substituted strontium hexaferrite $[21, 28-32]$. 

The magnetic behaviour of hexaferrite material is largely governed by the distribution of iron ions on the crystallographic lattice sites. In the M-type hexaferrite, $12\text{Fe}^{3+}$ ions are distributed at five different sublattices: three octahedral (12k, 2a, 4f2), one tetrahedral (4f1) and one trigonal bipyramidal (2b). Out of $12\text{Fe}^{3+}$ ions four have spin in downward direction i.e. $2\text{Fe}^{3+}$ ions at 4f1, $2\text{Fe}^{3+}$ ions at 4f2 while other $8\text{Fe}^{3+}$ ions have spin in upward direction i.e. $6\text{Fe}^{3+}$ at 12k, 1Fe at 2a, $1\text{Fe}^{3+}$ at 2b. The four upward and four downward spins cancel each other and the net magnetic moment is only due to the remaining four iron ions having spin in upward direction. So the total magnetic moment $20\mu\text{B}$ is due to uncompensated spin of electron in the upward direction $[32]$. 

---

**Table 4.4**

Saturation magnetization ($M_s$), remanent magnetization ($M_r$), remenence ratio $M_r/M_s$, coercivity ($H_c$) and magneton number ($n_B$) of SrNi$_x$Zr$_{12-2x}$O$_{19}$. 

<table>
<thead>
<tr>
<th>Parameters</th>
<th>x = 0.0</th>
<th>x = 0.2</th>
<th>x = 0.4</th>
<th>x = 0.6</th>
<th>x = 0.8</th>
<th>x = 1.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_s$ (emu/g)</td>
<td>60.16</td>
<td>62.03</td>
<td>66.50</td>
<td>68.63</td>
<td>70.20</td>
<td>66.64</td>
</tr>
<tr>
<td>$M_r$ (emu/g)</td>
<td>35.33</td>
<td>36.23</td>
<td>36.82</td>
<td>37.75</td>
<td>31.76</td>
<td>25.80</td>
</tr>
<tr>
<td>$M_r/M_s$</td>
<td>0.58</td>
<td>0.58</td>
<td>0.55</td>
<td>0.50</td>
<td>0.45</td>
<td>0.38</td>
</tr>
<tr>
<td>$H_c$ (Oe)</td>
<td>3001.4</td>
<td>2991.7</td>
<td>1719.3</td>
<td>1193.9</td>
<td>787</td>
<td>511.8</td>
</tr>
<tr>
<td>$n_B$ ($\mu$B)</td>
<td>11.43</td>
<td>11.87</td>
<td>12.82</td>
<td>13.32</td>
<td>13.73</td>
<td>13.12</td>
</tr>
</tbody>
</table>
The magneton number $n_B (\mu_B)$ was obtained using the equation

$$n_B = \frac{\text{Molecular weight} \times M_s}{5585}$$

where, $M_s$ is the saturation magnetization.

The behaviour of magnetic moment is same as that of saturation magnetization. The values of magneton number $n_B (\mu_B)$ increases up to $x = 0.8$ and then decreases with increase in Zr$^{4+}$ and Ni$^{2+}$ substitution due to the replacement of low magnetic moment of Zr$^{4+}$ and Ni$^{2+}$ as compared to Fe$^{3+}$. The behaviour of the magnetic moment of the sample is in good agreement with the saturation magnetization. The values of magneton number are given in Table 4.4.

**A C Susceptibility Measurements**

The A.C. Susceptibility measurements were carried out using double coil setup technique in the temperature range 300 K to 800 K.

---

**Fig. 4.13 Variation of $\chi_T/\chi_{RT}$ V/s temperature $T$ (K) of SrNi$_x$Zr$_x$Fe$_{12-2x}$O$_{19}$**
Curie temperatures of all the samples were determined using A.C. Susceptibility technique. The variation of $\chi_T/\chi_{RT}$ with temperature T (K) of SrNi$_x$Zr$_{1-x}$Fe$_{12-2x}$O$_{19}$ ($x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0$) are as shown in Fig. 4.14.

