Properties of nano ferrites are greatly influenced by the size and shape of the synthesized nano particles. Hence a comparative study on the structural and electrical properties of nano zinc ferrites of different crystallite size has significance. Zinc ferrite nanoparticles with different crystallite size distribution were prepared by sol-gel technique. Various techniques like the XRD, TEM, WD–XRF, were used to study the structural and morphological parameters of the prepared samples. An impedance analyzer was used to study the variation in electrical properties as a function of frequency, temperature and grain size. This chapter presents a detailed discussion on the above topics.
3.1 Introduction

Ferrites are ferrimagnetic oxides of iron and metals with general formula, $\text{MFe}_2\text{O}_4$ (Where M can be any divalent metal ions such as Co, Ni, Mn, Zn etc.). Nano scale spinel ferrites have been subjected to intense research due to their technological demand in high performance devices. Among the various ferrites, zinc ferrite finds a special position due to its high electromagnetic performance, excellent chemical stability, mechanical hardness and low coercivity etc, thus making it a potential candidate for soft magnets and as a low loss material at high frequencies [1, 2]. In bulk structure, zinc ferrite exhibits a normal spinel structure and shows paramagnetic behaviour at room temperature, with a Neel temperature of 10K [3]. But in a nano regime, it exhibits superparamagnetism [4 - 6].

Structural and electrical properties of nano particles depend on the size and shape of the nanoparticles. Preparation of nano particles of desired shape and size still remains a significant challenge to researchers. The method of preparation, the sintering temperature as well as the sintering time strongly influences the size and shape of nano particles and this in turn changes the properties of nano ferrites [7].

A survey of the literature reveals that the magnetic properties of zinc ferrites have been studied in plenty [6, 8 - 10]. But a systematic study on the dependence of electrical properties on particle size of zinc ferrite has not been reported much. Ferrites are very good dielectric materials with wide range of applications ranging from microwave frequencies to radio frequencies. Materials with high resistance and low dielectric loss find applications in microwave devices [11, 12]. In ferrites, temperature variation does not affect the carrier concentration but affects the mobility and hence the conductivity [13]. Thus the
conduction mechanism of ferrites is entirely different from that of the semiconductors. An investigation on the dielectric properties of ferrites will reveal information on the localized electric charge and hence will provide a greater understanding of the mechanism of dielectric polarization in ferrites [14, 15].

Zinc ferrite with varying particle size in the nano regime was prepared by sol–gel technique. Their structural and electrical properties were evaluated and correlated in this chapter.

3.2 Synthesis of Nano Zinc Ferrite

Nano sized zinc ferrite was prepared by sol-gel technique. The details of the preparation technique are already presented in section 2.2.1. The prepared sample was divided into five parts. One part was kept as such and was marked as ZF0, and each of the other four samples were fired at 300°C, 400°C, 500°C and 600°C for two hours and were marked as ZF300, ZF400, ZF500, ZF600 respectively. Cylindrical disc shaped pellets of diameter 10mm and thickness 2mm to 3mm were made from each of the sample by using a hydraulic press keeping a uniform pressure of 5 ton. These pellets coated with silver paste were then taken for dielectric and resistivity measurements.

3.3 Structural Characterization

3.3.1 TGA/DTA

The dried gel of the prepared zinc ferrite was used for TGA/DTA, the result is shown in Figure 3.1.
Endothermic peaks were observed before 380°C in the DTA Curve. From the figure it is also clear that the decomposition of the sample occurred through two steps. The first weight loss is observed in the range of 30°C to 180°C which could be due to the loss of moisture in the dried gel. The second weight loss from 330°C to 380°C which is accompanied by an endothermic curve in the DTA curve could be due to the combustion of nitrates and the remaining organic substances and rearrangement of oxides to form the spinel phase. There is no weight loss from 380°C onwards which shows the sample is thermally stable above this temperature.

