CHAPTER - IV

AC CONDUCTIVITY
4.0 Introduction

D C resistivity study only does not provide the clear picture of conduction mechanism in the bulk of polycrystalline ferrites. The bulk conductivity of polycrystalline material is influenced by grain size, grain to grain contacts and pores. Grains are moderately good conductors and also the outer layers, while the inter-grain contacts and pores are the regions of high resistivity. The high resistivity layers between grains are sandwiched between the regions of high conductivity. This situation therefore, is comparable with a parallel plate condensor. In this case the high resistivity layers between grain to grain contact act as a dielectric.

At low frequencies (almost dc level) the contribution of this to conductivity is constant but at higher frequencies the dielectric losses have considerable influence on the bulk conductivity of the polycrystalline material. At high frequencies dielectric losses occur due to relaxation process in the electric polarisation in the crystal lattice. Therefore, contribution to the conduction mechanism at higher frequencies becomes a complex phenomenon. The dispersion of dielectric constant and conductivity with frequency is therefore, rather expected. The contribution of imaginary part of dielectric constant at particular frequency can not be distinguished from the conductivity term. Therefore, to determine grain conductivity of the sintered polycrystalline
material, it is essential to establish the relation of the dielectric absorption spectrum between Koop's dispersion at low frequencies and dielectric losses at high frequencies.

4.1 Review of work done on A C conductivity measurements

The dielectric properties of ferrites basically depend on several factors such as method of preparation, chemical composition, grain structure and size. The dielectric constant and bulk conductivity of the polycrystalline materials show frequency dispersion \[1,2\]. From high frequency measurement of these parameters it is possible to determine their absolute values \[3\]. The measurement in the frequency range of \(10^2\) Hz to \(10^5\) Hz of the above said parameters have been reported by many workers \[3-14\]. Koop \[3\] gave a phenomenological theory of dispersion based on the Maxwell-Wagner interfacial polarization model for inhomogeneous dielectric structure.

The dispersion in dielectric constant and loss tangent (\(\tan \delta\)) with frequency is observed and is explained on the basis of \(Koop\) Maxwell-Wagner theory. \(Koop\) has observed high resistivity in Ni-Zn ferrites which is attributed to formation of poorly conducting regions. Rezlescu and Rezlescu \[8\] studied dielectric parameters as a function of composition, frequency and temperature for Cu-Zn Cu-Ni and Cu-Mn ferrites have explained the behaviour on the basis of Maxwell-Wagner polarisation process and Verwey type conduction mechanism. A sound correlation between the conduction mechanism and dielectric behaviour of the ferrites has been reported by Iwachi \[6\]. Ahmed et al \[15\] have studied dielectric behaviour of Co-Zn ferrite. They have shown that the dielectric
constant is proportional to ac conductivity.

The compositional dependence of dielectric constant of Co-Zn ferrites have been attributed by them to local displacement of charge carriers in the direction of applied field. The dependence of the dielectric properties of mixed ferrites of Co-Zn on the composition and temperature has been studied by Ramana Murthy [13]. He has observed increase in polarisation and dielectric constant with increase in zinc content and has attributed it to n-type behaviour. The dielectric properties of Ni-Zn ferrites have been studied by Murthy, et al [12]. They have observed decrease in dielectric constant \( (\varepsilon') \) with increase of frequency and have explained this behaviour on the basis of \( \text{Fe}^{2+} \) and \( \text{Fe}^{3+} \) electron exchange mechanism which cannot follow the frequency of the alternating field beyond a critical frequency.