The value of Curie temperature $T_c$ (K) was found to decrease with increasing Ni-Zr content ‘x’. This trend can be explained on the basis of the number of magnetic ions present in the two sub-lattices and their mutual contraction. The Curie temperature of Ni-Zr substituted strontium hexaferriate was also determined from D. C. resistivity and Loria technique \cite{33} the values are presented in Table 4.5. It is observed from Table 4.5 that the Curie temperature obtained from D. C. resistivity and Loria technique are in good agreement with AC susceptibility values.

<table>
<thead>
<tr>
<th>Composition ‘x’</th>
<th>Curie temperature $T_c$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DCR</td>
</tr>
<tr>
<td>0.0</td>
<td>742</td>
</tr>
<tr>
<td>0.2</td>
<td>709</td>
</tr>
<tr>
<td>0.4</td>
<td>672</td>
</tr>
<tr>
<td>0.6</td>
<td>638</td>
</tr>
<tr>
<td>0.8</td>
<td>599</td>
</tr>
<tr>
<td>1.0</td>
<td>563</td>
</tr>
</tbody>
</table>
Ni\textsuperscript{2+} and Zr\textsuperscript{4+} substituted SrFe\textsubscript{12}O\textsubscript{19} have been successfully synthesized by Sol-Gel auto combustion method. The X-ray diffraction pattern reveals the formation of M-phase hexagonal structure for all substitution levels of Ni\textsuperscript{2+} and Zr\textsuperscript{4+} without any secondary phases. The average grain size obtained from Scanning electron microscopy was found in the range of 40-90 nm. Energy dispersive spectroscopy analysis confirmed that the synthesized samples were near stoichiometric.

The values of resistivity and activation energy increases whereas the drift mobility decreases as Ni-Zr content ‘x’ increases. Both dielectric constant (\varepsilon’) and dielectric loss tangent (tan \delta) decreases as Ni-Zr content ‘x’ increases. The synthesized sample is more suitable for applications in microwaves devices.

The values of saturation magnetization and remenance magnetization increases up to x = 0.8 and then decreases for higher substitution while coercivity decreases continuously as Ni-Zr content increases. The magneton number (\mu B) increases up to x = 0.8 and then decreases with Ni\textsuperscript{2+} and Zr\textsuperscript{4+} substitution.

The Curie temperature obtained from DC resistivity, Loria technique and AC susceptibility decreases with increase in Ni-Zr substitution, and are in good agreement with each other.
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Chapter 5

RESULTS AND DISCUSSION ON SrZn$_{x}$Zr$_{x}$Fe$_{12-2x}$O$_{19}$ HEXAFERRITE NANOPARTICLES

5.1 INTRODUCTION

In the recent years, M-type hexagonal ferrites have been the interest of continuous research due to its low cost, perfect chemical stability, good thermal durability, corrosion resistivity, appropriate magnetic and electrical properties \cite{1}. Strontium ferrites (SrFe$_{12}$O$_{19}$) have been widely used in industrial applications such as permanent magnets, high density magnetic recording media, telecommunication, automobile, magneto optical and microwave devices \cite{2}.

The M-type hexagonal structure can be described as layers of closely packed oxygen ions, which are placed upon each other along the hexagonal c-axis. The structure is stacked alternately by spinel (S = Fe$_6$O$_8^{2+}$) and
hexagonal (R = SrFe₆O₁₉²⁻) layers [3]. The O²⁻ ions exists as close-packed layers with the Sr²⁺ substituting for an O²⁻ in every five hexagonal layers. The 24 Fe³⁺ ions are distributed in five interstitial crystallographic sites of close-packed layers namely, there octahedral (2a, 12k, 4f2), one tetrahedral (4f1) and one trigonal bipyramidal (2b) [4].

At present, several synthesis techniques such as chemical co-precipitation [5], glass crystallization [6], citrate precursor [7], micro emulsion [8], hydrothermal [9], sol-gel [10] and salt melt method [11] have been developed to prepare intrinsic and doped hexagonal ferrites.

In the present work, sol-gel auto combustion techniques have been used to prepare strontium ferrite. The advantage of chemical route is lower annealing temperature necessary in the crystallization process. Therefore varying the heat treatment in order to prepare nanocrystalline hexaferrite particles with narrow switching field distribution can control the crystal growth easier [12].