3.3.2 X–Ray Diffraction Studies

Figure 3.2 presents the XRD pattern of the zinc ferrite samples sintered at different temperatures. Comparison of the XRD patterns with the standard data (JCPDS Card No: 82 – 1042) confirms the formation of a single phased polycrystalline fcc spinel structure without any extra lines corresponding to any other crystallographic phases.
From figure 3.2, it is very evident that the crystallinity increases sharply as there is a decrease in the broadening of the peaks in the diffraction pattern when the firing temperature increases. The crystallite size of the samples and the error factor of the samples fired at different temperature were evaluated using the Debye Scherrer formula, from the most prominent peak (311) by fitting the curve with the function $P_{\text{Voigt1}}$ and is tabulated in Table 3.1.

**Table 3.1: Crystallite size, X-ray density and Lattice Strain**

<table>
<thead>
<tr>
<th>Firing Temperature (°C)</th>
<th>Crystallite Size (nm)</th>
<th>X-ray Density (gm/cm$^3$)</th>
<th>Crystallite Size from HW Plot (nm)</th>
<th>Lattice Strain ($\times 10^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As Prepared</td>
<td>12.7±0.2</td>
<td>5.13</td>
<td>14.2</td>
<td>-0.39</td>
</tr>
<tr>
<td>$T = 300$</td>
<td>16.8±0.3</td>
<td>5.18</td>
<td>24.7</td>
<td>0.90</td>
</tr>
<tr>
<td>$T = 400$</td>
<td>18.7±0.4</td>
<td>5.35</td>
<td>26.2</td>
<td>0.33</td>
</tr>
<tr>
<td>$T = 500$</td>
<td>19.2±0.3</td>
<td>5.37</td>
<td>29.0</td>
<td>0.69</td>
</tr>
<tr>
<td>$T = 600$</td>
<td>31.1±1.3</td>
<td>5.40</td>
<td>45.3</td>
<td>0.97</td>
</tr>
</tbody>
</table>

The Rietveld refinement technique was used to analyze the diffraction data, with the help of a profile fitting program GSAS, developed by Larson and Van Dreele [16]. The initial structural and microstructural parameters assigned for all the samples were: space group–Fd3m; wyckoff positions of metal and iron atoms as 8a and 16d and oxygen in (x,x,x) special position.
where \( x = 0.255 \) [17]. All the octahedral, tetrahedral and oxygen sites were assumed to be fully occupied. Figure 3.3 (a) – (c) shows three representative rietveld refinement plots for samples ZF0, ZF400 and ZF600.

![Rietveld refinement plots](image)

**Figure 3.3:** Rietveld refinement plots for samples (a) ZF0, (b) ZF400, (c) ZF600

The fitting quality of the experimental data was assessed applying the two parameters: the goodness of fit (\( \chi^2 \)) should tend to 1 and the two reliability factors \( R_p \) and \( R_{wp} \) (Weighted difference between measured and calculated values) should be less than 10\% [17].

Lattice strain and crystallite size were estimated using the powerful Hall-Williamson method [18]. The effect of size and strain induced broadening in the XRD peaks can be deconvoluted by considering the peak as a function of 20 [19, 20]. Hall–Williamson plots were plotted for all the samples and the average
crystallite size and lattice strain for all samples are given in table 3.1. Figure 3.4 (a) to (c) represents the H-W plots for the samples ZF0, ZF400 and ZF600.

![H-W plots for ZF0, ZF400, and ZF600](image)

**Figure 3.4 (a) – (c):** Representative Hall–Williamson plots of zinc ferrite

It is seen that the unfired sample ZF0 showed compressive strain (negative value of strain) while all the fired samples showed tensile strain (positive value of strain). This could be due to the fact that a strain depends on the sintering effects, effect of grain boundaries, stacking faults etc. [21]. From table 3.1 it can be seen that crystallite size obtained by the Scherrer equation is smaller, compared to the crystallite size calculated by the Hall-Williamson method. Generally crystallite size calculated by the Hall-Williamson method is more accurate, as it does not take into account the peak broadening due to any lattice strain or the effects of instrumental factors on peak broadening [22].
3.3.3 Transmission Electron Microscope

Figure 3.5 (a) to (f) shows TEM images of ZnFe$_2$O$_4$ samples and the size distribution histograms of the nanoparticles (ZF0, ZF400, ZF600).

