5.1. Introduction

Applications of ferrite materials in electronic technology depend on its electrical properties. Study of electrical properties not only gives information about the behavior of electrons, but also helps to understand the structure of materials to be used in various technologies [1]. Electrical properties of ferrites depends on several factors such as processing technique, sintering temperature, sintering time, chemical composition, frequency and dielectric constant of the materials, etc [2, 3]. At the same time, electrical properties depend on microstructure, grain size and distribution of grains inside the materials [4]. Therefore, properties of ferrites such as DC resistivity with respect to temperature, dielectric constant and dielectric loss tangent and AC conductivity with respect to frequency have been discussed in this chapter.
5.2. DC Resistivity

DC resistivity, the physical property of semiconducting material is required for the interpretation of various physical phenomena. Electrical conduction in ferrites can be explained on the basis of charge transfer mechanism. The understanding of electric charge transport mechanism in solid materials is to know whether the conductivity is ionic, electronic or partially mixed (i.e. ionic and electric). However, DC resistivity is important properties of metals, semiconductors and insulators, as it was affected by various factors such as grain size, porosity, temperature, etc [5]. DC resistivity of ferrites depends on chemical composition, sintering temperature, sintering time, porosity and presence of foreign materials or impurities, etc. DC resistivity with respect to temperature of semiconducting materials is expressed as follows:

\[ \rho = \frac{RA}{t} \quad (5.1) \]

Where \( R \) = resistance of the material, \( A = \) cross-sectional area of the pellet and \( t = \) thickness of the pellet.

DC resistivity is a temperature sensitive property; the diffusion of electric charge carriers from one ionic state to another is possible only when their energy exceeds certain limit known as activation energy (\( \Delta E \)). Activation energy is defined as the amount of energy required for hopping of electrons from one ion to other ions. DC resistivity of materials mainly depends on mobility of electric charge carriers as well as their concentration. Activation energy of semiconducting materials can be explained by using Arrhenius relation [6]:

\[ \rho = \rho_0 \exp \left( \frac{\Delta E}{K_B T} \right) \quad (5.2) \]

Where \( \rho = \) Resistivity, \( \rho_0 = \) Temperature independent constant, \( \Delta E = \) Activation energy, \( K_B = \) Boltzmann constant and \( T = \) Absolute temperature.

DC resistivity can be explained on the basis of actual location of distributed cations in the structure and electron hopping mechanism. Simultaneous availability of Fe\(^{2+}\) and Fe\(^{3+}\) ions in equivalent sites reveals the low
resistivity in ferrites. Hopping of 3d electrons among Fe\textsuperscript{2+} and Fe\textsuperscript{3+} ions arranged in octahedral sites can play substantial role in conduction process of electrons. However, higher resistivity is due to the occupation of divalent metal ions and trivalent metal ions in octahedral sites of ferrites. Therefore, electrical properties of ferrites depends on several factors such as synthesis technique, atmospheric condition, sintering temperature and time, composition, grain size and their distribution, etc [7].

5.2.1. Conduction Mechanism of Ferrites

Ferrites are magnetic semiconducting materials with low electrical conductivity which are quite different from usual semiconductors with respect to conduction mechanism. Carrier concentration of ferrites is almost constant, but mobility of charge carriers is affected by the temperature. Free electron theory fails to explain the conduction mechanism of ferrites as there is no Bloch type of wave functions since there are no free electrons [8]. Band theory of electrons is in accordance with increase in carrier concentration with respect to temperature, whereas electron-hopping model consider that the conductivity was due to change in mobility of electric charge carriers as a function of temperature. Hopping mechanism was due to Verwey and De-Boer [9], the conduction of electrons was due to the hopping of electrons between the ions of same elements present in more than one valence state and randomly distributed over crystallographic equivalent lattice sites. In ferrites conduction of electrons was due to the hopping of electrons between Fe\textsuperscript{3+} and Fe\textsuperscript{2+} ions present at octahedral site. Conduction mechanism gives the experimental evidences for the existence of polaron and its hopping process [10].

Ferrite the magnetic semiconductors are characterized by high conducting grains and are separated by highly non-conducting grain boundaries. The ferrites of high electrical resistivities are extensively used in many magnetic devices and soft magnetic alloys [11]. The decrease of DC resistivity of ferrites as a function of
temperature was due to the increase in drift mobility of electric charge carriers. Therefore, two mechanisms of conductivity of metal ions in ferrites is explained as follows:

\[
\begin{align*}
\text{Fe}^{2+} + \text{Fe}^{3+} &\rightarrow \text{Fe}^{3+} + \text{Fe}^{2+} + \Delta E \quad (5.3) \\
\text{M}^{2+} + \text{Fe}^{3+} &\rightarrow \text{M}^{3+} + \text{Fe}^{2+} + \Delta E \quad (5.4)
\end{align*}
\]

Where \( M \) = divalent metal ions, \( \Delta E \) = Activation energy.

