Chapter 4

RESULTS AND DISCUSSION ON SrNi₇ZrFe₁₂₋₂₅O₃₉ HEXAFERRITE NANOPARTICLES

4.1 INTRODUCTION

In the family of ferrites, M-type hexaferrite have extensive applications in telecommunication, microwave devices and magnetic recording media due to their good chemical stability, corrosion resistance, combined electrical and magnetic properties [1, 2]. These properties are strongly influenced by composition and synthesis methods. Ceramic method is commonly used for the synthesis of M-type hexagonal ferrite. However, ceramic method has inherent drawbacks which can be overcome in wet chemical methods. Wet chemical method produces particles of nanometer dimensions. The properties of nano-size ferrites are found to be superior and interesting as compared to their bulk counterpart [3].
Considering the importance of magnetic nano particles in several recent applications, nanoparticles of strontium hexaferrite have been widely investigated. The structural, morphological, electric and dielectric properties of these magnetic materials are related to purity, size and morphology of precursor powder. By modifying its microstructure and controlling its chemical composition, size and morphology its properties can be improved \cite{41}.

The magnetic and electrical properties of SrFe$_{12}$O$_{19}$ are strongly depends upon the size and shape of particles \cite{55}. Therefore, several methods have been used to prepare strontium ferrite including solid-state reaction \cite{66}, chemical co-precipitation \cite{77}, self-propagating high temperature synthesis \cite{88}, citrate precursor \cite{99}, ball milling \cite{101}, hydrothermal \cite{111}, sol-gel \cite{122} and salt melt method \cite{133}.

Nano-crystalline strontium hexaferrite (SrFe$_{12}$O$_{19}$) powder is a promising material for use as microwave absorbers in the gigahertz (GHz) range due to its high saturation magnetization, high coercivity, high electrical resistivity and because of its low dielectric and magnetic losses in the microwave frequency band \cite{144, 155}. The materials with high electrical resistivity and low dielectric constant values are more suitable for microwave devices \cite{166}. Owing to the applications of strontium hexaferrite in new emerging techniques the demand for the development of new magnetic materials has extraordinarily increased today.

The substitution of various cations in place of Fe$^{3+}$ ions has been extensively studied by various workers \cite{177-199}. In the present work tetravalent (Fe$^{5+}$) ions are substituted by divalent (Ni$^{2+}$) and tetravalent (Zr$^{4+}$) ions to improve the structural, electrical, dielectric and magnetic properties of strontium hexaferrite nanomaterials.
4.2 EXPERIMENTAL TECHNIQUES

4.2.1 Sample preparation

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, nickel nitrate Ni(NO$_3$)$_2$.6H$_2$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 SrNi$_x$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 de-ionized water and stirred on magnetic stirrer for ten minutes. 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 taken as 1:3. The solutions 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$^\circ$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$^\circ$C for 9 hrs to obtain pure SrNi$_x$Zr$_x$Fe$_{12-2x}$O$_{19}$ hexaferrite powder.

4.2.2 Characterization techniques

The thermal decomposition behavior of as prepared powder was examined by simultaneous thermo gravimetric analysis (TGA/DTA) using Shimadzu -DTG-60. The phase identification of the prepared sample was performed with the help of X-ray diffractometer (Rigaku Miniflux-II) in the 20 range from 20$^\circ$ to 80$^\circ$ at room temperature using CuK$\alpha$ radiation (wavelength $\lambda$ = 1.5406Å). The surface morphology of the prepared samples was studied by Scanning electron microscopy (Model No. LEO 1430) technique. The
stoichiometric proportion of the constituent ions was examined through the Energy dispersive spectroscopy (EDS) technique.

The Fourier transform infrared spectroscopy (FT-IR) spectra of all the calcined samples were recorded in the range of 4000-450 cm⁻¹. FT-IR spectra of all the samples have been taken to investigate the changes in the spectra due to the substitution of Fe³⁺ by Ni²⁺ and Zr⁴⁺ cations as a function of ‘x’ and heat treatment. 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.

The D.C. electrical resistivity measurements were carried out in the temperature range 300-923K using two probe method. As the resistivity of the Sr-hexaferrite is very high and it was not possible to use the four-point probe method because it is used for the samples having low resistance. The use of four-point probe method is also not suitable at high temperature due to un-stability of silver paste used for connections. While the two point probe method is suitable for the samples having high resistivity and at high temperature.