![TEM image and particle size distribution histogram of ZF0](image1.png)

**Figure 3.5 (a) & (b):** TEM image and particle size distribution histogram of ZF0

![TEM image and particle size distribution histogram of ZF400](image2.png)

**Figure 3.5 (c) & (d):** TEM image and particle size distribution histogram of ZF400

![TEM image and particle size distribution histogram of ZF600](image3.png)

**Figure 3.5 (e) & (f):** TEM image and particle size distribution histogram of ZF600
In all the TEM images, the nanoparticles appear to be spherical in shape though some of them are agglomerated. All the samples showed a narrow size distribution and the average particle size of the nanoparticles obtained from the TEM image analysis was found to be \((14 \pm 2)\) nm for ZF0, \((19 \pm 3)\) nm for ZF400 and \((36 \pm 2)\) nm for ZF600.

### 3.3.4 WD–XRF Elemental Analysis

The stoichiometry of the prepared powder samples were analyzed using the WD–XRF analysis. The compositional analysis of ZF0 and ZF400 are tabulated in table 3.2. From the table 3.2, it is clear that the samples showed the expected stoichiometry. The chemical purity of the samples were confirmed and no trace of any impurity was found.

<table>
<thead>
<tr>
<th>Elements Present</th>
<th>ZF0 Expected (wt%)</th>
<th>WD-XRF (wt%)</th>
<th>ZF400 Expected (wt%)</th>
<th>WD–XRF (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>46.331</td>
<td>46.991</td>
<td>46.331</td>
<td>46.370</td>
</tr>
<tr>
<td>Zn</td>
<td>27.121</td>
<td>26.521</td>
<td>27.121</td>
<td>26.170</td>
</tr>
</tbody>
</table>

### 3.4 Electrical Properties

The electrical properties of the prepared zinc ferrite were evaluated using the precision impedance analyzer, Wagner Kerr 6500B. Pellet shaped samples coated with silver paste on both sides were used for the evaluation of their electrical properties. The dielectric permittivity \((\varepsilon')\) of the samples were calculated using the equation [23].

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

where \(C\) is the capacitance of the pelletized samples, \(d\) is the thickness, \(A\) is the surface area and \(\varepsilon_0\) is the dielectric permittivity of free space.
AC conductivity ($\sigma_{AC}$) of the ferrite sample can be calculated from the values of loss tangent and dielectric permittivity [23].

$$\sigma_{AC} = 2\pi f \varepsilon_0 \varepsilon' \tan \delta$$  \hspace{1cm} .................................................. (3.2)

where $f$ is the frequency, $\varepsilon_0$ is the permittivity of free space and $\varepsilon'$ is the permittivity of the sample and $\tan \delta$ is the loss tangent. AC conductivity depends on temperature and frequency [24].

### 3.4.1 Frequency Dependence of Electrical Properties

#### 3.4.1.1 Dielectric Permittivity.

Figure 3.6 presents the variation of dielectric permittivity with frequency at 300K for the three representative samples ZF400, ZF500, ZF600. It is clear that the dielectric permittivity decreases with increase in frequency but remains a constant with further increase in the frequency. Ferrite can be considered as an inhomogeneous medium of two layer of Maxwell–Wagner type [25].

![Figure 3.6: Dielectric permittivity as a function of log f of zinc ferrites sintered at different temperatures](image)
The first layer consists of large ferrite grains which are good conductors. These grains are separated by a thin second layer consisting of grain boundaries which are poor conductors. According to the Rezlescu model [26], conduction in ferrites is due to the exchange of electrons between Fe$^{2+} \leftrightarrow$ Fe$^{3+}$ in the direction of an applied field. The space charge polarization at the interface is the reason for the high value of the dielectric permittivity at lower frequencies. The grain boundaries are found to be effective at low frequencies, while the grains are found effective at higher frequencies [15, 27]. This is the reason for the decrease in permittivity as the frequency increases. But at a still higher frequency, the electron exchange will not be able to follow the applied field and hence $\varepsilon'$ remains a constant after reaching a particular level of frequency.