Ferrites are good magnetic semiconductors and are expressed as follows:

\[
\sigma = e(\eta_e \mu_e + \eta_h \mu_h) \quad (5.5)
\]

Where, \( e \) = charge of electrons,

\( \eta_e \) = Concentration of electrons, \( \eta_h \) = Concentration of holes,

\( \mu_e \) = Mobility of electrons, \( \mu_h \) = Mobility of holes

Conduction mechanism of ferrites can be explained on basis of polaron hopping mechanism [12]. There are several experimental evidences for the existence of polarons and its hopping process [13].

### 5.2.2. Polarons and Hopping of Electrons

Electrons in crystal lattices interact through electrical charges with ions or atoms of lattices and produce local deformation of lattices in materials. The deformation follows that electrons move through the lattices and coupled with strain field is known as polarons. Polarons spread beyond the lattice constant is known as large polarons and strain field extends over a distance less than lattice constant is known as small polarons. The lattice displacement causes polarization of surrounding region with trapped electrons at the centre of potential well. If the potential well is deep enough, then the electrons may be trapped at the lattice site of ferrites and its electronic transition to the neighboring site can be estimated by thermal activation. The lattices are set into periodic vibrations and are quantized into phonons due to thermal activation. This process is known as hopping of electrons. The strength of interaction of lattices is expressed as electron-phonon coupling constant (\( \alpha \)) which is given as follows:
\[ \alpha = \frac{2E_d}{\hbar \omega} \]  \hspace{1cm} (5.6)

Where \( \omega \) = Longitudinal phonon frequency, \( E_d \) = Deformation energy, \( \hbar \) = Planck’s constant.

If the size of potential well is equivalent to ionic volume, then small polaron model is used as the interaction between nearest neighbor ions. The formation of small polarons is favored in semiconductors at certain temperature and behaves like a particle moving in narrow conduction band. At high temperature, small polarons may absorb one or more phonons showing the hopping mechanism. When tunneling time of electrons is less than the time of successive hopping transition, conduction of electrons by small polarons become a prominent mechanism. The detail analysis of conduction mechanism due to polarons hopping was given by Bosman and Van Daal [14]. Several research scientists reported that the conduction of electrons is mainly due to the hopping of small polarons [15, 16].

5.2.3. Experimental Details

DC resistivity of ferrites was measured by two-probe method. The final sintered pellet samples were well polished and coated with silver paste on both surfaces for good ohmic contact, after that the sample is fixed in the home made sample holder or conductivity cell and then it is kept in a digital temperature controlled muffle furnace. A constant voltage of about 5 V is provided using a stabilized power supply unit and the current at different temperature is measured by using a digital micro/nano ammeter. DC resistivity of the pellet samples was estimated using the relation:

\[ \rho = \frac{R \pi r^2}{t} \]  \hspace{1cm} (5.7)

Where \( R \) = Resistance of the pellet sample (in ohm), \( r \) = Radius of the pellet in cm, \( t \) = thickness of the pellet in cm.
Activation energy of ferromagnetic region, paramagnetic region and Curie
temperature were studied from the plot of ln ρ versus $\frac{10^3}{T}$. Activation energy of
the two regions were estimated using the following relation:

$$\Delta E = 1.982 \times m$$  \hspace{1cm} (5.8)

where $m =$ slope.
The drift mobility ($\mu_d$) of electrons for all samples was measured by using the
following relation:

$$\mu_d = \frac{1}{n\rho}$$  \hspace{1cm} (5.9)

where ‘$e$’ is the charge of electron, ‘$\rho$’ is the electrical resistivity and ‘$n$’ is the
charge carrier concentration.
The value of ‘$n$’ was calculated from the well known equation:

$$n = \frac{N\rho m_{Fe}}{M}$$  \hspace{1cm} (5.10)

Where ‘$M$’ is molecular weight, $N$ is Avogadro’s number, $P$ is number of iron
atoms in chemical formula of the ferrites and $\rho_m$ is density of the sample.
The density of samples was estimated using the relation:

$$\rho_m = \frac{m}{\pi r^2 L}$$  \hspace{1cm} (5.11)

Where ‘$m$’ is mass of the pellet, ‘$r$’ is the radius and ‘$L$’ is thickness of the pellet.