The abnormal dielectric behaviour in Cu-Cd ferrites have been reported by Kulkarni and Vaingankar [14]. They have attributed it to the p-type charge carriers due to \( \text{Cu}^{2+} \leftrightarrow \text{Cu}^{1+} \) (Hole exchange). The loss tangent \( (\tan\delta) \) decreases with increase of frequency [15]. However, the abnormal peaking behaviour in the dispersion of loss tangent \( (\tan\delta) \) is observed [16,17] and have attributed it to jump frequency approximately equal the frequency of applied field by Koop [3]. Another probable cause for the occurrence of peaking behaviour in the dispersion relation of loss tangent with frequency, the dispersion in dielectric constant \( (\varepsilon') \) is large in comparison with that of imaginary part of the complex dielectric constant \( (\varepsilon'') \). Which is just a consequence of loss-tangent relation [1].
The frequency dependence of the resistivity of zinc ferrite doped with \( \text{TiO}_2, \text{SiO}_2, \text{Sb}_2\text{O}_5, \text{Nb}_2\text{O}_5 \) have been studied by Wu et al [18]. They have observed that, the resistivity of ferrites containing \( \text{SiO}_2, \text{Nb}_2\text{O}_5 \) decreases with increase in frequency more rapidly than that of other kinds, and have attributed it to the formation of highly resistive compounds, according to the Wagner [19] inhomogeneous dielectric theory. The \( \text{TiO}_2 \) doped in zinc ferrite shows increase of resistivity due to formation of highly resistive grain boundary. The dielectric behaviour of \( \text{Ti}^{4+} \) substituted \( \text{Ni-Zn} \) ferrites shows decrease of dielectric constant with increase of frequency [16]. This behaviour is attributed to increase of \( \rho \text{dc} \). Similar results have been reported on \( \text{Li}^{1+} \) and \( \text{Ti}^{4+} \) substituted zinc ferrites [17]. The entire behaviour of dielectric relaxation intensity in ferrites can be explained on the basis of space charge polarisation due to the inhomogeneous structure as suggested by Maxwell [20] and Wagner [19].

The space charge is a function of charge carriers and dc resistivity. Therefore decrease of \( \text{Fe}^{3+} \) causes increase in dc resistivity so also, because of the hinderances and localisation effects [17]. Arias et al have discussed the effects of sodium and calcium on dielectric behaviour of \( \text{Ni-Zn} \) ferrites and have explained it on the above lines [21]. Murthy et al have studied dielectric behaviour at lower temperature in \( \text{Mn-Zn} \) ferrite and have observed peak in \( \varepsilon'' \) (imaginary part of dielectric constant) at low frequency. They have attributed it to the existence of one or more relaxation processes [22]. Iwauchi studied \( \text{Mn-Zn} \) ferrites and had measured the values of dielectric
constants of powder and sintered ferrites. He observed that powder samples have low dielectric constant (10-100) and sintered ones have high values of the order of 10^5 [23].

Karmer, et al have studied the dielectric properties of two series of Mn-Zn ferrites with different grain structure obtained by the change of firing temperature [24].

4.2 Theories of dielectric dispersion

Koop gave a phenomenological theory of dispersion based on the Maxwell-Wagner interfacial polarization model for inhomogeneous dielectric structure [3]. The inhomogeneous structure consists of highly conducting grains separated by poorly conducting layers. The high resistivity layer between the grains acts as dielectric material while low resistivity grains as plates of parallel plate capacitor. Therefore, measured value of capacitance $C_p$ and parallel resistance $R_P$ of the specimen composition from a capacitor with double layer dielectric results from equivalent circuit shown in figure 4.1(a). As shown in figure 4.1(a) the capacitance $C_1$ is due to boundary layer, and $C_2$ due to ferrite grains. If the area of parallel plate capacitor is $A$ then $C_1$ is given by

$$C_1 = \frac{\varepsilon_0 \varepsilon_1 A}{d_1},$$

and

$$C_2 = \frac{\varepsilon_0 \varepsilon_2 A}{d_2},$$

while

$$R_1 = \frac{\rho_1 d_1}{A},$$

and

$$R_2 = \frac{\rho_2 d_2}{A}.$$
Impedance

Equivalent circuit for an electrical ceramic with bulk and grain boundary components

\[
W = \frac{1}{R_2C_2} \quad \text{and} \quad W = \frac{1}{R_1C_1}
\]

Impedance plane response for circuit

(a)

(b)

(c)

Fig. 4.1 Inhomogeneous dielectric double layer structure.
where $\varepsilon_0$, $\varepsilon$ is the permittivity and $\rho$ the resistivity.

