Chapter 4

On the Electrical Properties of Nanostructured Manganese Zinc Mixed Ferrites

Temperature and frequency dependence of dielectric permittivity and dielectric loss of nanosized Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ (for x=0, 0.2, 0.4, 0.6, 0.8, 1) were investigated. Maxwell-Wagner theory together with Koop's phenomenological theory was effectively used to explain the dielectric behaviour of ferrites. The impact of zinc substitution on the dielectric properties of the mixed ferrite is elucidated. Strong dielectric dispersion and broad relaxation were exhibited by Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$. The variation of dielectric relaxation time with temperature suggests the involvement of a multiple relaxation processes. Cole-Cole plots were employed as an effective tool for studying the observed phenomena. The activation energies calculated from relaxation peaks and Cole-Cole plots were found to be consistent with each other and indicative of a polaron conduction. The electrical properties, dc conductivity and ac conductivity of nanosized Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ were investigated as a function of frequency, temperature and composition. The activation energy for dc conduction and the mobility of the charge carriers were estimated. The dc conductivity is then explained based on the small polaron conduction process. The frequency dependence of ac conductivity is studied by the power law $\sigma_a(\omega) = B \omega^n$ which is typical for charge transport by hopping or tunneling processes. The temperature dependence of $n$ is investigated to understand the conduction mechanism in the different compositions. The conduction mechanisms are mainly based on polaron hopping conduction. The activation energies for ac and dc conduction were calculated.

Publications


The electrical properties of materials in the nanoregime are totally different when compared to their bulk counterparts in the micron regime. The modification of dielectric properties when the particle size is reduced is attributed to a variety of reasons namely particle size, shape, boundaries and inclusions. This unique dielectric properties of nanosystems have been effectively used in various dielectric based applications such as capacitors, electronic memories and optical filters [1-3]. In addition, intensive studies on further exploitation of their dielectric properties in futuristic high tech devices are also being pursued. Yet the level of understanding of the dielectric properties of nanosystems is far from being satisfactory both from a qualitative and quantitative outlook.

Ferrite materials enjoy special significance in the field of electronic and telecommunication industry because of their novel dielectric and electrical properties which makes them useful in radiofrequency circuits, high quality filters, rod antennas, transformer cores, read/write heads for high speed digital tapes and other devices [4-6]. The electrical and dielectric properties of ferrites provide information necessary for the selection of these materials for specific applications. The properties of ferrites are sensitive to their composition and microstructure, which in turn are sensitive to their processing conditions. Nanoparticles of spinel ferrites by virtue of their unique electronic and physical structure display enhanced properties which may be harnessed for technological applications.

In ferrites, the dielectric properties are explained assuming that a heterogeneous structure consisting of grains and grain boundaries exist [7-9]. Dielectric relaxation was reported in micron sized particles in the frequency regime of 1-100 kHz. Dielectric dispersion and dielectric relaxation was found to change with grain size. In the case of nanometer sized particles the existence of a large number of interface dipoles can give rise to different relaxation processes.
resulting in a broader relaxation. Sharp dispersion and relaxation effect with multiple relaxation times are reported in ferrites in the nanoregime [10]. Dielectric properties are expected to be modified substantially because of the presence of nanosized grains and grain boundaries.

The dielectric permittivity of a material is found to depend on the frequency of measurement. It decreases from static permittivity ($\varepsilon_r$) at low frequencies to a smaller limiting value of ($\varepsilon_a$) at higher frequencies. This has been explained by Debye [11] and the difference in the values of $\varepsilon_r$ and $\varepsilon_a$ has been attributed to dipolar polarization and generally a single relaxation time is associated with the dielectric relaxation. In real dielectrics, different types of dipole species are present and these may give rise to several relaxation times instead of a single one. Hence R H Cole and K S Cole [12] modified Debye's equations to incorporate the effects of multiple relaxation times. These Cole-Cole plots based on these modified equations can be effectively used for studying the dielectric relaxation at the molecular level and for evaluation of the dispersion parameters [chapter2].

The frequency dependent ac conductivity and temperature dependent dc conductivity are the deciding factors for technological applications of ferrites. It is thought that electrical conduction in ferrites results from the thermal activation of electrons or positive holes along chains of neighbouring cations in the ionic lattice. The activation energy for transport mechanism is greatly reduced if the crystal lattice intrinsically contains cations of one element in more than one valence state. In the case of manganese zinc ferrites, electron hopping between $\text{Fe}^{3+} \leftrightarrow \text{Fe}^{2+}$ ions and hole hopping between $\text{Mn}^{2+} \leftrightarrow \text{Mn}^{3+}$ ions are found to be responsible for electrical conduction [13]. Thus conductivity is found to depend on the availability of $\text{Fe}^{2+}/\text{Fe}^{3+}$ ions and $\text{M}^{2+}/\text{M}^{3+}$ pairs in octahedral sites. In micron sized particles prepared by solid state reactions, sintering gives rise to the
of Fe$^{2+}$ and Mn$^{3+}$ ions. However in the nanoregime where no high temperature sintering is involved, presence of Fe$^{2+}$/Fe$^{3+}$ and Mn$^{3+}$/Mn$^{2+}$ will be dependent on the preparative conditions. A cation redistribution which is different from that of their bulk cousins is observed in nanoparticles of ferrites [14]. These factors are bound to play a major role in deciding the overall electrical properties of the nanosized manganese zinc ferrite. Nanoparticles of the series belonging to Mn$_{1-x}$ZnxFe$_2$O$_4$ (where x=0.0, 0.2, 0.4...1) were found to be exhibiting different structural and magnetic properties with respect to their bulk counterparts [chapter 3]. A reduction in lattice parameter, accompanied by reduced magnetization values, enhanced Curie temperature and a metastable cation distribution are all hall marks of nanosized manganese zinc ferrites.

