. For an alternating field the time required for polarization show a phase retardation of the charging current instead of 90° further.
It is advanced by some angle $90-\delta$ where $\delta$ is the loss angle, which gives,

$$\tan \delta = \frac{K''}{K} = \frac{\varepsilon''}{\varepsilon'}$$

where $K$'s represent dielectric constants and $\varepsilon$'s the permittivities. The loss factor $\tan \delta$ is the primary criterion for usefulness of dielectric as an insulating material.

The frequency dependence can be explained with the help of Maxwell–Wagner two-layer Model or the heterogeneous model of the polycrystalline structure of ferrites given by Koops (1951). According to this theory, in a dielectric structure two layers are formed: the first layer consists of ferrite grains of fairly well conducting (ferrous) ions, which is separated from the second layer a thin layer of poorly conducting substances, which forms the grain boundary. These grain boundaries are more active at lower frequencies. Hence the hopping frequency of electron between Fe$^{2+}$ and Fe$^{3+}$ ion is less at lower frequencies. As the frequency of the applied field increases, the conductive grains become more active by promoting the hopping of electron between Fe$^{2+}$ and Fe$^{3+}$ ions, thereby increasing the hopping rate (frequency). Thus, a gradual increase in conductivity with applied field frequency is observed. But at higher frequencies the rate of hopping between the ions can not follow the applied field frequency and it lags behind. This causes a dip in conductivity at higher frequencies.
5.5. EXPERIMENTAL MEASUREMENT:

The samples were subjected to various tests to assess their potential applications. The tests were carried out to investigate the electrical properties such as resistivity, thermo-electric power and the dielectric constant.

5.5.1. RESISTIVITY:

Sample preparation:

Powdered samples of Mn$_2$Zn$_{1-x}$Fe$_2$O$_4$, synthesized by the mechano-chemical and the wet chemical methods, were pressed into pellets of the size 1.0 cm in diameter and of thickness between 2-3 mm under 75KN pressure applied for about 5 minutes. Four sets of pellets were sintered in nitrogen atmosphere at temperatures: 1000$^\circ$C, 1100$^\circ$C, 1200$^\circ$C and 1300$^\circ$C, respectively, for 4 hours separately in a programmable Carbolite furnace with a heating and cooling rate of 5$^\circ$C min$^{-1}$. The pellets were silver pasted on either side for establishing good ohmic contacts with the electrodes.

Measurement:

The dc resistivity measurements on these samples were then carried out using standard two-probe method.
5.5.2. THERMO-ELECTRIC POWER:

Sample preparation:

Powdered samples of \( \text{Mn}_x\text{Zn}_{(1-x)}\text{Fe}_2\text{O}_4 \) prepared by mechanochemical and wet chemical methods were pressed into pellets of the size 1.0 cm in diameter and of thickness between 2-3mm under 75KN pressure applied for about 5 minutes. The pellets were silver pasted on either side for establishing good ohmic contacts with the electrodes.

Measurement:

The thermo-emf measurements of these samples were carried out from room temperature to 500\(^\circ\)C by maintaining a temperature difference between the two ends - hot and cold junction - of electrodes by 10\(^\circ\)C.

5.5.3. DIELECTRIC CONSTANT:

Sample preparation:

Powdered samples of \( \text{Mn}_x\text{Zn}_{(1-x)}\text{Fe}_2\text{O}_4 \) synthesized by mechanochemical and wet chemical methods were pressed into pellets of the size 1.0 cm in diameter and of thickness 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\(^\circ\)C, 1100\(^\circ\)C, 1200\(^\circ\)C and 1300\(^\circ\)C, respectively, for 4 hours separately in a programmable Carbolite furnace with a heating and cooling rate of 5\(^\circ\)C min\(^{-1}\). The pellets were
silver pasted on either side for establishing good ohmic contacts with the electrodes.

Measurement:

The dielectric measurements were carried out from room temperature to 550°C, with the variation of frequencies from 20Hz to 1MHz using Wayne Kerr precision LCR meter. The capacitance C was measured and the dielectric constant was calculated using the relation

\[ \varepsilon' = \frac{ct}{\varepsilon_0 A} \]

where 't' is the thickness of pellet, 'A' is Area of cross section of the pellet, '\varepsilon_0' is the permittivity of free space.