3.4.1.2 AC Conductivity

The variation of AC conductivity with applied frequency at room temperature for representative samples ZF400, ZF500, ZF600 is depicted in figure 3.7.

![Figure 3.7: Frequency dependence of AC conductivity](image)
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The Maxwell–Wagner type interfacial polarization model [25] can be used to explain the variation of AC conductivity with frequency. Initially the AC conductivity increased linearly, reached a maximum value and then suddenly decreased. As the applied frequency increases, the conducting grains become more effective at higher frequencies, due to their hopping between Fe$^{2+}$ and Fe$^{3+}$ ions. Thus a gradual increase in the AC conductivity with frequency was observed. From the figure 3.7 it is clear that the plots are almost linear, which point to a conduction due to small polaron hopping [28]. But if the frequency is increased beyond a point, the hopping of charge carriers are unable to follow the applied field frequency, resulting in a decrease in the conductivity values.

3.4.2 Temperature dependence of electrical properties

3.4.2.1 Dielectric permittivity

Figure 3.8 shows the variation of dielectric permittivity of a representative sample, ZF400, with temperature. All the other samples too showed a similar behavior with temperature. Polarization effect can be used to explain the dependence of permittivity on temperature. An initial increase in $\varepsilon'$ was found with increase in temperature. This can be the result of the enhancement of charge carriers with the increase in temperature [29].

A dispersion peak is observed in figure (3.8) with a transition temperature around 460K. This can be explained based on the fact that the polarization in ferrites is produced due to the valance exchange between various ions in the compound. The low ionization potential of the atoms in the ferrite spinel structure will free large number of dipoles with increase in temperature leading to the progressive increase in dielectric constant. But with further increase in temperature after a particular level the system will give rise to more degrees of freedom to the dipoles resulting in the increase of the
disorder of the system [30] thus decreasing the dielectric constant. Similar variation of dielectric constant with temperature was reported in terbium doped nickel ferrite [31], in zinc substituted nickel ferrite [32], lanthanum substituted Ni-Zn ferrite [30], and ytterbium substituted Li–Co ferrite [33].

![Figure 3.8: Dielectric permittivity as a function of temperature at a selected frequency, for ZF400](image)

The temperature dependent polarizations, namely the dipolar and interfacial polarizations are prominent at low frequencies. This is the reason for the large variation of dielectric constant with temperature at low frequencies. But at higher frequencies, the temperature dependence is insignificant. This is because of the fact that the polarizations that dominates at higher frequencies, namely the electronic and ionic polarizations, does not have significant temperature dependence [34].

### 3.4.2.2 AC Conductivity

The temperature dependence of AC conductivity of a representative sample, ZF400, for selected frequencies is shown in figure 3.9. All other samples also showed a similar behavior. Dielectric constant is directly
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proportional to the square root of conductivity [35], hence the temperature variation of AC conductivity shows a similar variation as that shown by the dielectric constant with temperature.

![Figure 3.9: Relation between AC conductivity and absolute temperature](image)

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Log ρAC (μΩ·m⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>340</td>
<td>-4.0</td>
</tr>
<tr>
<td>360</td>
<td>-3.5</td>
</tr>
<tr>
<td>380</td>
<td>-3.0</td>
</tr>
<tr>
<td>400</td>
<td>-2.5</td>
</tr>
<tr>
<td>420</td>
<td>-2.0</td>
</tr>
<tr>
<td>440</td>
<td>-1.5</td>
</tr>
<tr>
<td>460</td>
<td>-1.0</td>
</tr>
<tr>
<td>480</td>
<td>-0.5</td>
</tr>
<tr>
<td>500</td>
<td>0.0</td>
</tr>
<tr>
<td>520</td>
<td>0.5</td>
</tr>
</tbody>
</table>

The temperature dependence of AC conductivity can be explained using the Matliessen’s rule [36, 37].

\[
\rho(T) = \rho_r + \rho_{ph}(T) + \rho_e(T, \omega) \]