Dielectric properties like dielectric constant (ε’), dielectric loss (ε’’) and dielectric loss tangent (tan δ) were studied using LCR-Q meter as a function of logarithm of frequency. The capacitance of all the samples was measured in the frequency range of 50Hz to 5MHz.

Magnetization measurements at room temperature were performed using vibrating sample magnetometer (VSM) technique. Using M-H plots, the saturation magnetization (Ms), corecivity (Hc), remanence magnetization
(Mr), remanence ratio (Mr/Ms) and magneton number (nB) were calculated.

The Curie temperature is an important magnetic characteristic. It reveals the temperature of the transition of the magnetic materials from a ferromagnetic to a paramagnetic state. A.C. Susceptibility technique was used to determine Curie temperature (Tc) of all the samples. The A.C. susceptibility measurements were carried out using double coil setup in the temperature range 300 K to 800 K. The variation of A. C. susceptibility with temperature and composition ‘x’ is studied in the present work.

### 4.3 RESULTS AND DISCUSSION

#### 4.3.1 Thermal analysis

TGA/DTA plots for as synthesized samples of the strontium hexaferrite with the chemical composition SrNi$_{0.2}$Zr$_{0.2}$Fe$_{11.6}$O$_{19}$ are as shown in Fig. 4.1.

![TGA/DTA plot](image.png)

**Fig. 4.1** Thermo gravimetric and differential thermal analysis of SrNi$_{0.2}$Zr$_{0.2}$Fe$_{11.6}$O$_{19}$ hexaferrite
It can be observed from Fig. 4.1 that, the 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 calcinations temperature selected for all other composition of strontium hexaferrite was 950°C.

4.3.2 STRUCTURAL ANALYSIS

X-ray diffraction (XRD)

X-ray diffraction pattern for all synthesized samples is shown in Fig. 4.2.

![X-Ray diffraction patterns for SrNiₓZrₓFe_{12-2x}O_{19}]
X-ray diffraction analysis reveals that all the diffraction peaks seen in the XRD pattern well matches with the standard pattern of strontium hexa ferrite (JCPDS Card No. 84-1531). The analysis of XRD pattern revealed the formation of single phase M-type hexagonal structure.

Various structural parameters were calculated from XRD data using the following equations. The lattice constants a and c were calculated using the equation

$$\frac{1}{d_{hkl}^2} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}$$ \hspace{1cm} (4.1)

Where, $d_{hkl}$ is the crystal face distance and (hkl) is the miller indices.

The cell volume (V) is calculated using the equation

$$V = 0.8666 \ a^2 \ c$$ \hspace{1cm} (4.2)

The values of lattice parameters calculated using above equations are presented in the Table 4.1. It is evident from Table 4.1 that the lattice constant ‘a’ almost remains constant while ‘c’ increases with increase in Ni-Zr content ‘x’. This can be attributed to the fact that the ionic radii of Fe$^{3+}$ ions (0.64Å) is smaller than that of substituted cations Ni$^{2+}$ (0.69Å) and Zr$^{4+}$ (0.80Å). Both the lattice constant ‘a’ and ‘c’ increases linearly obeying Vegard’s law [20]. In the present case two Fe$^{3+}$ ions are replaced by Ni$^{2+}$ and Zr$^{4+}$ ions. The behaviour of lattice constant of the present samples is analogous to Ni-Zr substituted Sr ferrite prepared by chemical co-precipitation method [21].

The unit cell volume (V) calculated using the relation (4.2) is shown in Table 4.1 as a function of Ni-Zr content ‘x’. It is observed that unit cell volume increases with increasing Ni-Zr content ‘x’, which is attributed to increase in lattice constant ‘c’ of the present samples.
Table 4.1
Lattice constants (a and c), c/a ratio and cell volume (V) of SrNiₓZrₓFe₁₂₋₂ₓO₁₉.