5.6. RESULTS AND DISCUSSION:

The results obtained in the study of the resistivity, thermo-electric power and dielectric constant of the Mn-Zn ferrite samples, are tabulated and discussed in the following Sections.

5.6.1. RESISTIVITY:

Ferrite samples prepared by mechano-chemical method:

Variation of dc resistivity (logp) with different sintering temperatures (1000/ T) K for Mn_xZn_{(1-x)}Fe_2O_4 ferrite samples (with different compositions) prepared by the mechano-chemical method, is illustrated in the Fig.5.1 (a, b, c and d). It was observed that the dc resistivity decreases with increasing temperature indicating the semiconducting nature of the samples. This was due to the increase in drift
mobility of the charge carriers. Although the resistivity depends on the concentration of the Mn in the ferrite samples, in present study it was observed that it strongly depend on the sintering temperature. Resistivity values at 310K were varying between $5.721 \times 10^7$ ohm-cm and $9.365 \times 10^7$ ohm-cm for unsintered samples. The lowest was observed for Mn$_{0.7}$Zn$_{0.3}$Fe$_2$O$_4$ and the highest value was obtained for Mn$_{0.4}$Zn$_{0.6}$Fe$_2$O$_4$. These values of resistivity were found to be higher than that for bulk material [46]. This was because, in the case of nano material, microstructure with smaller grain contains a greater number of grain boundaries. The grain boundaries are the region of mismatch between the energy states of the adjacent grains and hence act as a barrier to the flow of electrons. The higher resistivity observed in this method thus may be attributed to the smaller grain size. The smaller grain size is also advantageous from the point of view of reducing Fe$^{2+}$ ions as oxygen advances faster in smaller grains thus keeping iron in the Fe$^{3+}$ state [47].

For the samples sintered at 1000$^\circ$C, the resistivity at 310K was found to vary between $3.962 \times 10^6$ ohm-cm and $3.526 \times 10^7$ ohm-cm with the value being highest for Mn$_{0.6}$Zn$_{0.4}$Fe$_2$O$_4$ sample. The values of resistivity for samples sintered at 1200$^\circ$C were found in the range between $1.194 \times 10^6$ ohm-cm and $7.850 \times 10^6$ ohm-cm. While the resistivity values obtained for samples sintered at 1300$^\circ$C at 310K were having the lowest value of $6.615 \times 10^5$ ohm-cm for Mn$_{0.7}$Zn$_{0.3}$Fe$_2$O$_4$ and the highest value being $4.481 \times 10^6$ ohm-cm for Mn$_{0.4}$Zn$_{0.6}$Fe$_2$O$_4$. 

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Many models have been suggested to account for the electrical properties and conduction mechanism in ferrites by various investigators, which have been reviewed by Klinger et al. [48]. However, the thermally activated hopping model is found to be the one, which can qualitatively and appropriately explain the electrical properties and behavior of Mn–Zn ferrite. In the hopping process the additional electron on a Fe$^{2+}$ ion requires lesser energy to move to an adjacent Fe$^{3+}$ ion on the equivalent octahedral lattice sites (B sites).

When external electric field is applied, these extra electrons hopping between Fe ions are responsible for the electrical conduction. Therefore, any change in the Fe$^{2+}$ ion content in the spinel ferrite lattice as also the distance between them is important for the intrinsic resistivity of Mn-Zn ferrite grains, including the intrinsic grain boundaries. If the introduction of another cation into the lattice causes a change in the valency distribution on the B sites, then the number of electrons potentially available for the transfer will be altered. On the other hand, the addition of foreign ions (impurity) can also change the distance between the B lattice sites; this is crucial for the conduction mechanism.

Thus, the formation of an intrinsic grain boundary in doped samples by the segregation of aliovalent ions must increase the resistivity. This gives rise to polycrystalline Mn-Zn ferrite with non ferrimagnetic grain boundary, ferrimagnetic outer grain region and ferrimagnetic conductive core. Thus the contribution to the bulk resistivity may be
considered as resistivity contribution coming from three different regions [49]. In order to establish a relation between the power loss due to eddy currents and the average grain diameter, a hypothetical brick wall model is applied. As per this model each layer can be represented by a resistance — capacitance (R-C) lumped circuit of high ohmic layers. When the resistivity of the bulk is much lower than the grain boundary layers, the equivalent circuit of the ferrite can be represented by a series of lumped R-C circuits of the grain boundary layers.