It is in this situation that a detailed investigation on the electrical properties of a series belonging to Mn$_{1-x}$ZnxFe$_2$O$_4$ assumes significance. The employment of Cole-Cole plot to evaluate various parameters namely, $\varepsilon_s$ (static dielectric constant), $\varepsilon_o$ (optical dielectric constant), $\alpha$ (spreading factor), $\tau_o$ (average relaxation time) and $\tau$ (molecular relaxation time) will definitely lead to an understanding of the phenomenon of dispersion occurring in the nanosized mixed ferrites. In this investigation manganese zinc ferrites belonging to the series Mn$_{1-x}$ZnxFe$_2$O$_4$ (for x=0, 0.2, 0.4, 0.6, 0.8 and 1) are synthesized by employing low temperature methods. In order to gain an insight into the phenomenon of dielectric dispersion and absorption, the dielectric properties of these ferrites in the frequency regime of 100 kHz - 8MHz are evaluated and the results are correlated. One can obtain information about the mechanism of conduction and evaluate the activation energy from the analysis of ac and dc conductivities. All these can lead to a good explanation and understanding of the electrical behaviour in ferrites.
4.1 Experimental

Manganese zinc ferrites belonging to the series Mn$_{0.6}$Zn$_{0.4}$Fe$_2$O$_4$ were prepared by using low temperature co-precipitation technique [chapter 3]. The powder samples were pressed into pellets having a diameter of 12mm and 2mm thickness. These pellets were then heat treated at 200°C before being subjected to different studies. Uniformity in heat treatment and pressure applied was ensured for all the samples in the series. The porosity of these samples (all compositions) was determined after evaluating their X-ray densities using the structural parameters derived from XRD measurements. The samples were found to be having a porosity of around 30% and we observed consistency in the values for all the compositions.

The dc conductivity of the sample was measured using a Keithley 236 Source meter and dielectric measurements were carried out on samples in the series using a home made dielectric cell and an HP 4285 LCR meter in the frequency range of 100 kHz - 8MHz over a temperature of 303 K-393 K. The data acquisition was automated by interfacing the LCR meter with a virtual instrumentation package called LabVIEW (National Instruments). Copper discs of same diameter as the pellets were used as contact electrodes and the measurements were carried out under rotary vacuum. Lead and fringe capacitance were eliminated before every run of the sample. Cole-Cole plots for different temperatures were drawn by the circle least square method utilizing the real and imaginary values of dielectric permittivity [15]. Dispersion parameters were evaluated from the Cole –Cole plots [chapter 2].

4.2 Scanning Electron Microscopy Analysis

Scanning electron micrographs of the samples are depicted in figure 4.1(a-d). It can be seen that the grains are uniformly sized and are in the
nanoregime. The micrographs show the presence of a large number of interfaces which have a direct bearing on the dielectric properties of these ferrites.
4.3 Dielectric Properties

4.3.1 Dielectric Dispersion

The variation of dielectric properties with frequency is depicted in figure 4.2 (a-f). It can be seen that the relative dielectric permittivity, $\varepsilon'$, exhibits an inverse dependence with frequency as reported in a number of ferrite compounds. It decreases with increase in frequency and remains a constant at higher frequencies. In our frequency regime of measurements (100 kHz - 8 MHz), it is the polarization due to interface dipoles which contribute to the overall dielectric properties of the sample [16, 17]. Earlier, theories like Maxwell Wagner theory of dielectric dispersion were employed to study the dispersion [7, 8]. It was assumed that the dielectric polarization had its origin in the heterogeneous structure of ferrites with grains and grain boundaries [18]. The effect of grain interfaces are more pronounced at lower frequencies where we observe relatively large values of $\varepsilon'$. The space charge polarization occurring at the interfaces at lower frequencies can also contribute to the dielectric permittivity at lower frequencies.