Now by equating the impedances (fig.4.1c) of basic and equivalent circuit (figure 4.1(b) the values of resistance and dielectric constant of parallel combination on the basis of Koops assumption can be written as,

$$
\rho_p = \rho_p^\infty + (\rho_p^0 - \rho_p^\infty) \left(1 + \omega^2 \tau^2\right)
$$

and

$$
\varepsilon_p = \varepsilon_p^\infty + (\varepsilon_p^0 - \varepsilon_p^\infty) \left(1 + \omega^2 \tau^2\right)
$$

where superscripts infinity($\infty$) and zero (0) refer to very high frequency and very low frequency respectively, $\tau$ relaxation constant and $\omega = 2\pi f$, where $f_p$ is the frequency of applied electric field. From equation 3 and 4 it is clear that the values of resistance ($\rho_p$) and the dielectric constant ($\varepsilon_p$) of equivalent parallel network are frequency dependent and therefore, show frequency dispersion.

If an alternating electric field of the form,

$$
E = E_0 \exp(j\omega t)
$$

is applied to a dielectric material the response is not instantaneous [25]. It is because of the complex nature of dielectric constant. According to Maxwell's equation it is given by,

$$
D = \varepsilon^* E
$$

where $\varepsilon^*$ is the dielectric constant of the medium. It is a complex quantity given by,

$$
\varepsilon^* = \varepsilon' - j\varepsilon''
$$
where \( \varepsilon' \) is real part and \( \varepsilon'' \) the imaginary part of dielectric constant, arising due to time lag between the response and stimulus provided. The phase angle \( \delta \) arising due to imaginary part of dielectric constant is given by \( \tan \delta = \varepsilon'' / \varepsilon' \). The losses in dielectric material are found to be proportional to \( \tan \delta \) and is frequency dependent. Therefore, imaginary dielectric constant also show the frequency dispersion. The real part of dielectric constant is given by,

\[
\varepsilon' = \varepsilon_0 + \frac{\varepsilon_\infty - \varepsilon_0}{1 + \omega^2 \tau^2}
\]

(8)

and the imaginary part of dielectric constant \( \varepsilon'' \) is given by,

\[
\varepsilon'' = \varepsilon_\infty - \varepsilon_0 \frac{\omega \tau}{1 + \omega^2 \tau^2}
\]

(9)

where \( \omega \), \( \varepsilon_0 \), \( \omega \), \( \tau \) are usual meaning discussed before. The equation of \( \tan \delta \) can be obtained by using above equation as,

\[
\tan \delta = \frac{\varepsilon_\infty - \varepsilon_0}{\varepsilon_0 + \varepsilon_\infty} \frac{\omega \tau}{1 + \omega^2 \tau^2}
\]

(10)

The dielectric properties of dipolar material are explained with characteristics, power law \([26]\). Frequency dependence of complex susceptibility above the loss peak frequency given by

\[
\chi^*(\omega) = (\varepsilon^*(\omega) - \varepsilon_\infty) \omega^0 [1 - \cot n \pi / 2] \omega^{n-1}
\]

(11)

where \( 0 < n < 1 \).

Materials in which charge transport is ionic or electronic, make significant contribution to the process of polarisation. The low frequency dispersion therefore, in these materials is very fast than that at higher frequency and is given by a power law given in equation (11). The low frequency dispersion (LFD) is
also characterised by the frequency independent ratio of the real and imaginary part of the dielectric constant. The low frequency dispersion is due to high polarization because of migration of charge carriers, influence of boundary phenomena in granular media like polycrystalline materials.

4.3 Polarisation in dielectrics

When an alternating field is applied to a ferrite material, it induces a polarisation in the material. The polarisation in multiphase material is given by,

\[ p = p_e + p_i + p_o + p_s \]  \hspace{1cm} (12)

where \( p_e \) - electronic polarisation [27]

\[ p_i \] - ionic polarisation

\[ p_o \] - orientational polarisation [28]

and \( p_s \) - space charge polarisation or (interfacial) [28]

In ferrites, the interfacial polarisation plays prominent role in deciding the conduction mechanism in the presence of applied electric field and a great deal about it has been explained by Maxwell [20] and Wagner [19].