As the samples in the present study were sintered from nanosized Mn-Zn ferrite particles in nitrogen atmosphere (reducing) without any additives, there was no possibility of formation of high resistivity ferrimagnetic outer grain boundary. Thus the resistivity will exclusively depend on the contribution from the non-ferrimagnetic grain boundaries and ferrimagnetic conductive core. It can be seen from SEM micrographs in Fig.5.2 (a, b, c and d) and 5.3 (a, b, c and d) that the samples sintered at 1000°C show small grain sizes with large non ferrimagnetic grain boundaries. Higher total surface area of the sample, which further increases due to the formation of fine (small) crystals, results in the high resistivity for the samples. With the increase in the sintering temperature for the samples, viz. 1100°C, 1200°C and 1300°C, the grain size increases without forming perfect crystals. This leads to low surface area and lower resistivity non-ferrimagnetic grain boundaries which accounts for the low value of resistivity at 310K for the samples sintered at these increasing temperatures.
Many researchers [50, 51] have observed that the increase in electrical conductivity as a function of sintering temperature and time results in higher density and grain growth. As a result, porosity correspondingly decreases and so does the number of grain boundaries. This is due to an increase in grain size. Therefore, it is concluded that sintering temperature and time play dominant role in deciding the electrical conductivity and microstructure of the particular ferrite.

Fig. 5.1.(a). Variation of resistivity (log\(p\)) with \(1000/T\) (K) for different unsintered Mn-Zn ferrite samples obtained by the mechano-chemical method.
Fig. 5.1.(b). Variation of resistivity (log$\rho$) with $1000/T$ (K) for different sintered Mn-Zn ferrite (1000°C) samples obtained by the mechano-chemical method.

Fig.5.1.(c). Variation of resistivity (log$\rho$) with $1000/T$ (K) for different sintered Mn–Zn ferrite (1200°C) samples obtained by the mechano-chemical method.
Fig. 5.1. (d). Variation of resistivity (logp) with 1000/T (K) for different sintered Mn-Zn ferrite (1300°C) samples, obtained by the mechano-chemical method.

Fig. 5.2. SEM micrographs of Mn$_{0.6}$Zn$_{0.4}$Fe$_2$O$_4$ ferrite (a) unsintered sample, and sintered, at (b)1000°C, (c)1100°C, (d)1200°C, (e) 1300°C by the mechano-chemical method.
Fig. 5.3. 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 by the mechano-chemical method.
Ferrite samples prepared by wet chemical method:

Similar variation of dc resistivity (logρ) with sintering temperatures (1000/T K) was noticed in the case of samples prepared by the wet chemical method. Fig.5.4 (a, b and c) illustrate these changes for samples with different Mn content. These samples also exhibit semiconducting nature as their dc resistivity decreases with increasing temperature. This phenomenon occurs due to an increase in the drift mobility of the charge carriers. In these samples the resistivity also is found to be strongly dependent on the sintering temperatures. Resistivity values at 310K are seen to vary between $7.281 \times 10^7$ ohm-cm and $2.176 \times 10^8$ ohm-cm for unsintered samples. The lowest for Mn$_{0.8}$Zn$_{0.2}$Fe$_2$O$_4$ and the highest value is seen for Mn$_{0.4}$Zn$_{0.6}$Fe$_2$O$_4$. These values of resistivity were found to be marginally higher than those samples obtained from the mechano-chemical method. The higher values of dc resistivity may be attributed to the stoichiometric compositions, better crystal structure and the improved nanostructure due to atomic level mixing in the aqueous medium in this wet chemical method.

For the samples sintered at $1200^\circ C$ the resistivity at 310K was found to vary between $4.380 \times 10^6$ ohm-cm and $9.841 \times 10^6$ ohm-cm with the highest being for the Mn$_{0.6}$Zn$_{0.4}$Fe$_2$O$_4$ sample. The values of resistivity for samples sintered at $1300^\circ C$ at 310K were found in the range- $9.179 \times 10^5$ ohm-cm as the lowest for Mn$_{0.7}$Zn$_{0.3}$Fe$_2$O$_4$ and $3.418 \times 10^6$ ohm-cm as the highest value, for Mn$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$. 