The aim of the present work is to study the effect of Zn-Zr doping on the structural, electrical and magnetic properties of strontium hexaferrite nanoparticles. Strontium ferrite possesses high electrical resistivity, magnetization and low dielectric losses. These properties are useful in the applications at high frequencies. The dielectric properties such as dielectric constant (ε') and dielectric loss tangent (tan δ) are very important for microwave applications. The dielectric constant (ε') affects the thickness of microwave absorbing layer and the dielectric loss tangent (tan δ) of a material determines dissipation of electrical energy. This dissipation may be due to electrical conduction, dielectric relaxation, dielectric resonance and loss from nonlinear processes [13].
Strontium hexaferrite (SrFe$_{12}$O$_{19}$) is used as a permanent magnet due to its high-uniaxial anisotropy, high-Curie temperature (743 K), large saturation magnetization (64 emu/g), high coercivity, excellent chemical stability and high-corrosion resistivity $^{[14-15]}$. It is a promising material for application in high-density magnetic recording media and microwave devices. Strontium hexaferrite is an unsuitable material for use in recording media due to its intrinsic coercivity of 6.4 kOe. The value of the coercivity has been reduced to 0.2 kOe by the substitution of Zn$^{2+}$, Co$^{2+}$, Mn$^{2+}$, Ti$^{4+}$, Ni$^{2+}$ and Ir$^{4+}$ but it is accompanied by a decrease in the saturation magnetization thus limiting its use in the recording media $^{[16-19]}$.

### 5.2 EXPERIMENTAL TECHNIQUES

#### 5.2.1 Sample synthesis

Analytical Reagent (AR) grade strontium nitrate Sr(NO$_3$)$_2$, ferric nitrate Fe(NO$_3$)$_3$.9H$_2$O, Zirconium nitrate ZrO(NO$_3$)$_2$.H$_2$O, Zinc nitrate Zn(NO$_3$)$_2$.9H$_2$O and Citric acid C$_6$H$_8$O$_7$.H$_2$O as a fuel were used as starting materials. According to the composition of SrZn$_x$Zr$_x$Fe$_{12-2x}$O$_{19}$ (where $x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0$), all the nitrates were separately dissolved in minimum amount of distilled water and stirred on magnetic stirrer for ten minutes. Then all the solutions have been mixed together and stirred on a magnetic stirrer until the nitrates were completely dissolved. The metal nitrate to citric acid ratio was 1:3. The solution were made with continuous stirring on magnetic stirrer, drop by drop ammonia solution was added to adjust the pH value to 7. Then the solution was heated on hot plate at 80°C with constant stirring until gel was formed. Instantaneously gel ignites with the formation of large amount of gas, resulting in to light weight
voluminous powder. The resulting precursor powder was calcined at 950 °C for 9 hrs to obtain pure SrZn₃ZrₓFe₁₂₋₂ₓO₁₉ hexaferrite powder.

5.2.2 Characterization techniques

The thermal decomposition behaviour of the as prepared powder was examined by TGA/DTA (Model Shimadzu DTG-60). The phase identification of the prepared samples was performed with the help of X-ray diffractometer (Rigaku Miniflux-II) in the 2θ range from 20° to 80° at room temperature using CuKα radiation (wavelength λ = 1.5406 Å).

The surface morphology of the prepared samples and the stoichiometric proportion of the constituent ions was studied by using Scanning electron microscopy (Model LEO 1430) equipped with Energy dispersive spectroscopy (EDS). The Fourier transform infrared spectra of all the calcined samples were recorded in the range of 4000 - 450 cm⁻¹ using Perkin-Elmer spectrophotometer.

The D.C. electrical resistivity measurements were carried out in the temperature range 300 – 923 K using two probe method. Dielectric properties like dielectric constant (ε’), dielectric loss (ε’’), and dielectric loss tangent (tan δ) were studied using LCR-Q meter [Model 4192, HP make] as a function of logarithm of frequency.

The magnetic parameters such as saturation magnetization (Ms), remenaneance magnetization (Mr), remenaneance ratio (Mr/Ms), coercivity (Hc) and magneton number (nB) were obtained at room temperature using vibrating sample magnetometer (VSM) technique. The A.C. Susceptibility technique was used to determine Curie temperature (Tc) of all the samples.
5.3 RESULTS AND DISCUSSION

5.3.1 Thermal analysis

The TGA/DTA plot for an as-synthesized sample of strontium hexaferrite with the composition SrZn$_{0.2}$Zr$_{0.2}$Fe$_{11.6}$O$_{19}$ is shown in Fig. 5.1. It can be observed that removal of water takes place around 100 °C. The exothermic peak at around 250 °C corresponds to the crystallization of the M-phase of the strontium hexaferrite nanoparticles. The decomposition of hydroxide takes place from 400 °C - 800 °C. Above 900 °C no further weight loss occurred indicating that all organic constituents were eliminated and the formation of strontium hexaferrite starts. Thus, the calcination temperature selected for all other compositions of strontium hexaferrite was 950 °C.