In electronic polarisation, the centre of gravity of negative electrons is shifted relative to the positive nucleus in an electric field. In ionic polarisation the displacement of positive and negative ions relative to one another takes place. The orientational polarisation is due to the orientation of electric dipoles in the presence of external field.
The above mentioned processes of polarisation are schematically presented in figure 4.2(a), while the range of frequency within which, each process contributes the total polarisation is shown in figure 4.2(b). From the figure 4.2(b) it is clear that electronic polarisation is over the entire range of visible frequency, while ionic polarisation is in the infrared region. The range of orientational polarisation is wide enough ranging from $10^4$ Hz to $10^{10}$ Hz. The low frequency range is covered by space charge polarisation.

4.4 Experimental technique

The ac conductivity study of Cd$_x$Cu$_{1-x}$Fe$_{2-y}$Gd$_y$O$_4$ ferrites ($x=0.0, 0.2, 0.4, 0.6, 0.8$ and $1.0$ for $y=0.0, 0.1$ and $0.3$) was carried out by using L.F. impedance/gain phase analyser (Model 4194A Hewlet Packard) at ERTL, Bombay. The measurement of $C_p, R_p,\tan \delta$, were carried out in the frequency range of 100 Hz to 5 MHz. The dielectric constant $\varepsilon'$ and ac resistivity $(ac)$ were calculated by using the relation equation 12,13 respectively,

$$\varepsilon' = \frac{C_p d}{\varepsilon_0 A}$$  \hspace{1cm} (12)

where $C_p$ - parallel capacitance

$\varepsilon_0$ - permittivity of free space

$d$ - thickness of pellet

$A$ - area of the pellet

and

$$\rho \ (ac) = \frac{R_p A}{d} \ (\text{ohm-cm})$$  \hspace{1cm} (13)

where $R_p$ - parallel resistance.
Fig. 4.2 (a) - Schematic representation of different mechanisms of polarization.

Fig. 4.2 (b) - Frequency dependence of several contributions to the polarizability.
4.5 Results and Discussion

The frequency dependence of \((\varepsilon')\) the dielectric constant is presented in figures 4.3, 4.4 and 4.5 for \(y=0.0, 0.1\) and 0.3 respectively. From figure 4.3 it is clear that the dispersion of the dielectric constant \((\varepsilon')\) can be explained by the Koop's phenomenological theory. The dispersion of \(\varepsilon'\) is high in all samples at low frequency, below 1 MHz, except for \(x = 0.8\). This is indicative of the electronic and ionic conduction, which has significant contribution to the polarisation process. The low frequency dispersion is due to high polarisation because of migration of charge carriers and boundary phenomena in polycrystalline material. The dispersion in \(x=0.8\) is high, below 10KHz, i.e. at still lower frequencies compared to the above mentioned compositions. It means that, in this composition the polarisation process reach its saturation limit below 10 KHz. This behaviour can be attributed to strong electronic conduction having predominant contribution to polarisation process at lower frequency.

The n-type behaviour and a comparatively lower activation energy in this composition has been observed. (Chapter 3A,3B). The addition of \(\text{Cd}^{2+}\) in \(\text{CuFe}_2\text{O}_4\) shows increase of activation energy and dc resistivity upto 60\% composition, therefore, these compositions show increasing trend of dielectric constant. However, beyond 60\% Cd content the decrease of dc resistivity and activation energy \(\triangle E\) is observed. Therefore, \((\varepsilon')\) in these compositions is found to decrease. The relation between dielectric constant \((\varepsilon')\) and ac conductivity is well known [6].
Fig. 4-3 Plot of dielectric constant ($\varepsilon'$) with frequency for $\text{Cd}_{x}\text{Cu}_{1-x}\text{Fe}_{2-y}\text{Gd}_y\text{O}_4$ ferrite system.