(3.3)

where ρ(T) is the total resistivity, ρ_r the residual resistivity due to the impurities and lattice defects, \( \rho_{ph}(T) \) is the contribution due to the electron-phonon and \( \rho_e(T, \omega) \) is the contribution from the electron-spin wave scattering, caused by localized charge carriers at high temperature. As temperature increases, the AC conductivity also gets increased due to the increase in the thermally enhanced drift mobility of the charge carriers [28, 38]. Further increase in temperature leads to large thermal energy. This leads to a very strong lattice vibration resulting in the scattering of charge carriers caused by their collision with the vibrating lattice.
This will dampen the mobility of the charge carriers and will in turn make conductivity temperature independent [37].

3.4.3 Dependence of Electrical Properties on Grain Size

The conductivity and permittivity of ferrites depend on many factors like grain size, grain boundaries, porosity and stoichiometry. For polycrystalline materials, it has generally been reported that the resistivity increases with decrease in the grain size [39]. Smaller the grain size, larger will be the number of insulating grain boundaries and higher will be the restriction to the flow of electrons. But when the sintering temperature is increased, the grain size too increases and as a result the resistivity of the ferrites gets reduced. The variation of dielectric constant with sintering temperature is shown in figure 3.10

![Figure 3.10: Variation of AC dielectric constant of ZnFe$_2$O$_4$ with sintering temperature at selected frequency](image)

Dielectric constant is inversely proportional to the resistivity in ferrites [29]. Hence dielectric constant is expected to increase with increase in the sintering temperature, but a reverse trend is observed in our present work up to a sintering temperature of 600°C. The high value of permittivity and the low value
of resistivity for the samples sintered at a low temperature may be due to the presence of a localized stage in the forbidden energy gap which arises due to the lattice imperfections in it. These localized stages will lower the energy barriers for the electron flow. Because of the larger surface area of the smaller grain boundaries, there will be two contributors to the polarization namely polarization due to the larger surface and polarization due to the grain boundaries, thereby increasing the total polarization. Similar variation of dielectric constant with particle size has been reported by Mathew et al. [40]

AC conductivity can be correlated to the Barrier hopping model [41].

\[
\sigma(\omega) = \frac{\pi^3}{24} N^2 \epsilon' R^2 \omega 
\]

where \(N\) is the concentration of defect sites, \(R\) is the hopping distance, \(\epsilon'\) is the dielectric permittivity. The variation of AC conductivity with sintering temperature is depicted in figure 3.11.

**Figure 3.11**: Variation of AC conductivity of ZnFe\(_2\)O\(_4\) with sintering temperature at selected frequency

When the sintering temperature increases, the crystallization too increases reducing the imperfection. This decreasing concentration of defect sites (N), thus reduces the value of AC conductivity. Hence samples fired at a higher temperature or samples with a greater crystallite size will have a lower
value of conductivity. Similar results were reported by Mathew et al. [40]. This also can be explained in terms of increase in the structural perfection with increase in the sintering temperature.

3.5 Conclusions

Zinc ferrite nanoparticles were synthesized by sol–gel technique. The prepared samples were sintered at different temperatures for two hours and zinc ferrite of various crystallite sizes was obtained. The X-Ray diffraction analysis showed the formation of a single phase spinel structure without any secondary phase. The Rietveld analysis technique was used for the XRD analysis. The lattice strain and crystallite size were calculated from the Hall–Williamson plot. The TEM analysis revealed that the prepared nanoparticles were spherical in shape and slightly agglomerated. Purity of the samples was confirmed by the WD–XRF analysis. Variation of dielectric permittivity and AC conductivity were found to be in good agreement with the Koop’s phenomenological theory of dielectric dispersion. The almost linear increase of AC conductivity with frequency points to conduction due to small polaron hopping. Both dielectric constant and AC conductivity were found to increase with temperature. The correlated barrier-hopping model was used to explain the enhancement of electrical properties with decrease in the particle size.

References

Chapter 3


Effect of Sintering Temperature on Structural and Electrical Properties of Zinc Ferrite


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