5.2.4. Results and Discussion

Variation of DC resistivity with respect to temperature for Ni$_{1-x}$Mg$_x$Fe$_2$O$_4$
(with $x=0.0, 0.1, 0.2, 0.3, 0.4$ and $0.5$) ferrites are shown in figure 5.1. It is observed
that DC resistivity decreases with increase in temperature shows semiconducting
nature of ferrites as it was due to the thermally activated drift mobility of electric
charge carriers [17]. Variation of DC resistivity as a function of temperature depends on the purity of materials, sintering temperature and sintering time which influences the microstructure and composition of samples. Conduction
mechanism of ferrites was explained on the basis of Verwey and De Boer
mechanism [9] which involves the exchange of electrons between the ions of same elements present in more than one valence state.

Conduction of electrons in ferrites was due to the hopping of electrons from Fe\(^{2+}\) to Fe\(^{3+}\) ions. Exchange of electrons between Fe\(^{2+}\) ↔ Fe\(^{3+}\) + e\(^-\) is responsible for n-type charge carrier and exchange of holes between Ni\(^{3+}\) ↔ Ni\(^{2+}\) + e\(^+\) and Mg\(^{2+}\) ↔ Mg\(^{1+}\) + e\(^+\) are responsible for p-type charge carriers in ferrites [18]. DC resistivity mainly depends on distribution of cations in ferrites as well as difference in ionic size of the cations [19]. Figure 5.1 shows that at a particular temperature the change in slope occurs in all ferrite samples, it was due to the transition of phase from ferromagnetic to paramagnetic region [20]. Activation energy of paramagnetic region (ΔE\(_1\)) and ferromagnetic region (ΔE\(_2\)) were estimated through the slopes of DC resistivity curve before and after phase transition using equation 5.8. In table 5.1, activation energy of paramagnetic region (ΔE\(_1\)) varies from 1.33 eV–2.96 eV and activation energy of ferromagnetic region (ΔE\(_2\)) varies from 0.716 eV – 0.854 eV. It is clear that the activation energy of paramagnetic region is higher than that of ferromagnetic region and is in good agreement with the theory of Irkin and Turor [21]. The estimated value of activation energy is in good agreement with each other for other spinel ferrites [5, 7, 8]. The lowering of activation energy in ferromagnetic region was due to the spin disordering effect.

Figure 5.2 shows the temperature dependence of drift mobility (\(\mu_d\)) of ferrites. It is observed that the increase of drift mobility with increase in temperature was due to the overcome of activation energy barrier by the charge carriers. In the present system, it is observed that the mobility of charge carrier was found to increase with increase in temperature it was due to the hopping of electrons between Fe\(^{2+}\) and Fe\(^{3+}\) ions and also due to the decrease of DC resistivity with respect to temperature [9].
Fig. 5.1. Variation of DC resistivity as a function of temperature for Ni$_{1-x}$Mg$_x$Fe$_2$O$_4$ ($x = 0.0, 0.1, 0.2, 0.3, 0.4$ and $0.5$) ferrites

Fig. 5.2. Variation of Drift mobility with temperature for Ni$_{1-x}$Mg$_x$Fe$_2$O$_4$ ($x = 0.0, 0.1, 0.2, 0.3, 0.4$ and $0.5$) ferrites
Table 5.1. The activation energy of paramagnetic ($\Delta E_1$) and ferromagnetic ($\Delta E_2$) regions

<table>
<thead>
<tr>
<th>x content</th>
<th>Activation Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta E_1$</td>
</tr>
<tr>
<td>0.0</td>
<td>1.33</td>
</tr>
<tr>
<td>0.1</td>
<td>1.65</td>
</tr>
<tr>
<td>0.2</td>
<td>1.46</td>
</tr>
<tr>
<td>0.3</td>
<td>1.50</td>
</tr>
<tr>
<td>0.4</td>
<td>2.85</td>
</tr>
<tr>
<td>0.5</td>
<td>2.96</td>
</tr>
</tbody>
</table>

5.3. Dielectric Properties of Ferrites

5.3.1. Introduction

The term “Dielectric” was introduced by M. Faraday to describe materials through which the electric field can penetrate. Ferrite materials are electrical insulators having dielectric strength, dielectric constant and dielectric loss tangent tailored for electronic device applications. Ferrite materials with high dielectric constant are applicable to increase the storage capacity of charge in capacitors. But, low dielectric constant materials are sought to reduce inductive cross talk and noise production in electrical circuits. In high voltage insulator applications, high electrical resistivity and high dielectric strength are required.