$\text{Cd}_x\text{Cu}_{1-x}\text{Fe}_{2-y}\text{Gd}_y\text{O}_4$

($\gamma = 0.0$)

Symbol $x$

- $x = 0.0$
- $x = 0.2$
- $x = 0.4$
- $x = 0.6$
- $x = 0.8$
- $x = 1.0$

$10^4 \text{K}$ $50 \text{K}$ $200 \text{K}$ $1 \text{MHz}$ $5 \text{MHz}$ $f$ (Hz)

$\varepsilon'$
Fig. 44  Plot of dielectric constant ($\varepsilon'$) with frequency for $\text{Cd}_x\text{Cu}_{1-x}\text{Fe}_{2-y}\text{Gd}_y\text{O}_4$ ferrite system.
Fig. 4.5 Variation of dielectric constant with frequency of \( \text{Cd}_{x}\text{Cu}_{1-x}\text{Fe}_{17}\text{Ge}_{3}\text{O}_{4} \) ferrite system.
The variation of dielectric constant \( \varepsilon' \) with log frequency for \( y=0.1 \) and 0.3 (Gd substituted) is presented in figure 4.4,4.5 respectively. From the above mentioned figures it is clear that, the values of dielectric intensity is decreased on Gd substitution. So also, the frequency limits of low frequency dispersion in these compositions have been lowered from 1 MHz to 10 KHz.

The decrease of dielectric intensity and dispersion with frequency in substituted ferrites can be explained on the basis of space charge polarisation [19,20]. In the present case the decrease of dielectric intensity can be attributed to increase of ac resistivity \( \rho_{ac} \), and the activation energy \( \Delta E \). The substitution of Gd\(^{3+}\) for Fe\(^{3+}\), reduces number of Fe\(^{2+}\)/Fe\(^{3+}\) ratio and the charge carrier concentration participating in Verwey conduction mechanism. The process of polarisation may have affected by the hinderances caused by Gd\(^{3+}\) to the conduction and polarisation process [24] which in turn affects the dielectric intensity. The effect of Ti\(^{4+}\) substitution in zinc ferrite on the dielectric behaviour have been reported in literature [16,17] and have explained the lowering of dielectric intensity due to reduction of Fe\(^{2+}\)/Fe\(^{3+}\) ratio, reduction in carrier concentration and hinderances of the substituents to charge transport and process of polarisation.

The dispersion of ac log resistivity \( \rho_{ac} \) with frequency, for \( y=0.0,0.1 \) and 0.3 (Gd\(^{3+}\) concentration) are presented in figure 4.6,4.7 and 4.8 respectively. The dispersion of ac log resistivity with frequency show a rather normal trend. However, rate of
Fig. 4-6  Plot of a.c. log resistivity with frequency for $Cd_xCu_{1-x}Fe_{2-y}GdyO_4$ ferrite system.
Fig. 4.7 Plot of a c log resistivity with frequency for $\text{Cd}_x\text{Cu}_{1-x}\text{Fe}_{2-y}\text{GdyO}_4$ ferrite system.
Fig. 4.8 Variation of ac resistivity with frequency of \( C_d \cdot C_u \cdot Fe_i \cdot Gd \cdot 3O_4 \) ferrie system.
dispersion is found to be comparatively high in Gd$^{3+}$ substituted samples ($y=0.1$ and $0.3$) than that of unsubstituted ones ($y=0.0$). The frequency dependence of ac resistivity of TiO$_2$,SiO$_2$,Sb$_2$O$_5$,$\text{Nb}_2\text{O}_5$ substituted zinc ferrite has been studied by Wu et al [18]. They have observed faster dispersion rate of AC resistivity with frequency in compounds of which resistance is increased on substitution. In the present case, the faster rate of dispersion in Gd$^{3+}$ substituted compositions ($y=0.1$ and $y=0.3$) is observed which can be attributed to formation of highly resistive compound according to the Wagner's [19] inhomogeneous dielectric theory. The high value of dc resistivity, and increase of activation energy ($\Delta E$) is observed in these compositions from our dc electrical resistivity study which supports the above statement [28]. The contribution to increase of dc resistivity in substituted compositions may also due to the increase of porosity in these compositions (Chapter-2B).