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Fig. 5.4. Variation of resistivity (log ρ) with $1000/T$ (K) for various Mn-Zn ferrite (a) unsintered samples, and sintered, at (b) 1200°C and (c) 1300°C samples obtained by the wet chemical method.
Fig. 5.5. 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 obtain by the wet chemical method.
The resistivity values obtained in the present studies for both the methods of preparation, namely mechano-chemical and wet chemical method, were higher compared to the resistivity values of $10^5$ ohm-cm reported [52, 53] in the surveyed literature.

The higher resistivity values seen for the samples obtained by the mechano-chemical method as well as those prepared by the wet chemical method amply confirm that both these methods yield Mn-Zn ferrite having grain size in the nanometer range. This observation is in conformity with the particle size calculated from the XRD data (3.5.9, Table 3.9) and with the conclusion drawn from the other experimental results (3.5.7, Fig.3.7).

5.6.2. THERMO-ELECTRIC POWER:

Ferrite samples prepared by mechano-chemical method:

The variation of Seebeck coefficient ($Q$) with temperature (K) for the $\text{Mn}_{(x)}\text{Zn}_{(1-x)}\text{Fe}_2\text{O}_4$ (where $x = 0.40, 0.50, 0.60, 0.80$) unsintered samples prepared by the mechano-chemical method is shown in Fig.5.6. (a, b, c and d).

It can be seen from the figures that all the samples prepared by this method show a negative value of Seebeck coefficient ($Q$), indicating that the electrons were the majority charge carriers. Thus all the samples show n-type semiconductor behaviour. The mechanism of conduction in all these samples is predominantly due to the hopping of electrons from
Fe\(^{2+}\) to Fe\(^{3+}\) ions. It is also evident from the figures that the value of Seebeck coefficient increases with increasing Mn content in the samples. Among all the samples prepared by the mechano-chemical method, Mn\(_{0.4}\)Zn\(_{0.6}\)Fe\(_2\)O\(_4\) sample show lower (numerical) Q value of -186 uV/K while Mn\(_{0.8}\)Zn\(_{0.2}\)Fe\(_2\)O\(_4\) has the highest (numerical) Q value of -452 uV/K.
Fig. 5.6. Variation of Seebeck coefficient with Temperature (K) for various Mn-Zn ferrite unsintered samples obtained by the mechano-chemical method.
Ferrite samples prepared by wet chemical method:

Similarly, the variation of Seebeck coefficient \( Q \) with temperature \( K \) for \( \text{Mn}^{(x)}\text{Zn}^{(1-x)}\text{Fe}_2\text{O}_4 \) unsintered samples, with various compositions, prepared by wet chemical method is shown in Fig. 5.7. (a, b, c, d).

It can be seen from the figures that, like the samples prepared by the mechano-chemical method, all the samples prepared by the wet chemical method also show an identical trend of a negative value of Seebeck coefficient \( Q \), indicating that the electrons are the majority charge carriers. In other words, all the samples show n-type semiconductor behaviour. The mechanism of conduction in all these samples is also predominantly due to the hopping of electrons from \( \text{Fe}^{2+} \) to \( \text{Fe}^{3+} \) ions. It is also evident from the graphs that the values of Seebeck coefficient increases with decreasing zinc concentration.

However, the samples prepared by the wet chemical method were found to show overall higher values of Seebeck coefficient as compared to the mechano-chemical method. The lowest (numerical) value was seen in case of \( \text{Mn}_{0.4}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4 \) which is \(-285 \ \text{uV/k}\) and the highest (numerical) was for \( \text{Mn}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4 \) equal to \(-782 \ \text{uV/k}\).
(a) Graph showing the relationship between temperature in K and $\sigma_{\text{inum}} \times 10^2$, with data points for $0.4 \text{Mn}$.

(b) Graph showing the relationship between temperature in K and $\sigma_{\text{inum}} \times 10^2$, with data points for $0.5 \text{Mn}$.
Fig. 5.7. Variation of Seebeck coefficient with Temperature (K) for various Mn-Zn ferrite unsintered samples obtained by the wet chemical method.

While investigating the thermo-electric power of Mn-Zn ferrite with various compositions of Mn (0.2, 0.4, 0.6, 0.8 and 1.0), Ravinder and Latha [54] observed that except for the composition of 0.8 in Mn-Zn ferrite, all other compositions showed n-type of behaviour, where as,
sample with Mn composition of 0.8, indicated p-type behaviour. However all the Mn-Zn ferrite samples prepared by both the methods discussed in the present study showed n-type behaviour for all the compositions of Mn (0.4, 0.6, 0.7 and 0.8).