---

Fig. 5.1. Thermo gravimetric and differential thermal analysis of SrZn$_{0.2}$Zr$_{0.2}$Fe$_{11.6}$O$_{19}$ hexaferrite.
5.3.2 STRUCTURAL ANALYSIS

X-ray Diffraction (XRD)

Fig. 5.2 shows the X-ray diffraction pattern for all the synthesized samples. X-ray diffraction analysis reveals that all the diffraction peaks seen in the XRD pattern well matches with the standard pattern of strontium hexaferrite (JCPDS Card No. 84-1531). The analysis of XRD pattern revealed the formation of single phase M-type hexagonal structure.

![X-ray diffraction patterns of SrZn\textsubscript{x}Zr\textsubscript{x}Fe\textsubscript{12-2x}O\textsubscript{19}](image)

---

**Fig. 5.2** X-ray diffraction patterns of SrZn\textsubscript{x}Zr\textsubscript{x}Fe\textsubscript{12-2x}O\textsubscript{19}
Lattice constants (a and c), cell volume (V), were calculated from XRD data using the equations (4.1) and (4.2) respectively and the values are reported in the Table 5.1.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>x = 0.0</th>
<th>x = 0.2</th>
<th>x = 0.4</th>
<th>x = 0.6</th>
<th>x = 0.8</th>
<th>x = 1.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (Å)</td>
<td>5.870</td>
<td>5.877</td>
<td>5.883</td>
<td>5.891</td>
<td>5.900</td>
<td>5.910</td>
</tr>
<tr>
<td>c (Å)</td>
<td>23.06</td>
<td>23.10</td>
<td>23.14</td>
<td>23.18</td>
<td>23.22</td>
<td>23.28</td>
</tr>
<tr>
<td>c/a</td>
<td>3.9284</td>
<td>3.9305</td>
<td>3.9333</td>
<td>3.9348</td>
<td>3.9355</td>
<td>3.9390</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>689.28</td>
<td>692.00</td>
<td>694.74</td>
<td>697.53</td>
<td>700.51</td>
<td>703.44</td>
</tr>
</tbody>
</table>

It is evident from Table 5.1 that, the lattice constant ‘a’ almost remains constant while ‘c’ increases with increase in Zn-Zr content ‘x’. This is due to the smaller ionic radii of Fe³⁺ ions (0.64Å) as compared to that of the substituted cations Zn²⁺ (0.74Å) and Zr⁴⁺ (0.80Å). Both the lattice constant ‘a’ and ‘c’ increases linearly obeying Vegard’s law [20]. In the present case two Fe³⁺ ions are replaced by Zn²⁺ and Zr⁴⁺ ions. According to Verstegen and Stevels [21] c/a parameter ratio may be used to quantify the structure type, as the M-type structure can be assumed, if the ratio is observed to be lower than 3.98.
The unit cell volume ($V$) calculated is shown in Table 5.1 as a function of Zn-Zr content ‘$x$’. It is observed that unit cell volume increases with increasing Zn-Zr content ‘$x$’, which is attributed to increase in lattice constant ‘$c$’ of the present samples.

X-ray density ($\rho_x$), bulk density ($\rho_m$) and porosity ($P$), crystallite size ($D$) were calculated from XRD data using the equations (4.3, 4.4, 4.5, 4.6) respectively and their values are tabulated in Table 5.2.