The dispersion of loss tangent ($\tan \delta$) with frequency for $y=0.0,0.1$ and $0.3$ are presented in figures 4.8,4.9 and 4.10 respectively. The trend of dispersion of loss tangent for ($y=0.0$) is similar to that expected for ferrites except for $x=0.4$ and $1.0$, which show peaking behaviour. The maximum in $\tan \delta$ for $x=0.4$ occurs at about 10 KHz while for $x=1.0$ at 150 KHz. Figure 4.9 (for $y=0.1$) show peaking behaviour in the dispersion relation of $\tan \delta$ with frequency except for $x=0.0$. The peak frequencies for $x=0.2$ and $0.4$, it is 100 KHz and for $x=0.6$ 10 KHz while for $x=0.8$, 1 KHz. The peak frequency is found to be decreased with increase of Cd content. The variation of $\tan \delta$ with frequency for
Fig. 4-9 Plot of loss tangent ($\tan \delta$) against frequency for $\text{Cd}_x\text{Cu}_{1-x}\text{Fe}_2\text{O}_4$ ferrite system.

$\text{Cd}_x\text{Cu}_{1-x}\text{Fe}_2\text{O}_4$

Symbol | $x$
--- | ---
$\bullet$ | 0.0
$\circ$ | 0.2
$\Delta$ | 0.4
$\times$ | 0.6
$\blacksquare$ | 0.8
$\bigcirc$ | 1.0

--- $f$ (Hz) ---
Fig 4.10 Plot of loss tangent ($\tan \delta$) against frequency for $\text{Cd}_x\text{Cu}_{1-x}\text{Fe}_{2-y}\text{GdyO}_4$ ferrite system.
Fig. 4.11 Variation of loss tangent with frequency of \( \text{Cd}_x \text{Cu}_{1-x} \text{Fe}_{1.7} \text{Gd}_{304} \) ferrite system.
y=0.3, show rather a normal dispersion relation except a peaking behaviour for x=1.0.

The decrease of $\tan \delta$ with frequency is rather expected in ferrites [15]. However, an increase of $\tan \delta$, with frequency is somewhat abnormal. The peaking behaviour in mixed ferrites of Cu-Ni [8], Cu-Cd [14], Ti substituted Ni-Zn ferrites [16] have been reported in literature. The peaking behaviour in $\tan \delta$ versus frequency plots is attributed by different workers [3,16] to jump frequency equal to the frequency of applied field. According to Koop [3], the maximum in loss tangent in frequency relation is due to large variation in ( $\varepsilon''$ ) the imaginary component of dielectric constant in comparison to $\varepsilon'$ the real part. However, the abnormal peaking behaviour in copper containing ferrites [14] has been attributed by Vaingankar et al. to the presence of p-type charge carriers in addition to n-type given by Cu $^{2+}$ Cu $^{1+}$ exchange on octahedral lattice site of spinel structure [14].

The peaking behaviour in this case therefore, may be attributed to higher rates of dispersion of ( $\varepsilon'$ ) in substituted samples with respect to $\varepsilon''$, and also, due to the presence of p-type charge carriers contributing to the charge transport. The presence of p-type charge carriers in copper rich composition, y=0.3 & In Gd $^{3+}$ substituted samples x $\leq$ 0.2 are observed from the thermoelectric power measurement (Chapter 3B), which supports the results obtained. The values of loss tangent ($\tan \delta$) are also found to decrease on substitution, which supports the increase in the values of ac resistivities of substituted compositions.
The microstructure of the material is also important in deciding the dielectric constant, loss tangent (\(\tan \delta\)) and ac resistivity [14,30]. In the present case, it is found that the substitution of Gd\(^{3+}\) increases the porosity, and decreases the grains size, which may also have reflected in decreasing the values of complex dielectric constant and loss tangent (\(\tan \delta\)). The decrease of dielectric intensity in the present case may be attributed to the decrease of grain size, and is in conformity with the results discussed by Kramer, et al [14].
References