Many researchers have reported a similarity between conduction process and dielectric polarization in ferrites [10]. Normally, for Manganese zinc ferrites, the conduction process is explained on the basis of electron hopping between Fe$^{2+}$ and Fe$^{3+}$ and hole hopping between Mn$^{2+}$ and Mn$^{3+}$ on the octahedral sites. In the Rezlescue Model, the hopping of electrons/holes results in the local displacements of the electrons/holes which collectively contribute to the total polarization [19]. Denecke et al. observed the presence of Mn$^{3+}$ ions in octahedral sites in co-precipitated manganese zinc ferrite nanoparticles prepared using highly basic solution [20]. The electrons exchanging between Fe$^{2+}$ and Fe$^{3+}$ ions and the holes that transfer between Mn$^{3+}$ and Mn$^{2+}$ ions are responsible for electric conduction and dielectric polarization in manganese zinc ferrites. At higher frequencies, the frequency of electron/hole exchange will not be able to follow
Figure 4.2 Dielectric Permittivity vs. Frequency plot of (a) MnFe$_2$O$_4$
(b) Mn$_{0.8}$Zn$_{0.2}$Fe$_2$O$_4$ (c) Mn$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ (d) Mn$_{0.2}$Zn$_{0.8}$Fe$_2$O$_4$
(e) Mn$_{0.2}$Zn$_{0.8}$Fe$_2$O$_4$ and (f) ZnFe$_2$O$_4$. 
Figure 4.3 Dielectric Permittivity vs. temperature plot of (a) MnFe$_2$O$_4$
(b) Mn$_{0.8}$Zn$_{0.2}$Fe$_2$O$_4$
(c) Mn$_{0.6}$Zn$_{0.4}$Fe$_3$O$_4$
(d) Mn$_{0.4}$Zn$_{0.6}$Fe$_2$O$_4$
(e) Mn$_{0.2}$Zn$_{0.8}$Fe$_2$O$_4$ and (f) ZnFe$_2$O$_4$
the applied electric field thus resulting in a decrease in polarization. Consequently the dielectric permittivity attains a constant value.

The temperature dependence of $\varepsilon'$ at selected frequencies is shown in figure 4.3(a-f). As the temperature increases, the orientations of interface dipoles are facilitated and this enhances the dielectric permittivity.

At lower frequencies the rapid increase in dielectric constant with temperature is mainly due to polarization due to interfacial dipoles which are strongly dependent on temperature [17]. As temperature increases, the accumulation of charges on the grain boundaries increases which causes an increase in the interfacial polarization. This is at lower frequencies. Therefore the dielectric polarization increases resulting in an increase of $\varepsilon'$ with temperature at lower frequencies.

4.3.2 Dielectric Absorption

Dielectric absorption in a material is characterized by $\tan\delta$ and dielectric loss ($\varepsilon''$) values. It can be seen that $\tan\delta$ and $\varepsilon''$ values when plotted against frequency exhibit relaxations at specific frequencies and temperatures (figure 4.4(a-f) and 4.5 (a-f)). Dielectric relaxation occurs when the hopping frequency of charge carriers is equal to the frequency of the applied field [21]. However it is to be noted that a relaxation can be noticed in the case of manganese rich compositions while for the zinc rich compositions the relaxation is found to be absent (figure 4.5 (e-f)). This may be due to the reduction in number of hopping charges available for hopping as the zinc concentration increases. There also is a likelihood that the relaxation peaks corresponding to these compositions lie outside the frequency range of measurement.
Figure 4.4 Tan δ vs. Temperature plot of (a) MnFe$_2$O$_4$ (b) Mn$_{0.8}$Zn$_{0.2}$Fe$_2$O$_4$
(c) Mn$_{0.6}$Zn$_{0.4}$Fe$_2$O$_4$ (d) Mn$_{0.4}$Zn$_{0.6}$Fe$_2$O$_4$ (e) Mn$_{0.2}$Zn$_{0.8}$Fe$_2$O$_4$ and (f) ZnFe$_2$O$_4$
Figure 4.5 Dielectric loss vs. Log(f) plot of (a) MnFe$_2$O$_4$, (b) Mn$_{0.8}$Zn$_{0.2}$Fe$_2$O$_4$, (c) Mn$_{0.6}$Zn$_{0.4}$Fe$_2$O$_4$, (d) Mn$_{0.4}$Zn$_{0.6}$Fe$_2$O$_4$, (e) Mn$_{0.2}$Zn$_{0.8}$Fe$_2$O$_4$, and (f) ZnFe$_2$O$_4$. 
4.3.3 Effect of Zinc Substitution on dielectric properties

The zinc substitution has a direct influence in modifying the dielectric characteristics. The variation of $\varepsilon$ with zinc compositions is studied for different temperatures and different frequencies (figure 4.6 (a-b)).

![Figure 4.6 Dielectric Permittivity vs. zinc content (a) at 303 K and (b) at 8MHz](image)

The dielectric permittivity decreases with increase in zinc content. With increasing zinc content there is a decrease in manganese ions ($\text{Mn}^{3+}$) and consequently the presence of $\text{Fe}^{2+}$ ions in the octahedral sites is also reduced. Hence the number of $\text{Mn}^{3+}/\text{Mn}^{2+}$ and $\text{Fe}^{3+}/\text{Fe}^{2+}$ pairs available for hole and electron hopping will be less in number as we increase the zinc content. As a result hopping decreases and the charged species are accumulated at the grain boundaries. Therefore the resistance of the grain boundaries increases and hence the probability of charged species to cross over the grain boundaries decreases. This will subsequently result in reduced hopping and dielectric polarization which is manifested in low permittivity values in zinc rich compositions.

Figure 4.7 (a-b) depicts the effect of zinc substitution on the $\tan \delta$ of the $\text{Mn}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ series. A reduction in dielectric absorption values is seen with an
increase in zinc concentration. A decrease in the Fe$^{2+}$/Fe$^{3+}$ and Mn$^{2+}$/Mn$^{3+}$ pairs available for conduction with increase in zinc concentration can be thought of as one of the reasons for this type of behaviour in manganese zinc ferrites.