| Parameters | $x = 0.0$ | $x = 0.2$ | $x = 0.4$ | $x = 0.6$ | $x = 0.8$ | $x = 1.0$
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$D$ (nm)</td>
<td>44.76</td>
<td>41.43</td>
<td>47.45</td>
<td>46.07</td>
<td>41.95</td>
<td>36.43</td>
</tr>
<tr>
<td>$\rho_x$ (g cm$^{-3}$)</td>
<td>5.11</td>
<td>5.14</td>
<td>5.16</td>
<td>5.19</td>
<td>5.21</td>
<td>5.24</td>
</tr>
<tr>
<td>$\rho_m$ (g cm$^{-3}$)</td>
<td>3.00</td>
<td>3.10</td>
<td>3.16</td>
<td>3.23</td>
<td>3.31</td>
<td>3.38</td>
</tr>
<tr>
<td>$P$ (%)</td>
<td>0.41</td>
<td>0.37</td>
<td>0.36</td>
<td>0.36</td>
<td>0.36</td>
<td>0.35</td>
</tr>
</tbody>
</table>

It is evident from Table 5.2 that the X-ray density ($\rho_x$) increases due to larger molar mass of substituted samples. This behaviour of X-ray density is attributed to the fact that the cell volume increases due to rise in molar
masses of the doped metal cations. The bulk density ($\rho_m$) was found to increase with increase in Zn-Zr content ‘x’ in strontium hexaferrite system. The values of bulk density are smaller than that of the X-ray density which is due to the presence of unavoidable pores during the heating. The porosity (P) was found to decrease with increase in Zn-Zr content ‘x’ of the present system.

The crystallite size obtained from XRD data is in the range of 36-47 nm. The major problem with the high density recording media is the media noise which results from coupling between magnetic grains. It is found that interaction between small size grains is generally less significant. A magnetic grain size of less than 50 nm is more suitable for to obtain the low signal-to-noise ratio [22].

**Microstructural analysis**

The surface morphology and microstructure of SrZn$_x$Zr$_x$Fe$_{12-2x}$O$_{19}$ hexaferrite system were observed by scanning electron microscopy (SEM) technique. The images obtained by scanning electron microscopy are as shown in Fig. 5.3. The surface of synthesized samples appears to be a mixture of individual nanoparticles of well crystalline nature and aggregates formed as a resultant of agglomeration of individual nanoparticles.

These SEM images were used to obtain the grain size. The grain size was calculated using linear intersect method. The results indicate that all the particles have a proper hexagonal shape. The average grain size calculated from SEM was found in the range of 40-90 nm.
Fig 5.3 Scanning Electron Microscopy Pattern for SrZn$_2$Zr$_x$Fe$_{12-2x}$O$_{19}$

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Compositional Analysis

The EDAX plots gives the evidence of Sr$^{2+}$, Fe$^{3+}$, Zn$^{2+}$, and Zr$^{4+}$ ions with proper ratio confirming the desired stoichiometric composition. The results of energy dispersive spectroscopy are in good agreement with its nominal composition. The energy dispersive X-ray analysis plots for all the samples are shown in Fig. 5.4.

Fig. 5.4 Energy dispersive spectroscopy pattern for SrZn$_{x}$Zr$_{x}$Fe$_{12-2x}$O$_{19}$
Fourier Transform Infrared Spectroscopy

The Fourier transform infrared spectra (FT-IR) of SrZn$_x$Zr$_{3-x}$Fe$_{12-2x}$O$_{19}$ samples were recorded using KBr pellet method on Perkin-Elmer spectrophotometer. FT-IR spectra of all the annealed samples were recorded in the range of 4000-450 cm$^{-1}$ at room temperature. The FT-IR spectra are generally used to investigate the chemical and structural changes that take place during the combustion process and to reveal the mechanism of self-propagating combustion. FT-IR spectra of all the samples have been taken to investigate the changes in the spectra due to the substitution of Fe$^{3+}$ by Zn$^{2+}$ and Zr$^{4+}$ cations as a function of ‘x’ and heat treatment.

The FT-IR spectra for all the synthesized samples are as shown in Fig 5.5 (a, b and c). The absorption bands between 450 cm$^{-1}$ and 565 cm$^{-1}$ appear when heat treatment is performed on gel and increases with heat treatment which is attributed to the formation of hexaserrite [23]. Large band around 3525 cm$^{-1}$ and 2926 cm$^{-1}$ is attributed to the stretching modes of vibration of H$_2$O molecules and the band corresponds to 1713 cm$^{-1}$ and 1691 cm$^{-1}$ is due to the deformation of H$_2$O molecules.