Dielectric loss tangent is the ratio of imaginary permittivity to the real permittivity of dielectric materials. Operating frequency of dielectric materials is capable for operating within the range, while supplying the acceptable performance and/or without excessive power loss. Dielectric properties can be defined by the behavior of dielectric materials in parallel plate capacitor. This is a
pair of conducting plates, parallel to one another and separated by a distance \( d \), i.e. as small as compared with the linear dimension of conducting plates.

**Fig. 5.3.** Schematic representation of polarization of dielectrics in an electric field

When dielectric materials are subjected to AC electric field, then there is relative displacement of positive and negative charges which show degree of polarization [22]. The quantity of dielectric constant depends on degree of polarization or charge displacement that occurs in dielectric materials. For air, the dielectric permittivity is \( \approx 1 \) and for ionic solids, the dielectric permittivity \( \approx 5 \) to 10. There are various possibilities of the polarization mechanism or conduction of dielectric materials which depends on the behavior of chemical bond i.e. electron density distribution in dielectric materials. On the basis of polarization mechanism [23, 24], the polarizations in dielectric materials are divided into four types and are shown in figure 5.3. They are:
1. Electronic polarization ($\alpha_e$) (Frequency range 10-10^{18} Hz).
2. Ionic polarization ($\alpha_i$) (Frequency range 10-10^{14} Hz).
3. Orientation (Dipolar) polarization ($\alpha_d$) (frequency range 10-10^{10} Hz).
4. Space charge polarization ($\alpha_s$) (Frequency range 10-10^4 Hz).

![Graph showing frequency dependence of total polarizability of solid dielectric materials]

**Fig. 5.4.** Frequency dependence of total polarizability of solid dielectric materials

1) Electronic polarization is common to all dielectric materials i.e. it is the shift of centre of gravity of +ve charged nucleus and -ve charged electrons in electric field of the dielectric materials. If electric field is applied to an atom, electronic structure of an atom gets disturbed and concentration of electrons on either side of +ve field of the nucleus shows dipole moment to an atom temporarily in dielectric materials.

2) If ionic bonded dielectric materials are placed in electric field, it deforms elastically the bonds between ions that cause redistribution of charges within the materials. In an ionic crystal, electrons are distributed in such a way that the individual ions are isolated and due to the shift of positive
and negative ions relative to each other polarization occurs and is called ionic polarization.

3) When electric field is applied to the dielectric materials having certain amount of dipoles, the dipoles revolve to line up with applied electric field and it shows temporary polarization of the materials. The presence of permanent electric dipoles that exist in absence of electric field is called orientation polarization.

4) Space charge polarization in dielectric materials occurs due to the change in electrical resistivity. When dielectric materials are subjected to applied electric field at high temperature, then the charges accumulates at the interface of materials due to sudden change in conductivity. Charge accumulation occurs with opposite polarity at opposite parts in less electrical resistivity leading to the origin of dipole moment under less resistivity of the materials.

5.3.2. Effect of Frequency on Dielectric Properties

Relationship between dielectric constant and frequency describes the dielectric dispersion characteristics of materials. The decrease of dielectric constant monotonically with increase in frequency is called as relaxation dispersion for dipoles and interfacial polarization. The ionic and electronic type of polarization experiences the dispersion of resonance where the dielectric constant decreases first and then reaches a constant value at higher frequency [25]. Electrical resistivity and dielectric constant for polycrystalline ferrites shows dispersion behavior with respect to frequency and this is explained with the help of Koops phenomenological theory [26]. According to Koops, two layer model for inhomogeneous dielectric structure comprising well conducting grains separated by low conducting layers or grain boundaries. These layers constitute a condenser in which ferrite grains and their boundaries have different property that leads to two parallel resistance and capacitance circuits connected in series,
one for the grains and the other for grain boundaries. The conducting grains and less conducting grain boundaries are separated by voids or pores gives rise to less conducting and non-conducting matrix of polycrystalline ferrites which shows the interfacial polarization explained by Maxwell and Wagner [27, 28].

In ferrites, grain boundaries are effective at lower frequency region whereas the grains are effective at higher frequency region [29]. Dielectric constant decreases steeply at low frequency and remains constant at higher frequency was due to the contribution of electronic polarizability to the polarization.