![Graph](image)

**Figure: 4.7 tanδ vs. zinc content** (a) at 303 K and (b) at 8MHz

We have suggested that the dielectric polarization can be explained based on the hopping of charge carriers. A relaxation occurs when the hopping frequency equals the applied frequency. The evaluation of the activation energy can provide more insight on the transport properties of ferrites [22].

### 4.3.4 Activation Energy from relaxation peaks

The condition for observing a maximum in the dielectric loss of a dielectric material is given by the relation [21],

$$\omega \tau' = 1$$

where $\tau'$ is the relaxation time and

$$\omega = 2\pi f_{\text{max}}$$

(4.1)

The value of $f_{\text{max}}$ can easily be observed from figure 4.4(a-f). The relaxation time $\tau$ can be determined from equation (4.1). Then $\tau$ can be written as,

$$\tau' = \tau_0 \exp\left(\frac{E_d}{k_B T}\right)$$

(4.2)
where $\tau_0$ is the pre exponential constant which equals the relaxation time at infinitely high temperatures, $k_B$ is the Boltzmann's constant, $T$ is the temperature in degree absolute and $E_d$ the activation energy for dielectric relaxation.

![Graph showing $\tau'$ vs. temperature](image)

**Figure 4.8** Relaxation time ($\tau$) vs temperature

The variation of $\tau'$ with temperature is shown in figure (4.8) which showed a decrease in relaxation time with temperature. This point towards the possibility of existence of multiple relaxation mechanisms with a distribution of relaxation times in the nanosystems.

From the slope of the graph between $\ln \tau'$ vs. $1000/T$, $E_d$ the activation energy for dielectric relaxation can be determined (figure 4.9).

![Graph showing $\ln \tau'$ vs. $1000/T$](image)

**Figure 4.9** $\ln \tau'$ vs. $1000/T$ (K$^{-1}$)
The hopping depends on the activation energy which is associated with the electrical energy barrier experienced by the electrons during hopping. Since \( \tau = \frac{1}{2P} \) where \( P \) is the hopping probability, the decrease in relaxation time with temperature results in an increase in hopping probability with temperature.

The activation energy for dielectric relaxation for MnFe\(_2\)O\(_4\), Mn\(_{0.8}\)Zn\(_{0.2}\)Fe\(_2\)O\(_4\) and Mn\(_{0.6}\)Zn\(_{0.6}\)Fe\(_2\)O\(_4\) is calculated and found to be 0.329eV, 0.412eV and 0.497eV respectively. The large values of activation energy points towards polaron hopping. The observation of a relatively large value of activation energy and relaxation nature of dielectric loss suggests two distinct conduction processes namely Quantum mechanical tunneling through the barrier separating the two equilibrium positions and the classical hopping of a carrier over the barrier or some combination or a variant of the two[23-24].

The presence of a strong dielectric dispersion and broad relaxation peaks in the dielectric loss spectra are indicative of multiple relaxations. Therefore Cole-Cole plots were employed as an effective tool for studying the observed phenomena [26]. Knowledge of dispersion parameters can help reveal the dynamics of the relaxation phenomena in these materials.

### 4.3.5 Cole-Cole Analysis

The Cole-Cole plots corresponding to the compositions of MnFe\(_2\)O\(_4\) and Mn\(_{0.8}\)Zn\(_{0.2}\)Fe\(_2\)O\(_4\) were plotted since a relaxation in \( \varepsilon'' \) was found absent for all composition with \( x \) greater than 0.2. They are shown in figure 4.10(a-c) and figure 4.11(a-c). From the Cole-Cole analysis, the dispersion parameters of these two compositions were evaluated. The dispersion parameters like \( \varepsilon_\infty \) (static dielectric constant), \( \varepsilon_\alpha \) (Optical Dielectric constant), \( \alpha \) (Spreading factor), \( \tau_0 \) (Average Relaxation Time) and \( \tau \) (Molecular Relaxation Time) of the two samples are evaluated and they are tabulated and their variation with temperature is analyzed.
The optical dielectric constant (\(\varepsilon_0\)) is found to be increasing with temperature (figure 4.12), while the static dielectric constant is found to decrease (figure 4.13).
However the variation of the two limiting values of dielectric permittivity within the measured temperature range was not very large. The spreading factor is a measure of the broadening of the relaxation time (figure 4.14).

The average relaxation time is the effective time constant for the relaxation involved while molecular or intrinsic relaxation time is the time constant for the immediate molecular dipole relaxation.
Both average relaxation time and molecular relaxation time decreases with increasing temperature (table 4.1). The rise in temperature causes a reduction in the mean time of stay of dipoles resulting in a decrease of relaxation time with temperature. Hence, as relaxation time decreases with temperature there is a decrease in spreading factor. Activation energy for dielectric relaxation can be calculated from the slope of $\ln \tau$ vs. $1000/T$ plot (figure 4.15). The activation energy calculated for the MnFe$_2$O$_4$ and Mn$_{0.8}$Zn$_{0.2}$Fe$_2$O$_4$ are 0.315 eV and 0.426 eV respectively. These values were found to be in very good agreement with those calculated from relaxation peaks (0.329 eV for MnFe$_2$O$_4$ and 0.412 eV for Mn$_{0.8}$Zn$_{0.2}$Fe$_2$O$_4$) The activation energy is found to be increasing with zinc substitution.
Table 4.1 Dispersion Parameters from Cole-Cole Analysis