The large band at 1057 cm$^{-1}$ can be assigned for the presence of NO$_3^-$ ions, for the higher concentration of Zirconium and nickel in the strontium hexaserrite lattice the intensity of this band decreases. Such a modification in the intensity could be related to the shape of the particles in the samples [24, 25]. The absorption bands at about 949 cm$^{-1}$ is attributing to the metal oxygen stretching vibration of strontium hexaserrite [26, 27].
Fig. 5.5 (a) FT-IR spectra of SrZn$_{x}$Zr$_{1-x}$Fe$_{12-2x}$O$_{19}$ samples.
Fig. 5.5 (b) FT-IR spectra of SrZn$_x$Zr$_x$Fe$_{12-2x}$O$_{19}$ samples.
Fig. 5.5 (c) FT-IR spectra of SrZn$_2$Zr$_x$Fe$_{12-2x}$O$_{19}$ samples.
5.3.3 ELECTRICAL PROPERTIES

D. C. Electrical resistivity measurements

The D. C. electrical resistivity measurements were carried out within the temperature range of 300-923 K using two point probe method. The resistivity ($\rho$) was calculated using the equation (4.7).

The variation of D.C. electrical resistivity with reciprocal of temperature (1000/T) is as shown in Fig. 5.6. It is clear from Fig. 5.6 that the resistivity plot exhibit semiconducting behaviour and obeys Arrhenius relation given by equation (4.8).

![Graph showing variation of resistivity with temperature](image)

**Fig. 5.6 Variation of Log $\rho_{\text{d.c.}}$ versus 1000/T for SrZn$_x$Zr$_{x}$Fe$_{12-2x}$O$_{19}$.**

The activation energy (Ea) was also calculated from D.C. electrical resistivity data. The activation energy increases on changing from the ferrimagnetic to paramagnetic region. This is due to the fact that the
ferrimagnetic state is an ordered state while the paramagnetic state is disordered, thus charge carrier require more energy for the conduction. It is found that the activation energy in paramagnetic region is greater than that of ferromagnetic region, is due to the volume expansion of the samples during the magnetic transitions [28, 29].

The calculated values for activation energy in both paramagnetic region (E_p) and ferrimagnetic region (E_f) are tabulated in Table 5.3.

<table>
<thead>
<tr>
<th>Composition ‘x’</th>
<th>Activation energy in (eV)</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E_p</td>
<td>E_f</td>
<td>ΔE = E_p - E_f</td>
<td></td>
</tr>
<tr>
<td>0.0</td>
<td>0.6251</td>
<td>0.182</td>
<td>0.4431</td>
<td></td>
</tr>
<tr>
<td>0.2</td>
<td>0.5528</td>
<td>0.144</td>
<td>0.4088</td>
<td></td>
</tr>
<tr>
<td>0.4</td>
<td>0.5202</td>
<td>0.1445</td>
<td>0.3747</td>
<td></td>
</tr>
<tr>
<td>0.6</td>
<td>0.4801</td>
<td>0.1401</td>
<td>0.3400</td>
<td></td>
</tr>
<tr>
<td>0.8</td>
<td>0.4307</td>
<td>0.1264</td>
<td>0.3043</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>0.3051</td>
<td>0.0373</td>
<td>0.2678</td>
<td></td>
</tr>
</tbody>
</table>

The effect of Zn-Zr substitution on the activation energy (E_a) is shown in Fig. 5.7. It is clear from Fig. 5.6 and 5.7 that the value of resistivity and
activation energy decreases as Zn-Zr content ‘x’ increases. This decrease in D.C. electrical resistivity (ρ) and activation energy (Ea) is due to electron hopping and occupancy of doped ions at different lattice sites. The Zr\textsuperscript{4+} ions occupy 4f\textsubscript{t} (tetrahedral) as well as 2b (trigonal bipyramidal) sites where as the Zn\textsuperscript{2+} ions occupy 4f\textsubscript{t} (tetrahedral) site \textsuperscript{[30, 31]}. The occupation of tetrahedral sites by Zn\textsuperscript{2+} and Zr\textsuperscript{4+} ions would force some of Fe\textsuperscript{3+} ions to migrate from tetrahedral site to octahedral site. The large number of Fe\textsuperscript{3+} ions at octahedral site would consequently enhance the electronic hopping between Fe\textsuperscript{2+} and Fe\textsuperscript{3+} sites causing the D.C. electrical resistivity (ρ) and activation energy (Ea) to decrease.