Ravinder et al. [55-57], further in their studies on substituted Mn-Zn ferrite with cerium, erbium and gadolium also observed that in all these substituted Mn-Zn ferrites the conduction is due to the electrons. These substituted ferrites show n-type of semiconductor behaviour.

**5.6.3 DIELECTRIC CONSTANT:**

Results of variation of dielectric constant, with the frequency and the temperature, are given in this section.

**5.6.3.1 FREQUENCY DEPENDENCE OF DIELECTRIC CONSTANT:**

**Ferrite samples prepared by mechano-chemical method:**

The capacitance values were recorded at various frequencies for the ferrite samples prepared by the mechano-chemical method. The variation of dielectric constant with the frequency for $\text{Mn}_{(x)}\text{Zn}_{(1-x)}\text{Fe}_2\text{O}_4$ samples is shown in Fig.5.8. (a), (b) and (c).
It can be seen from the figures that the value of the dielectric constant decreases with increasing frequencies and that a very low value is shown at higher frequencies for all the unsintered as well as sintered samples at different sintering temperatures. This can be explained on the basis of space charge polarization model of Maxwell [42] Wagner [43], and the Koop's phenomenological theory [6]. The decrease of dielectric constant at higher frequency can be explained on this basis, by assuming that the solid is composed of well conducting grains separated by poorly conducting grain boundaries. The electrons reach the grain boundary by hopping and if the resistance of the grain boundary is high enough, electrons pile up at the grain boundaries and produce polarization. However, as the frequency of the applied field is increased beyond a certain value, the electrons cannot follow the alternating field. This decreases the possibility of further electrons reaching the grain boundary and as a result the polarization decrease [6, 42].

The decrease of dielectric constant with increase in frequency as observed in the case of mixed ferrites is a normal dielectric behavior. This normal dielectric behavior was also observed by several other investigators [58, 59]. Reddy et al. have studied the variation of dielectric constant with frequency for ferrites [60]. They have explained the behavior qualitatively as due to the fact that the electron exchange between Fe$^{3+}$ and Fe$^{2+}$ ions cannot follow the frequency of the externally applied alternating field beyond a certain limit. The large decrease in dielectric constant validates the two-layer model assumption [61]. The large values of dielectric
constant at lower frequencies have been attributed to the predominance of the species like Fe$^{2+}$ ions, interfacial dislocation pile ups, oxygen vacancies, grain boundary defects etc.

The values of dielectric constant at 310K and 20Hz frequency were seen to vary between $8.3587 \times 10^3$ and $1.6803 \times 10^4$ for unsintered samples. The lowest was observed for Mn$_{0.8}$Zn$_{0.2}$Fe$_2$O$_4$ and the highest value for Mn$_{0.4}$Zn$_{0.6}$Fe$_2$O$_4$ respectively.

The dielectric constant for all the unsintered samples is lower than the corresponding bulk value at room temperature. Latha et al. [62] have reported a dielectric constant of $(17-32) \times 10^5$ at 308K measured at a frequency of 5 kHz for Mn–Zn ferrite in bulk form synthesized by ceramic method. This low value of dielectric constant may be attributed to homogeneity, better symmetry, uniform smaller grains. Smaller grains contain large surface boundaries and are the regions of high resistance. This reduces the interfacial polarization and hence the dielectric constant was found to be lesser than that reported for the bulk materials.

For the samples sintered at 1100°C, the values vary between $7.4730 \times 10^4$ and $1.3472 \times 10^6$, the lowest and the highest were for Mn$_{0.8}$Zn$_{0.2}$Fe$_2$O$_4$ and Mn$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ respectively. It can be seen that samples sintered at 1300°C have higher values of dielectric constant. The highest value $1.9268 \times 10^7$ was obtained for Mn$_{0.4}$Zn$_{0.6}$Fe$_2$O$_4$ sample (at ambient temperature) for 20Hz frequency which is comparable to the
reported values. In the case of samples sintered at 1300°C, the lowest value of dielectric constant was 6.8240×10^5 for Mn_{0.8}Zn_{0.2}Fe_{2}O_{4} sample.