5.3.3. Experimental Details

(a) Measurement of Dielectric Properties

All samples in the form of pellets were well polished and coated with silver paste on both surfaces for good ohmic contact (electrical contact), then they are used for the measurement of dielectric properties. The silver pasted pellet samples of ferrites are used to estimate the parallel capacitance (Cp) and dielectric loss tangent (tanδ) at room temperature in the frequency range of 20 Hz to 1 MHz (by using two probe method) using an LCR meter bridge (Model: PSM1700) at Materials Science Lab, Physics Department, Karnatak University Dharwad. The dielectric constant of ferrites was estimated by using the relation as follows:

\[ \varepsilon' = \frac{C_p \times t}{\varepsilon_0 A} \]  

(5.12)

Where \( C_p \) – Parallel capacitance, \( t \) – Thickness of the pellet, \( A \) – Cross sectional area of the pellet (\( \pi r^2 = \frac{\pi d^2}{4} \)) and \( \varepsilon_0 \) – Permittivity of free space = \( 8.854 \times 10^{-14} \) F-cm\(^{-1}\).

(b) AC conductivity

AC conductivity of dielectric materials (\( \sigma_{ac} \)) is related to the dielectric relaxation caused by localized free electric charge carriers. Frequency dependence of AC
conductivity was estimated using dielectric constant ($\varepsilon'$) and dielectric loss tangent ($\tan\delta$) i.e.

$$\sigma_{AC} = \varepsilon'\varepsilon^0\omega\tan\delta$$  \hspace{1cm} (5.13)

where $\varepsilon'$ = Dielectric constant, $\varepsilon^0$ = Permittivity of free space, $\tan\delta$ = Dielectric loss tangent and $\omega$ = Angular frequency.

5.3.4. Results and Discussion

(1) Variation of dielectric constant and dielectric loss tangent with respect to frequency

Variation of dielectric constant with respect to frequency is shown in figure 5.5. It is observed that dielectric constant decreases steeply at lower frequency and remains constant at higher frequency indicates usual dielectric dispersion behavior of semiconducting materials. High dielectric constant at lower frequency and low dielectric constant at high frequency shows the large dielectric dispersion behavior which was due to the Maxwell-Wagner type of interfacial polarization \[27, 28\], which is in good agreement with Koops phenomenological theory \[26\]. Variation of dielectric constant with respect to applied frequency was due to the charge transport relaxation \[30\]. Maximum dielectric constant was due to the availability of space charge polarization at the grain boundaries \[31\]. Polarization effects are inefficient beyond certain frequency \[25\]. At low frequency region all types of polarization contributes, but as the frequency increases polarizations with large relaxation times cease to respond and hence the decrease in dielectric constant \[32-34\].

Variation of dielectric loss tangent with respect to frequency is shown in figure 5.6. Dielectric loss tangent causes due to the collective behavior of two species of charge carriers (p-type and n-type) of the polarization \[35\]. Physical significance of dielectric loss tangent is the energy dissipation in dielectric materials which is proportional to the imaginary part of dielectric constant. At
higher frequency, dielectric loss tangent is low if domain wall motion is inhibited and magnetization is forced to change by the rotation [36]. When relaxation time is large as compared to the period and frequency of applied field, dielectric loss tangents are small [37].

(2) **AC conductivity Measurement with respect to frequency**

In order to understand the type of polarons responsible for conduction of electrons, variation of AC conductivity with respect to frequency at room temperature was carried out by using dielectric constant and dielectric loss tangent. From figure 5.7, it is observed that AC conductivity increases with increase in frequency and was due to the hopping of electric charge carriers among the localized state and it is confirmed that the conduction of electrons was due to the hopping of small polarons. Infact, the polaron type of conduction mechanism is reported by Austin and Mott [38] and Appel et al [39]. The polarons are classified as small polarons and large polarons. However, in large polaron model, AC conductivity decreases with increases in frequency. In case of small polaron model, AC conductivity increases with increase in frequency. Therefore, frequency dependent conduction of electrons was due to small polarons as explained by Alder and Feinleib [40]. However, a slight decrease in AC conductivity at certain frequency was due to the mixed polaron (i.e. small and large) in ferrites [41].
Fig. 5.5. Variation of Dielectric constant with frequency for Ni$_{1-x}$Mg$_x$Fe$_2$O$_4$ ferrites

Fig. 5.6. Variation of Dielectric loss with frequency for Ni$_{1-x}$Mg$_x$Fe$_2$O$_4$ ferrites
Fig. 5.7. AC conductivity with respect to frequency at room temperature for Ni$_{1-x}$Mg$_x$Fe$_2$O$_4$ ferrites
5.4. References