![Graph](image)

**Fig. 5.7 Variation of activation energy (eV) with Zn-Zr content ‘x’ of the series SrZn\textsubscript{x}Zr\textsubscript{x}Fe\textsubscript{12-2x}O\textsubscript{19}.

The D.C. electrical resistivity data was also used to calculate the drift mobility (μ\textsubscript{d}) using the equation (4.9) and (4.10). The drift mobility increases with increase in temperature in the semiconductor region due to
hopping of charge carriers from one site to another site. The D.C. electrical resistivity decreases whereas the drift mobility increases. The variation of drift mobility ($\mu_d$) with the reciprocal of temperature (1000/T) is as shown in Fig. 5.8.

Fig. 5.8 Variation of drift mobility ($\mu_d$) versus 1000/T for SrZn$_x$Zr$_x$Fe$_{12-2x}$O$_{19}$.

Dielectric measurements

The frequency dependence of dielectric constant ($\varepsilon'$), dielectric loss ($\varepsilon''$) and dielectric loss tangent (tan $\delta$) were studied at room temperature for all samples. The dielectric constant ($\varepsilon'$) is calculated using the equation (4.11). The variation of dielectric constant ($\varepsilon'$) as a function of logarithm of frequency is as shown in Fig. 5.9.
The dielectric structure of ferrite consists two layers of which first layer consist of large number of grains and other layer consists of grain boundaries that acts as highly resistive medium at lower frequencies as described by Maxwell-Wanger model [32]. The polarization in ferrite is similar to conduction process by electron exchange between Fe$^{2+}$ and Fe$^{3+}$ ions. When microwaves enter in dielectric material, their speed decreases by a factor nearly equal to the square root of the dielectric constant ($\varepsilon'$). Therefore the relative speed that an electromagnetic signal can travel in the material is determined by the dielectric constant ($\varepsilon'$) of that material.

**Fig. 5.9** Variation of dielectric constant ($\varepsilon'$) of SrZn$_x$Zr$_x$Fe$_{12-2x}$O$_{19}$ with logarithmic frequency.

It can be seen that the dielectric constant is larger at low frequencies than at high frequencies. This is due to the fact that the amplitude of vibration of the ions is much greater at the lower frequencies (lower than natural
frequency of vibration of the ions), therefore most of the dipoles get the chance to be aligned in the direction of the electric field and the amplitude of vibration of the ions is much smaller at higher frequencies (higher than natural frequency of vibration of the ions) which means that large number of dipoles cannot follow upon the electric field variation and the net polarization in the material is no longer in phase with the electric field so that $\varepsilon'$ becomes small [33].

The variation of dielectric loss tangent (tan $\delta$) as a function of logarithm of frequency is as shown in Fig. 5.10.

![Graph showing variation of tan $\delta$ with log F]

**Fig. 5.10 Variation of dielectric loss tangent (tan $\delta$) of SrZn$_x$Zr$_x$Fe$_{12-2x}$O$_{19}$ with logarithmic frequency.**

From Fig. 5.9 and 5.10 it is clear that the values of dielectric constant ($\varepsilon'$) and dielectric loss tangent (tan $\delta$) increases as Zn-Zr content ‘x’ increases. This is because the mechanism of polarization in ferrite is similar to that of
the conduction process. If some of iron ions migrate from tetrahedral site to octahedral site due to occupation by Zn$^{2+}$ and Zr$^{4+}$ a decrease in D.C. electrical resistivity and increase in the value of dielectric constant ($\varepsilon'$) and dielectric loss tangent (tan $\delta$) would take place. The dielectric constant and dielectric loss tangent data are in good agreement with the resistivity, activation energy and drift mobility data.

The dielectric loss factor ($\varepsilon''$) was calculated using the equation (4.12). The variation of dielectric loss factor ($\varepsilon''$) with frequency is shown in Fig. 5.11. It is evident from Fig. 5.11 that the dielectric loss factor increases with increase in Zn-Zr content ‘x’ in similar manner to that of dielectric constant ($\varepsilon'$). High values for dielectric loss factor ($\varepsilon''$) at lower frequencies are observed due to impurities, crystal defects and moisture [34].