Some investigators [47, 63] have reported that there is a strong correlation between the conduction mechanism and the dielectric behavior of the ferrites, with the conjecture that the mechanism of the polarization process in ferrites is similar to that of the conduction process. They observed that the electronic exchange between Fe^{2+} ↔ Fe^{3+} results in local displacement that determine the polarization behavior of the ferrites. The dependence of the dispersion of dielectric constant on composition can be explained on the basis of the available ferrous ions on octahedral sites [64]. As the frequency of the externally applied electric field increases gradually, and though the same number of ferrous ions are present in the ferrite material, the dielectric constant decreases. This reduction occurs because, beyond a certain value of frequency of the externally applied field, the electronic exchange between ferrous and ferric ions cannot follow the alternating field, since the field changes are too fast. The variation of dispersion with composition can also be explained on the same basis.
Fig. 5.8. Variation of dielectric constant with Log f for various Mn-Zn ferrites (a) unsintered samples, and sintered, at (b) 1100°C and, (c) 1300°C samples prepared by the mechano-chemical method.
Ferrite samples prepared by wet chemical method:

As in the case of the samples prepared by the mechano-chemical method, the variation of dielectric constant with frequency for Mn\(_{x}\)Zn\(_{1-x}\)Fe\(_2\)O\(_4\) samples prepared by the wet chemical method can be seen in Fig. 5.9. (a), (b) and (c).

The value of the dielectric constant decreases with increase in frequency as in the case of samples prepared by mechano-chemical method. These samples were also found to have very low values at higher frequencies for all the unsintered as well as sintered samples.

The dielectric constant values at 310K and 20Hz frequency were in the range of 1.0811\(\times\)10\(^3\) and 3.2613\(\times\)10\(^3\) for unsintered samples. The observed lowest was for Mn\(_{0.5}\)Zn\(_{0.5}\)Fe\(_2\)O\(_4\) and the highest for Mn\(_{0.4}\)Zn\(_{0.6}\)Fe\(_2\)O\(_4\) samples. For the samples sintered at 1100\(^\circ\)C the values vary between 5.4980\(\times\)10\(^3\) and 1.5942\(\times\)10\(^4\) for Mn\(_{0.6}\)Zn\(_{0.4}\)Fe\(_2\)O\(_4\) and Mn\(_{0.4}\)Zn\(_{0.6}\)Fe\(_2\)O\(_4\), respectively. Samples sintered at 1300\(^\circ\)C, have the dielectric constant value in the range 7.5735\(\times\)10\(^5\) and 1.8704\(\times\)10\(^6\) measured at room temperature at 20Hz frequency. The highest was for the Mn\(_{0.4}\)Zn\(_{0.6}\)Fe\(_2\)O\(_4\) sample.

The dielectric constant values for wet chemical method were found to be on the lower side in comparison with the samples prepared by the mechano-chemical method. These low values of dielectric constant may be attributed to the homogeneity, better symmetry and the uniform smaller grains in the case of samples prepared by wet chemical method.
Fig. 5.9. Variation of dielectric constant with Log $f$ for various Mn-Zn ferrites (a) unsintered samples, and sintered, at (b) 1100°C and, (c) 1300°C samples prepared by the wet chemical method.
5.6.3.2 TEMPERATURE DEPENDENCE OF DIELECTRIC CONSTANT:

Ferrite samples prepared by mechano-chemical method:

In the case of ferrites, the dielectric constant is found to be directly proportional to the temperature up to a certain value. There are several reports [65-67] wherein the variation of dielectric constant of ferrites with temperature has been studied. In the present study, the dielectric constant values were recorded as a function of temperature at a fixed frequency of 20Hz. The results obtained for the Mn$_x$Zn$_{(1-x)}$Fe$_2$O$_4$ samples prepared by the mechano-chemical method are illustrated in Fig.5.10 (a), (b) and (c).