<table>
<thead>
<tr>
<th>T(K)</th>
<th>$\varepsilon_\infty$</th>
<th>$\varepsilon_a$</th>
<th>$\alpha$</th>
<th>$\varepsilon''$</th>
<th>$\tau_0 \times 10^8$ sec</th>
<th>$\tau \times 10^8$ sec</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MnFe</td>
<td>Zn0.2</td>
<td>MnFe</td>
<td>Zn0.2</td>
<td>MnFe</td>
<td>Zn0.2</td>
</tr>
<tr>
<td>373</td>
<td>85.85</td>
<td>43.75</td>
<td>6.41</td>
<td>5.16</td>
<td>0.326</td>
<td>0.289</td>
</tr>
<tr>
<td>363</td>
<td>84.02</td>
<td>43.83</td>
<td>6.11</td>
<td>5.12</td>
<td>0.308</td>
<td>0.293</td>
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<td>44.05</td>
<td>6.02</td>
<td>5.06</td>
<td>0.302</td>
<td>0.299</td>
</tr>
<tr>
<td>343</td>
<td>85.67</td>
<td>45.12</td>
<td>5.78</td>
<td>4.85</td>
<td>0.314</td>
<td>0.324</td>
</tr>
<tr>
<td>333</td>
<td>89.97</td>
<td>47.43</td>
<td>5.65</td>
<td>4.67</td>
<td>0.341</td>
<td>0.357</td>
</tr>
</tbody>
</table>

$\varepsilon_\infty$ – Static dielectric constant
$\varepsilon_a$ – Optical Dielectric constant
$\alpha$ – Spreading Factor
$\varepsilon''$ – Dielectric Loss
$\tau_0$ – Average Relaxation Time
$\tau$ – Molecular Relaxation Time
4.4 AC Conductivity Studies

The variation of ac conductivity with frequency and temperature is given in figure 4.16 (a-f). It is observed that initially the ac conductivity increases with frequency, reaches a maximum and then decreases. As the frequency of the applied field increases, hopping of charge carriers also increases thereby increasing the conductivity. But at higher frequencies, the hopping of charge carriers could not follow the applied field frequency and it lags behind the applied frequency resulting in a decrease in the ac conductivity values.

The increase of ac conductivity with frequency and temperature could also be explained on the basis of Koops model which assumes that ferrite samples act as a multilayer capacitor [7-8]. According to this model, at low frequencies, the conductivity is due to the grain boundaries, while the dispersion at higher frequencies is due to the conducting grains.

AC conductivity decreases with zinc concentration as in the case of dc conduction indicating decrease in the availability of charge carriers with increasing zinc content (figure 4.17). With increasing zinc content, there is a decrease in manganese ions (Mn$^{3+}$) and consequently the presence of Fe$^{2+}$ ions in the octahedral sites is also reduced. Hence the number of Mn$^{3+}$-Mn$^{2+}$ and Fe$^{2+}$-Fe$^{3+}$ pairs available for hole and electron hopping will be less in number as the zinc content is increased. As a result, hopping decreases and charged species accumulate on the grain boundaries. Therefore the resistance of the grain boundary increases and hence the probability of charged species crossing over the grain boundaries decreases. This eventually reduces conductivity with increasing zinc substitution. So there is relatively large number of hopping pairs in manganese ferrite compared with the other compositions.
Figure 4.16 Variation of ac conductivity with frequency and temperature of
(a) MnFe$_2$O$_4$ (b) Mn$_{0.8}$Zn$_{0.2}$Fe$_2$O$_4$ (c) Mn$_{0.6}$Zn$_{0.4}$Fe$_2$O$_4$ (d) Mn$_{0.4}$Zn$_{0.6}$Fe$_2$O$_4$
(e) Mn$_{0.2}$Zn$_{0.2}$Fe$_2$O$_4$ (f) ZnFe$_2$O$_4$
In the case of zinc ferrite the presence of hopping pairs may be entirely due to the presence of zinc ions in the octahedral sites which give rise to electron hopping $\text{Fe}^{2+}$-$\text{Fe}^{3+}$ pairs. It is interesting to see that (figure 4.16 (a-f)) in manganese rich compositions, the increase in ac conductivity with frequency and temperature in the kHz region is diminutive while in the case of zinc rich samples there is marked increase in conductivity with temperature and frequency in this regime. Hence different conduction mechanism can be expected in these compositions.

The real part of ac electrical conductivity consists of two terms [25]

$$\sigma = \sigma_1(T) + \sigma_2(\omega,T)$$

(4.3)

The first term is the temperature dependent dc conductivity which is related to the drift of electric charge carriers and follows an Arrhenius relation given by

$$\sigma_1(T) = \sigma_0 \exp \left(-\frac{E_a}{k_BT}\right)$$

(4.4)
where $E_a$ is the activation energy for electric conduction. $\sigma_0$ the pre-exponential factor. The activation energy at different frequencies can be found out by plotting $\ln \sigma_{ae}$ vs temperature from eqn 4.4 (figure 4.18).