**Fig. 5.11** Variation of dielectric loss factor ($\varepsilon''$) of SrZn$_x$Zr$_{12-2x}$Fe$_{12-2x}$O$_{19}$ with logarithmic frequency.
5.3.4 MAGNETIC PROPERTIES

Vibrating Sample Magnetometer Measurement

The magnetic properties of all the samples were studied using vibrating sample magnetometer (VSM) technique. Magnetization (M) versus applied field (H) plots for all the samples exhibit ferromagnetic behavior. All the samples saturates well.

The hysteresis loops for Zr$^{4+}$ and Zn$^{2+}$ substituted strontium hexaferrite samples are depicted in Fig. 5.12. The saturation magnetization (Ms) and remanence magnetization (Mr) increases while the coercivity (Hc) decreases for Zn-Zr substitution.

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**Fig. 5.12** Hysteresis plots of SrZn$_x$Zr$_{x}$Fe$_{12-2x}$O$_{19}$ samples
The width of the hysteresis loop decreases with the increase in Zn-Zr concentration indicating the decrease in coercivity of the materials. The saturation magnetization depends upon the number of uncompensated spin of electrons in Sr-hexaferrite. The 12 ferric ions in Sr-hexaferrite are distributed over 5 different sub-lattice sites. Out of these 5 sublattices, 3 are octahedral (2a, 12k and 4f2), one tetrahedral (4f1) and one trigonal bipyramidal (2b). The number of ferric ions present at sub-lattices 12k are 6,1 ferric ion is present at 2a site and 1 ferric ion at 2b site have the spin of electrons in the upward direction. While, the number of ferric ions present at sub-lattices 4f2 are 2 and 2 ferric ions at 4f1 having downward spins [33].

According to the configuration of Fe$^{3+}$, there are 5 unpaired electrons in the 3d orbital, each Fe$^{3+}$ ion has the magnetic moment of 5μB. Out of 12, the 8 ferric ions have the electronic spin in upward direction and other 4 have spin in downward direction. The 4 upward and 4 downward electronic spins cancel each other and the net magnetic moment is due to the remaining 4 ferric ions having spin in upward direction. So the total moment is 20 μB per formula unit in the M-type hexaferrites [35].

The values of saturation magnetization, remanence magnetization, remanence ratio and coercivity obtained from hysteresis loop data are listed in Table 5.4. From Table 5.4, it is clear that the magnetic properties were influenced by Zr$^{4+}$ and Zn$^{2+}$ substitution in the strontium hexaferrite. The values of saturation magnetization and remanence magnetization increases with the increase in Zn-Zr contents up to a concentration of x= 0.4 and then decreases. This can be explained on the basis of the occupancy of Zn$^{2+}$ and Zr$^{4+}$ ions at different lattice sites. Both the dopants are nonmagnetic ions (Zn$^{2+}$ and Zr$^{4+}$) would replace the iron ions from the
sites having spins in downward direction. As they replace iron ions at the tetrahedral (4f1) sites. The net increase in the spin of the Fe3+ ions in the upward direction causes the total magnetic moment and the saturation magnetization to increase.

The decrease in saturation magnetization Ms and remanence magnetization Mr for the samples with \( x > 0.4 \), is due to the presence of large amount of nonmagnetic Zn2+ and Zr4+ (\( x > 0.4 \)) ions. These nonmagnetic ions would decrease the super exchange interactions between 4f1-12k and 4f2-2a to result in a decrease in the saturation magnetization.

This abrupt fall in both the properties is due to the loss of magnetic collinearity leading to the spin canting. It is well known that in M-type hexaferrites, the 12k, 4f2 (octahedral) and 2b (trigonal bipyramidal) sites are the major contributors to their magneto-crystalline anisotropy. Replacement of Fe3+ from 4f1 and 2b sites by doping with nonmagnetic Zn2+ and Zr4+ions would have a negative impact on magneto-crystalline anisotropy.

Consequently, a decrease in coercivity with an increase in Zr–Zn content is expected to result. The coercivity decreased with the increase in Zn–Zr content due to decrease in magneto-crystalline anisotropy. There are few examples in which the saturation magnetization increased and at the same time the coercivity decreased with substitutions in M-type hexaferrites.

The increase in the saturation magnetization and remanence, together with the decrease in coercivity, makes the materials more suitable for the applications in magnetic recording media. Our results on the magnetic properties of Zr–Zn substituted strontium hexaferrite are in good