It can be seen from these figures that for all the samples dielectric constant ($e'$) increase with increasing temperature. Initially at lower temperature, the ($e'$) increases gradually as the thermal energy supplied to the samples is not sufficient to free the localized dipoles. When a certain temperature is reached, the thermal energy liberates more localized dipoles, and the field accompanying the applied frequency tries to align them in its direction. Thus, there is a sharp increase in the dielectric constant, reaching a peak. The temperature at which the dielectric constant is maximum (peak) is called the transition temperature. Beyond the transition temperature, the thermal energy added to the system overcomes the field effect and decreases the internal viscosity of the system giving rise to more degrees of freedom to the dipoles, and increasing the entropy (degree of randomness) of the system, thus resulting in the decrease in the
The dielectric constant values observed for the unsintered samples up to 550°C were in the range $5.0829 \times 10^5$ (for Mn$_{0.4}$Zn$_{0.6}$Fe$_2$O$_4$) to $1.4867 \times 10^7$ (for Mn$_{0.7}$Zn$_{0.3}$Fe$_2$O$_4$). The dielectric constant values for the samples sintered at 1100°C and 1300°C were in the range $1.36 \times 10^6$ - $4.4026 \times 10^8$ and $2.8613 \times 10^7$ - $4.5073 \times 10^9$ respectively. With the instrument employed for the measurements of the capacitance as a function of temperature, it was possible to obtain the transition temperature of only Mn$_{0.8}$Zn$_{0.2}$Fe$_2$O$_4$ ferrite sample sintered at 1300°C. The transition temperature of this sample was found to be 535°C.
Fig. 5.10. Variation of dielectric constant with temperature for various Mn-Zn ferrite (a) unsintered samples, sintered, at (b) 1100°C and (c) 1300°C obtained by the mechano-chemical method.
Ferrite samples prepared by wet chemical method:

The variation of dielectric constant with temperature, at frequency of 20Hz, for the Mn_{x}Zn_{1-x}Fe_{2}O_{4} samples prepared by the wet chemical method is shown in Fig.5.11 (a), (b) and (c).

It can be seen from the figures that the Mn-Zn ferrite samples obtained by this method also follow the same pattern as seen in the case of the mechano-chemical method for all the samples that is the dielectric constant (\epsilon') increases with increasing temperature. The values of dielectric constant for the unsintered samples were in the range 6.3682 \times 10^{5} - 8.4891 \times 10^{6} the lowest being for Mn_{0.7}Zn_{0.3}Fe_{2}O_{4} and the highest for Mn_{0.5}Zn_{0.5}Fe_{2}O_{4}. Similarly, in the case of the samples sintered at 1100^0C and 1300^0C, the values of dielectric constant were in the range of 2.3192 \times 10^{6} - 8.4934 \times 10^{7} and 2.3882 \times 10^{7} - 3.4278 \times 10^{8} respectively.

The dielectric constant values were lower for the wet chemical method as compared to the values obtained for the samples prepared by the mechano-chemical method, for the same composition. Better homogeneity, symmetry and the uniform smaller grains in the case of the samples obtained by the wet chemical method may be the reason for lower values of the dielectric constant.
Fig. 5.11. Variation of dielectric constant with temperature for various Mn-Zn ferrite (a) unsintered samples, sintered, at (b) 1100°C and (c) 1300°C obtained by the wet chemical method.
The decrease in values of the dielectric constant with increase in the frequency and secondly, the increase in values of the dielectric constant with the increase in the temperature, observed in the present studies for the samples prepared by the novel methods, are in agreement with the theories well documented for ferrite materials.

5.6.3.3 DIELECTRIC LOSS FACTOR:

**Ferrite samples prepared by mechano-chemical method:**

The variation of dielectric loss factor (tan δ) with the applied frequency for the ferrite samples is shown in Fig. 5.12. (a) and (b). It is observed that, for all the samples the value of tan δ decreases as the frequency is increased and reaches a constant value at higher frequency (1MHz) for unsintered as well as for the sintered samples.
Fig. 5.12. Variation of relative loss factor with log f for Mn-Zn ferrites (a) unsintered (b) sintered at 1300°C samples, obtained by the mechano-chemical method.

Ferrite samples prepared by wet chemical method:

Similarly, the variation of dielectric loss factor (tan δ) with the applied frequency, for the Mn-Zn samples prepared by the wet chemical method, is illustrated in Fig. 5.13. (a) and (b). It is clearly seen from the
figures, that for all the samples the tan δ value decreases as the frequency is increased and reaches to a constant value at 1 MHz for the unsintered as well as for the sintered samples.

Fig.5.13. Variation of relative loss Factor with log f for various Mn-Zn ferrite (a) unsintered (b)sintered at 1200°C samples, obtained by the wet chemical method.
REFERENCES:


