Chapter V

RESULTS AND DISCUSSION ON MAGNETIC AND ELECTRICAL PROPERTIES OF \( \text{Co}_{1+x}\text{Zr}_x\text{Fe}_{2-2x}\text{O}_4 \) SPINEL FERRITE NANOPARTICLES

5.1 INTRODUCTION

Ferrites are magnetic ceramics of great importance in many technological applications on account of their various electrical, dielectric and magnetic properties. Ferrites with cubic spinel structure forms an important class of magnetic materials and exhibit interesting electrical and magnetic properties. Owing to their numerous applications ferrites are being studied from last six to seven decades with a view to understand and improve their properties for suitable applications. On account of their combined electric and magnetic properties they show wide applications in technology, particularly at high frequency [1, 2]. Ferrite materials find high frequency applications due to their high permeability and permittivity [3-7]. These materials are being used in transformer cores, antennas, radio frequency coil and radar absorbing materials (RAM) [8].

The literature report mainly focuses on nanosize magnetic materials having significant potential for many applications. Research in this area for better and improved materials still continues as they find some new applications. During the last decades there has been an interest in developing and understanding the basic magnetic and electrical properties of spinel ferrite at nanometric scale. The progress made in the area of nanotechnology in the recent years has motivated the
scientist and technologist to synthesize spinel ferrites in nanometric size and characterize them for their structural, electrical and magnetic properties. It is well known that the properties of spinel ferrites are changed when the size of the particle reduces from bulk to nano.

In the recent years, the design and synthesis of magnetic particles of spinel ferrites in nanosize has been the focus of intense fundamental and applied research due to their enhanced properties that are different from those of their bulk counterparts [9]. Technological demand of high performance devices has triggered the synthesis and research in nanoscale spinel ferrite. Nanosize spinel ferrites find applications in high density magnetic data storage [10], microwave absorbing material [11], magnetic resonance imaging [12], targeted drug delivery [13], magnetic fluids [14], biotechnology [15] etc.

Cobalt ferrite is a well known hard magnetic material with inverse spinel structure. The saturation magnetization and coercivity of cobalt ferrite is higher than the other nickel, manganese spinel ferrites [16]. Cobalt ferrite is the most important and abundant magnetic materials that have large magnetic anisotropy, moderate saturation magnetization, remarkable chemical stability and mechanical hardness, which make it good candidate for the recording media [17, 18].

The chemical composition method of synthesis, nature of dopant, site preference of dopants etc parameters strongly influences the structural, electrical and magnetic properties of spinel ferrites [19, 20].
In the present study the effect of zirconium substitution, electrical, dielectrical and magnetic properties of nanocrystalline cobalt ferrite prepared by sol-gel auto combustion method is reported. The magnetic property of spinel ferrite materials depends on the magnetic interaction between cations and magnetic moments, which are situated in the tetrahedral (A) and octahedral [B] sites.

5.2 EXPERIMENTAL DETAILS

In this work the nanosize samples of zirconium substituted cobalt ferrites \( \text{Co}_{1+x}\text{Zr}_x\text{Fe}_{2-2x}\text{O}_4 \) system with \( x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5 \) and 0.6 were synthesized by sol-gel auto combustion method. X-ray diffraction, scanning electron microscopy and infrared spectroscopy techniques were employed to characterize the prepared samples of \( \text{Co}_{1+x}\text{Zr}_x\text{Fe}_{2-2x}\text{O}_4 \) system.

The magnetic properties of \( \text{Co}_{1+x}\text{Zr}_x\text{Fe}_{2-2x}\text{O}_4 \) system were investigated using pulse field hysteresis loop technique at room temperature by applying magnetic field of 2 Tesla. Using magnetization (M) versus applied magnetic field (H) plots obtained from pulse field hysteresis loop technique, the saturation magnetization, coercivity and remanence magnetization were obtained as a function of zirconium content \( x \).

The electrical properties of \( \text{Co}_{1+x}\text{Zr}_x\text{Fe}_{2-2x}\text{O}_4 \) system were investigated in the temperature range 300 to 800 K using two probe technique. The pellets in circular shape with 10 mm diameter and 3 mm thickness with silver coating were used for
the measurement of DC electrical resistivity. Using resistivity plots activation energy of all the samples was obtained.

5.3 RESULTS AND DISCUSSIONS

5.3.1 MAGNETIC PROPERTIES

The magnetic properties of the present zirconium doped cobalt ferrites Co$_{1+x}$Zr$_x$Fe$_{2-2x}$O$_4$ system with $x = 0.0$, 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6 were investigated using pulse field hysteresis loop technique. The plots of magnetization (M) verses applied magnetic field (H) are shown in Fig 5.1.

![M-H plots recorded at room temperature for Co$_{1+x}$Zr$_x$Fe$_{2-2x}$O$_4$](image_url)
The values of saturation magnetization (Ms), coercivity (Hc), remanence magnetization (Mr) and magneton number (n_B) are summarized in Table 5.1.

Table 5.1: Saturation magnetization (Ms), Remanence magnetization (Mr), Coercivity (Hc), Remanence ratio (Mr/Ms) and Magneton number (n_B) for Co_{1+x}Zr_{x}Fe_{2-2x}O_{4} system.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Ms (emu/g)</th>
<th>Mr (emu/g)</th>
<th>Hc (Oe)</th>
<th>Mr/Ms</th>
<th>n_B (μB)</th>
</tr>
</thead>
<tbody>
<tr>
<td>‘x’</td>
<td>Mr/Ms</td>
<td>n_B (μB)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Obs.</td>
<td>Cal.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.00</td>
<td>61.29</td>
<td>54.45</td>
<td>1357</td>
<td>0.88</td>
<td>2.57</td>
</tr>
<tr>
<td>0.10</td>
<td>47.38</td>
<td>39.97</td>
<td>1360</td>
<td>0.84</td>
<td>2.07</td>
</tr>
<tr>
<td>0.20</td>
<td>45.03</td>
<td>35.34</td>
<td>1280</td>
<td>0.78</td>
<td>1.83</td>
</tr>
<tr>
<td>0.30</td>
<td>40.52</td>
<td>28.07</td>
<td>1212</td>
<td>0.69</td>
<td>1.90</td>
</tr>
<tr>
<td>0.40</td>
<td>34.97</td>
<td>24.42</td>
<td>1188</td>
<td>0.69</td>
<td>1.70</td>
</tr>
<tr>
<td>0.50</td>
<td>21.30</td>
<td>16.10</td>
<td>1144</td>
<td>0.75</td>
<td>1.07</td>
</tr>
<tr>
<td>0.60</td>
<td>26.12</td>
<td>17.97</td>
<td>982</td>
<td>0.68</td>
<td>1.36</td>
</tr>
</tbody>
</table>
Saturation Magnetization (Ms)

It can be seen from the Table 5.1 that the saturation magnetization decreases with increase in zirconium content \(x\). The decrease in saturation magnetization is due to the substitution of nonmagnetic \(Zr^{4+}\) in cobalt spinel ferrite. The zirconium ions owing to their large ionic radii occupy octahedral site by replacing \(Fe^{3+}\) ions. The main contributions of magnetic properties come from \(Fe^{3+}\) on octahedral [B] site. The net magnetic moment is given by [21]

\[
M = M_B - M_A \quad \ldots 5.1
\]

Where, \(M_A\) and \(M_B\) represent the total magnetic moment of the A and B sublattices, respectively. The doping of zirconium ions reduces the super-exchange interaction and therefore saturation magnetization decreases. Considering the ionic magnetic moments of cobalt, ferric and zirconium as 3 \(\mu_B\), 5 \(\mu_B\) and 0 \(\mu_B\) and using cation distribution data (reported in previous chapter), the net magnetization was calculated and reported in Table 5.1.

The observed and calculated magnetic moments agree closely for low zirconium content \(x\). For \(x > 0.2\) the observed and calculated magnetic moments shows large variation suggesting canting spin structure. Further, the decrease in magnetization can be attributed to the fact that due to substitution of zirconium ions spin canting takes place. The collinear ferrimagnetic arrangement changes into non-collinear arrangement on substitution of zirconium ions. Overall, the substitution of zirconium ions in cobalt spinel ferrite reduces the saturation magnetization of the present system (Table 4.8).
**Magneton number (nB)**

Magneton number $n_B$ for all the samples was calculated by using the equation [22].

$$n_B = \left( \frac{\text{Mol. Weight} \times M_s}{5585} \right) \mu_B \ldots 5.2$$

and their values are presented in **Table 5.1**. As like saturation magnetization, magneton number of zirconium doped cobalt ferrite decreases as Zr content $x$ increases in cobalt ferrite.

**Coercivity (Hc)**

The values of coercivity were obtained from hysteresis plots (M-H plots) and are presented in **Table 5.1**. It can be observed from the table 5.1 that all the samples show high values of coercivity confirming the nanocrystalline nature. Further it can be observed that the coercivity decreases with increase in zirconium content $x$. The decrease in coercivity values can be attributed to the substitution of nonmagnetic zirconium ions in cobalt ferrite.

In general the coercivity of polycrystalline ferrites depends upon magnetocrystalline anisotropy constant, average grain size, domain wall energy and several other parameters. The decreases in magnetic coercivity suggest the decrease in magnetic losses. Hysteresis loss is proportional to the coercivity of the material.
Remanence Magnetization (Ms)

The values of remanence magnetization (Ms) were obtained from hysteresis plots (M-H plots) and are presented in Table 5.1. It can be observed from the table 5.1 that the remanence magnetization decreases with increase in zirconium content x. The decrease in remanence magnetization values can be attributed to the substitution of nonmagnetic zirconium ions in cobalt ferrite.

Remanence Ratio (Mr/Ms)

The ratio of remanence magnetization to saturation magnetization called as remanence ratio (Mr/Ms) of all the samples are presented in Table 5.1. It can be observed from the table 5.1 the remanence ratio decreases with increase in zirconium content x.

The decrease in crystallite size and increase in the canting angle gives evidence that saturation magnetization and other magnetic parameters decreases as a result of spin canting due to decrease in particle size. The observed magnetic behaviour cannot be perfectly explained on the basis of Neel’s theory. Yafet-Kittel model (YK) can explained the magnetic behaviour of the present samples.

Thus, the substitution of zirconium in cobalt ferrite leads to decrease in saturation magnetization, magneton number, coercivity and remanence magnetization magnetic properties. Our results on magnetic properties are similar to other Er, Ti, Zn substituted cobalt ferrite material [23-25].
5.3.2 ELECTRICAL PROPERTIES

5.3.2.1 DC Electrical Resistivity

The measurements of DC resistivity ‘ρ’ for all the samples of the Co_{1+x}Zr_xFe_{2-2x}O_4 ferrite system were carried out in the temperature range 300-800 K using standard two probe method. The D.C. electrical resistivity plots of all the samples are shown in the Fig. 5.2

Fig. 5.2: Variation of dc electrical resistivity with reciprocal of temperature for Co_{1+x}Zr_xFe_{2-2x}O_4
It is clear from the resistivity plots that the electrical resistivity of all Zr$^{4+}$ substituted cobalt spinel ferrite samples decreases with increase in temperature, thus exhibiting semiconducting behavior obeying the well-known Arrhenius relation. It is also seen from Fig. 5.2 that there are two regions of conduction with different activation energies. The change in slope is observed in each resistivity plot at a particular temperature which may correspond to Curie temperature of the sample. The increase in conductivity may be due to the hopping of electrons between Fe$^{2+}$ and Fe$^{3+}$.

**Activation Energy**

The activation energy $E_g$ for each sample in the ferrimagnetic and paramagnetic region was calculated from the resistivity plots. The values of activation energy for all Zr$^{4+}$ substituted cobalt spinel ferrite samples are listed in Table 5.2.

Table 5.1: Activation energy in paramagnetic ($E_p$) and ferrimagnetic ($E_f$) region for Co$_{1+x}$Zr$_x$Fe$_{2-2x}$O$_4$ system

<table>
<thead>
<tr>
<th>Comp. ‘x’</th>
<th>$E_p$ (eV)</th>
<th>$E_f$ (eV)</th>
<th>$\Delta E$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>0.08</td>
<td>0.04</td>
<td>0.04</td>
</tr>
<tr>
<td>0.10</td>
<td>0.13</td>
<td>0.04</td>
<td>0.09</td>
</tr>
<tr>
<td>0.20</td>
<td>0.73</td>
<td>0.57</td>
<td>0.16</td>
</tr>
<tr>
<td>0.30</td>
<td>0.69</td>
<td>0.52</td>
<td>0.17</td>
</tr>
<tr>
<td>0.40</td>
<td>0.81</td>
<td>0.63</td>
<td>0.18</td>
</tr>
<tr>
<td>0.50</td>
<td>0.85</td>
<td>0.65</td>
<td>0.20</td>
</tr>
<tr>
<td>0.60</td>
<td>0.92</td>
<td>0.69</td>
<td>0.23</td>
</tr>
</tbody>
</table>
It is found from Table 5.1 that activation energy increases with Zr$^{4+}$ substitution.

It is also evident from Table 5.1 that the activation energy in paramagnetic region is greater than ferrimagnetic region.

5.3.2.2 Dielectric Properties

The dielectric properties for the present samples can be explained on the basis of the mechanism of polarization process in ferrite, which is similar to that of conduction process. The electronic exchange Fe$^{3+} \leftrightarrow$ Fe$^{2+}$ gives the local displacement of electrons in the direction of an applied field, which induces polarization in ferrites.

Dielectric constant ($\varepsilon'$)

The variation of dielectric constant ($\varepsilon'$) with logarithm of applied electric field frequency for all Zr$^{4+}$ substituted cobalt spinel ferrite samples is observed as shown in Fig 5.3, it can be seen that the dielectric constant ($\varepsilon'$) initially decreases rapidly with increase in frequency up to the certain frequency; however, it remains fairly constant for higher frequencies. The decrease in dielectric constant ($\varepsilon'$) with increase in frequency can be explained by considering the solid as composed of well conducting grains separated by the poorly conducting grain boundaries. The decrease in dielectric constant ($\varepsilon'$) at lower frequencies is explained based on space charge polarization and attributed to the fact that ferroelectric regions are surrounded by non-ferroelectric regions similar to the relaxor ferroelectric
The dielectric constant attains a constant value only at higher frequencies due to electronic polarizability.

![Graph showing variation of dielectric constant with log f for Co$_{1+x}$Zr$_x$Fe$_{2-2x}$O$_4$](image)

**Fig.5.3: Variation of dielectric constant $\epsilon'$ with log f for Co$_{1+x}$Zr$_x$Fe$_{2-2x}$O$_4$**

**Dielectric loss ($\epsilon''$)**

The dielectric loss ($\epsilon''$) factor is considered to be the most important part of the total core loss in ferrites. The variation of dielectric loss as a function of frequency is shown in **Fig. 5.4.** It can be observed from fig.5.4 that dielectric loss ($\epsilon''$) decreases exponentially with increase in frequency and is shown in **Fig 5.4.** The decrease in dielectric loss is almost similar to that of dielectric constant. The
decrease in imaginary part of dielectric constant i.e. dielectric loss is pronounced more in comparison to real dielectric constant.

![Graph showing variation of dielectric loss $\varepsilon''$ with log f for Co$_{1+x}$Zr$_x$Fe$_{2-2x}$O$_4$](image)

**Fig. 5.4: Variation of dielectric loss $\varepsilon''$ with log f for Co$_{1+x}$Zr$_x$Fe$_{2-2x}$O$_4$**

**Dielectric loss tangent (tan $\delta$)**

The variation of dielectric loss tangent (tan $\delta$) as a function of frequency is shown in **Fig 5.5** calculated from dielectric constant and dielectric loss shows decreasing trend with increasing frequency. The values of tan $\delta$ depend on a number of factors such as a carrier concentration and structural homogeneity.
The dielectric loss tangent decreases exponentially with increase in frequency. The observed behavior of dielectric loss tangent can be explained on the basis of Maxwell-Wagner interfacial polarization.

![Graph showing variation of dielectric loss tangent (tanδ) with log f for Co₁₊ₓZrₓFe₂₋₂ₓO₄](image)

**Fig 5.5: Variation of dielectric loss tangent (tanδ) with log f for Co₁₊ₓZrₓFe₂₋₂ₓO₄**

The compositional dependence of various dielectric properties shows that the dielectric constant, dielectric loss and dielectric loss tangent all decreases as zirconium content x increase.

The properties of spinel ferrites that are of prime concern to users or designers are mainly dielectric properties such as dielectric constant, dielectric loss and dielectric tangent or loss factor.
5.4 CONCLUSIONS

- The substitution of zirconium ions in cobalt ferrite results in decrease of magnetic properties and increase of electrical properties in general.

- The saturation magnetization (Ms), coercivity (Hc) and remanence magnetization (Mr) all these magnetic parameters get decreased as zirconium content x increases in the lattice of cobalt ferrite.

- The magneton number calculated from the values of saturation magnetization also decreases with increase in zirconium content x.

- The substitution of zirconium in cobalt ferrite leads to canting structure.

- The DC resistivity of all the samples decreases with increase in temperature exhibiting the semiconducting behaviour.

- The activation energy in paramagnetic region ($E_p$) is more than that of ferrimagnetic ($E_f$) region.

- The dielectric constant ($\varepsilon$), dielectric loss ($\varepsilon''$) and dielectric loss tangent ($\tan \delta$) decreases exponentially with increase in frequency.

- The dielectric constant ($\varepsilon$), dielectric loss ($\varepsilon''$) and dielectric loss tangent ($\tan \delta$) decreases with increase in zirconium content x.
REFERENCES