![Graph](image_url)

**Figure 4.18** $\ln \sigma_{ae}$ vs $1000/T$ for Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ at 4MHz

From the slope of the linear region of the graph, $E_a$ for electrical conduction at 4MHz is determined. The variation of activation energy with zinc content indicates an increasing trend with increasing zinc content (figure 4.8). Since both hole hopping between Mn$^{3+}$-Mn$^{2+}$ and Fe$^{2+}$-Fe$^{3+}$ electron hopping can happen in these ferrites, the activation energy calculated can be taken as an average of the activation energies for the two hopping processes and should be less than 0.21eV [20]. The higher activation energies are associated with polaron conduction. In ferrites, the cations are surrounded by close packed oxygen anions and hence can be treated as isolated from each other. There will be little direct overlap of the charge clouds or orbitals. Hence a localized electron model is appropriate in the case of electrons. When the charge carriers are localized, charge transport take place via phonon assisted hopping between localized sites. Localization of the charge carriers may give rise to the formation of polarons and the charge transport may be considered between the nearest neighbour sites [10].
Hence polaron conduction can be expected in these ferrites as indicated by dielectric measurements. The temperature and frequency dependent ac conductivity in equation (4.4) which is related to the dielectric relaxation caused by the localized charge carriers is given by the power law [26].

\[ \sigma_2(\omega, T) = B(T)\omega^n(T) \]  

(4.5)

where \( B \) is the parameter having the unit of conductivity and \( n \) is a dimensionless parameter.

Since ac conductivity is frequency dependent in the lower temperature region, the power law (equation 4.5) can be applied to the experimental data by plotting the graph \( \log\sigma_{ac} \) vs. \( \log\omega \) for different compositions. This is done for the frequency region where \( \sigma_{ac} \) is exhibiting an increase with frequency. The value of \( n \) is estimated from the slope of the \( \log\sigma_{ac} \) vs. \( \log\omega \) graphs. The dependence of \( n \) with temperature is plotted and is shown in figure 4.19(a-f).

It is known that variation of \( n \) with temperature can throw light on the conduction mechanism [27, 28]. If \( n \) increases with temperature, small polaron tunneling is the predominant mechanism [29]. A minimum value of \( n \) followed by an increase suggests that the predominant conduction is by overlapping large polaron tunneling mechanism [30]. Under such circumstances \( n \) is temperature independent and quantum mechanical tunneling is the possibility [31]. The correlated barrier hopping [32] is usually associated with decrease of \( n \) with temperature. It can be seen that the behaviour of \( n \) is different in the manganese rich and zinc rich compositions. This observation indicated a different conduction mechanism in these compositions. In manganese rich compositions of the series \( \text{Mn}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4 \) for \( x \leq 0.5 \) the value of \( 'n' \) is found to be increasing with temperature (figure 4.19 (a-c)). This is characteristic of small polaron tunneling and can be explained based on small polaron tunneling model for ac conduction [29].
Figure 4.19 Variation of ‘n’ with temperature for (a) MnFe₂O₄ (b) Mn₀.₈Zn₀.₂Fe₂O₄ (c) Mn₀.₆Zn₀.₄Fe₂O₄ (d) Mn₀.₄Zn₀.₆Fe₂O₄ (e) Mn₀.₂Zn₀.₈Fe₇O₄ and (f) ZnFe₂O₄
The frequency exponent $n$ based on this model is evaluated as,

$$n = 1 - \frac{4}{\ln \left( \frac{1}{\omega \tau_0} \right) - \frac{W_H}{k_B T}}$$

(4.6)

where $k_B$ is the Boltzmann’s constant, $T$ the temperature, $W_H$ is the barrier height for infinite site separation, $\tau_0$ the relaxation time and $\omega$ the angular frequency. According to this model, the ac conductivity is given by

$$\sigma(\omega) = \frac{\pi^4 e^2 k_B T N(E_F)}{24} \frac{\omega R_w^4}{\alpha}$$

(4.7)

where $e$ is the electronic charge, $k_B$ is the Boltzmann’s constant, $T$ the temperature and $\alpha$ is the spatial extent of polaron, $N(E_F)$ the density of states at the Fermi level and $R_w$ is the tunneling distance.

However in the case of zinc rich compositions of $\text{Mn}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ upto $\text{Zn}=0.8$ the variation of ‘$n$’ is found to be different (figure 4.19(d)-4.19(e)). The value of ‘$n$’ decreases with temperature, reaches a minimum and then increases. This behaviour is in accordance with the variation of ‘$n$’ in overlapping large polaron tunneling model (OLPT) of ac conduction [33].

The frequency exponent ‘$n$’ is given by the equation

$$n = 1 - \frac{8 \alpha R_w + \frac{6 \beta W_{HO} r_p}{R_w}}{\left( 2 \alpha R_w + \frac{\beta W_{HO} r_p}{R_w} \right)^2}$$

(4.8)

where $\beta$ is $1/k_B T$, $k_B$ is the Boltzmann’s constant, $T$ is the temperature in degree absolute, $r_p$ is the polaron radius separation and $W_{HO}$ is the barrier height for infinite site separation, $\alpha$ the spatial extent of the polaron, $N(E_F)$ the density of states at the Fermi level and $R_w$ is the tunneling distance.

The ac conductivity for OLPT model is given by [30]
The maximum resistivity is observed in the case of zinc ferrite where a decrease of \( n \) with temperature is found (figure 4.19f). This variation of \( n \) with temperature is similar to that predicted by correlated barrier hopping conduction model using the equation, [32]

\[
\frac{n}{1} = 1 - \frac{6k_B T}{W_{\nu} + k_B T \ln (\omega \tau_{\nu})} \tag{4.10}
\]

The correlated barrier hopping model predicts ac conductivity as

\[
\sigma(\omega) = \frac{\pi^3}{24} [N(E_F)]^2 \varepsilon \varepsilon_0 \omega R_\sigma \tag{4.11}
\]

Where \( N(E_F) \) the density of states at the Fermi level, \( \varepsilon \) the dielectric permittivity of the medium \( \varepsilon_0 \) is the free space permittivity and \( R_\sigma \) the hopping distance.

It has been found that apparently the mechanism of ac conduction in nanostructured manganese zinc ferrites is found to be different for different compositions. The formation of small non overlapping polarons in the manganese rich compositions may be directly related to the availability of more hopping charge pairs in these ferrites. When there is a reduced number of hopping charges, the spatial extent of the polaron may extend to several inter atomic distances resulting in the formation of overlapping large polarons. Hence Overlapping Large Polaron Tunneling conduction is observed in the zinc rich compositions. Since pristine zinc ferrite is free of Mn\(^{2+}\)-Mn\(^{3+}\) pairs, it is to be expected that in ZnFe\(_2\)O\(_4\), the conductivity is predominating because of Fe\(^{3+}\)-Fe\(^{2+}\) electron hopping in the lattice. But the formation of these hopping ion pairs depends on the occupancy of Zn\(^{2+}\) ions in the octahedral sites preferentially. So the observed conduction mechanism in zinc ferrite is correlated Barrier hopping conduction based on hopping of charge carriers between two sites over a barrier separating...
them. A clear understanding of the conduction mechanism in nanostructured ferrites remain elusive unless and until the conductivity measurements are carried out for a wide range of frequencies and over a wide temperature range.

4.5 DC Conductivity Studies

The dc conductivity values varied between $10^{-5}$ S/m to $10^{-9}$ S/m for pristine manganese ferrite to pristine zinc ferrite. The variation of conductivity with temperature indicates the semiconducting nature of the ferrites (figure 4.20). But a localized electron model is more appropriate in the case of ferrites rather than the collective electron band model (for semiconductors).

![Figure 4.20 Variation $\sigma_{dc}$ with temperature](image)

Based on hopping model, electron hopping between Fe$^{2+} \leftrightarrow$Fe$^{3+}$ ions and hole hopping between Mn$^{3+} \leftrightarrow$ *Mn$^{2+}$ ions collectively contribute to the conductivity in these ferrites. Hence the conductivity depends largely on the availability of charge carriers and their mobility. The dc conductivity decreases with increasing zinc content as in the case of ac conductivity and pure zinc ferrite is found to possess very high resistivity values. The decrease in conductivity can hence explained on the basis of decrease in hopping pairs. The activation energy
for dc conduction is evaluated from Arrhenius relationship and is given in Table 4.2. The activation energy for dc and ac conduction is found to be different. This may be due to the frequency and temperature dependence of ac conduction. But both the values exhibit a decrease with zinc content indicating an increase in resistivity.

Since the conductivity in ferrites directly depends on the mobility of charge carriers, the evaluation of the mobility values can throw light on the nature of charge carriers involved in conduction. The mobility \( \mu \) of the charge carriers was calculated from the experimental values of the electrical conductivity \( (\sigma) \) and charge carrier concentration \( (n_e) \) using the expression [34].

\[
\mu = \frac{\sigma}{n_e e}
\]  

(4.12)

where \( e \) is electrical charge of the carrier.

The charge carrier concentration can be determined using the relation

\[
n_e = \frac{N_a X_s P_{Fe}}{M}
\]  

(4.13)

where \( N_a \) is the Avogadro number, \( X_s \) the sintered density and \( P_{Fe} \) is the number of Fe atoms in one mol of the ferrite and \( M \) the molecular weight.

The mobility obtained for different samples and its variation with temperature is shown in figure (4.21). It can be noticed that the mobility increases with temperature and decreases with zinc concentration. The mobility is found to lie in the range \( 10^{-10} \) to \( 10^{-12} \) cm\(^2\)/V.sec. This mobility is found to be lower than that for electrons \( (10^{-4} \) cm\(^2\)/V/sec) and holes \( (10^{-8} \) cm\(^2\)/V.sec) [39]. These mobility values are found to be the same as that of the mobility of small polarons. So it is reasonable to assume that small polarons are involved in the conduction process in these ferrites.
A small polaron is created when an electron gets trapped at a given site as a consequence of the displacement of adjacent atoms or ions. The entire defect then migrates by an activated hopping mechanism. Low value of mobility, temperature independent Seebeck co-efficient and thermally activated hopping are important characteristics of small polaron conduction.

The polaron radius \( r_p \) [35] for all the compositions was calculated by employing the relation

\[
r_p = \frac{1}{2} \left( \frac{\pi}{6N} \right)^{\frac{1}{3}}
\]

where \( N \) is the number of interstitial sites per unit volume \((96/a^3)\). In spinel ferrites 64 octahedral (A) sites and 32 tetrahedral (B) sites are available per unit volume.

The calculated values of \( r_p \) for different zinc concentrations are found to be \(-0.5\) Å. Since the polaron radius is lower than the hopping distance (inter ionic distance between octahedral sites - 2.93Å). Small polaron hopping is a possibility in these compositions.

The expression for conductivity in small polaron conduction [36] is given by the equation

\[
\sigma = \frac{e^2}{4\pi^2} \frac{1}{r_p^2}
\]
\[ \sigma = \frac{A}{T} \exp\left(-\frac{E_A}{k_B T}\right) \]  
(4.15)

where \( T \) is temperature in degree absolute and \( E_A \) is the activation energy for conduction and \( A \) is a constant. The value of \( A \) is given by

\[ A = \frac{\nu_{ph} N e^2 R^2 c(1-c) \exp(2\alpha R)}{k_B} \]  
(4.16)

where \( N \) is the number of ion sites per unit volume, \( R \) average intersite spacing, \( c \) is the fraction of sites occupied by polaron, \( \alpha \) is the electron wave function decay constant, \( \nu_{ph} \) is optical phonon frequency and \( k_B \) is the Boltzmann’s constant.

Further, in order to check whether the conduction process obeys Small Polaron Hopping, a graph is plotted with \( \log \sigma T \) on the Y-axis and \( 1/T \) on the X-axis (figure 4.22).

![Figure 4.22 log \( \sigma T \) vs \( 1/T \)](image)

We obtained straight line graphs for different compositions which points to the possibility of small polaron assisted transport in these mixed ferrites [37]. The inferences arrived based on the above discussions are tabulated and are shown in table 4.2.
<table>
<thead>
<tr>
<th>Composition Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$</th>
<th>Activation energy for</th>
<th>AC Conduction (eV)</th>
<th>DC Conduction (eV)</th>
<th>AC Conduction Mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnFe$_2$O$_4$</td>
<td>0.372</td>
<td>0.303</td>
<td>Small Polaron Tunnelling</td>
<td></td>
</tr>
<tr>
<td>Mn$<em>{0.8}$Zn$</em>{0.2}$Fe$_2$O$_4$</td>
<td>0.344</td>
<td>0.292</td>
<td>Small Polaron Tunnelling</td>
<td></td>
</tr>
<tr>
<td>Mn$<em>{0.6}$Zn$</em>{0.4}$Fe$_2$O$_4$</td>
<td>0.388</td>
<td>0.31</td>
<td>Small Polaron Tunnelling</td>
<td></td>
</tr>
<tr>
<td>Mn$<em>{0.4}$Zn$</em>{0.6}$Fe$_2$O$_4$</td>
<td>0.468</td>
<td>0.348</td>
<td>Overlapping Large Polaron Tunnelling</td>
<td></td>
</tr>
<tr>
<td>Mn$<em>{0.2}$Zn$</em>{0.8}$Fe$_2$O$_4$</td>
<td>0.473</td>
<td>0.358</td>
<td>Overlapping Large Polaron Tunnelling</td>
<td></td>
</tr>
<tr>
<td>ZnFe$_2$O$_4$</td>
<td>0.833</td>
<td>0.495</td>
<td>Correlated Barrier Hopping</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.2 Activation energy and ac conduction mechanism in Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$

4.6 Conclusion

The frequency and temperature dependence of the dielectric parameters of Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ nanoparticles were studied. The low frequency dielectric dispersion was explained in terms of Maxwell-Wagner theory of interfacial polarization. The effect of grains and grain interfaces were found to be enhanced in the nanoregime. The mechanism of dielectric polarization was found to be similar to that of conduction process involving the hopping/tunneling of charge carriers. The decrease in $\varepsilon$ and $\varepsilon''$ with zinc substitution point to the decrease in availability of Mn$^{2+}$-Mn$^{1+}$ and Fe$^{2+}$-Fe$^{3+}$ pairs with increasing zinc. The tan$\delta$ and $\varepsilon''$ exhibit strong relaxation peaks and relaxation time $\tau$ was estimated from these relaxations. The activation energy for dielectric relaxation determined from $\tau$ values suggested a conduction involving polaron hopping or tunneling. The presence of dielectric relaxation implies the existence of multiple relaxation
processes occurring in the system. Signatures corresponding to the existence of multiple relaxation times were evident from the Cole-Cole plot. Cole-Cole plots provide dispersion parameters and their temperature dependence was also studied. The transport behaviour of nanosized Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ is evaluated by measuring the dc conductivity and ac conductivity. Both ac and dc conductivity are found to decrease with increasing zinc content. This was confirmed by the increase in activation energy with zinc substitution. The higher values of activation energy indicated a conduction mechanism involving hopping of polarons. The evaluation of drift mobility and polaron radius confirmed small polaron conduction as the conduction mechanism responsible for dc conductivity. The frequency dependent term of ac conductivity was analysed and the frequency parameter ‘n’ for the different compositions are evaluated. Based on the variation of $n$ with temperature, appropriate conduction mechanisms are proposed for the different compositions. However scope exists for elaborate theoretical studies on this type of polaron conduction mechanisms in ferrites.

References