<table>
<thead>
<tr>
<th>Structural 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>5.876</td>
<td>5.880</td>
<td>5.885</td>
<td>5.890</td>
<td>5.895</td>
</tr>
<tr>
<td>c (Å)</td>
<td>23.06</td>
<td>23.10</td>
<td>23.13</td>
<td>23.17</td>
<td>23.21</td>
<td>23.26</td>
</tr>
<tr>
<td>c/a</td>
<td>3.9284</td>
<td>3.9312</td>
<td>3.9336</td>
<td>3.9371</td>
<td>3.9405</td>
<td>3.9457</td>
</tr>
<tr>
<td>V(Å³)</td>
<td>689.28</td>
<td>691.44</td>
<td>693.76</td>
<td>696.00</td>
<td>698.18</td>
<td>700.28</td>
</tr>
</tbody>
</table>

X-ray density (ρₓ), bulk density (ρₘ) and porosity (P) were calculated using the equations 4.3, 4.4 and 4.5 respectively.

\[ \rho_x = \frac{ZM}{N_A V} \]  \hspace{1cm} 4.3

where, Z is the number of formula units in unit cell, M is the molecular mass of the sample and Nₐ is the Avogadro’s number.

\[ \rho_m = \frac{m}{\pi r^2 h} \]  \hspace{1cm} 4.4

where, m is the mass of the pellet, h is the height of the pellet and r is the radius of the pellet.

\[ P = 1 - \frac{\rho_m}{\rho_x} \]  \hspace{1cm} 4.5
The crystallite size was calculated using the Scherrer formula for which the most intense peak (114) was considered.

\[
D = \frac{k\lambda}{\beta \cos(\theta)}
\]

where, \(\lambda\) is the X-ray wavelength, \(\beta\) is the full width at half maximum, \(\theta\) is the Bragg angle and \(k = 0.89\).

The values of X-ray density \((\rho_x)\), bulk density \((\rho_m)\), porosity \((P)\) and crystallite size \((D)\) are presented in Table 4.2.

<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>(D) (nm)</td>
<td>44.76</td>
<td>41.46</td>
<td>47.41</td>
<td>46.03</td>
<td>41.91</td>
<td>36.46</td>
</tr>
<tr>
<td>(\rho_x) (g cm(^{-3}))</td>
<td>5.11</td>
<td>5.13</td>
<td>5.15</td>
<td>5.17</td>
<td>5.19</td>
<td>5.22</td>
</tr>
<tr>
<td>(\rho_m) (g cm(^{-3}))</td>
<td>3.00</td>
<td>3.08</td>
<td>3.15</td>
<td>3.23</td>
<td>3.30</td>
<td>3.37</td>
</tr>
<tr>
<td>(P) (%)</td>
<td>0.41</td>
<td>0.38</td>
<td>0.37</td>
<td>0.37</td>
<td>0.36</td>
<td>0.36</td>
</tr>
</tbody>
</table>

It is clear from Table 4.2 that, the X-ray density \((\rho_x)\) increases due to larger molar mass of substituted samples. The bulk density \((\rho_m)\) also increases whereas porosity \((P)\) decreases with Ni-Zr content ‘x’. The crystallite size obtained from XRD data is in the range of 36-47 nm, indicating the nano crystalline nature of the present samples.
Morphology

The images obtained by scanning electron microscopy are shown in Fig. 4.3. 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. 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. 4.3 Scanning Electron Microscopy pattern for SrNi$_x$Zr$_x$Fe$_{12-2x}$O$_{19}$
Compositional Analysis

The energy dispersive X-ray analysis plots for all the samples are shown in Fig. 4.4. The results of energy dispersive spectroscopy are in good agreement with its nominal composition. The EDAX plots gives the evidence of Sr$^{2+}$, Ni$^{2+}$, Zr$^{4+}$ and Fe$^{3+}$ ions with proper ratio confirming the desired stoichiometric composition.

![Energy dispersive spectroscopy plots](image)

Fig. 4.4 Energy dispersive spectroscopy pattern for SrNi$_x$Zr$_y$Fe$_{12-2y}$O$_{19}$
Fourier Transform Infrared Spectroscopy

FT-IR spectra of all the annealed samples were recorded in the range of 4000-450 cm⁻¹. They show two main absorption bands with the characteristics of formation of ferrites. The spectra of these samples generally contain the bands observed in SrFe₁₂O₁₉. However, there are some additional bands as well as some changes in the position and intensity of the SrM bands which give valuable information about the site occupation of the substituted cations.

The FT-IR spectra for typical samples are as shown in Fig 4.5 (a, b and c). This spectrum shows the various absorption bands at various positions for different functional groups present in the sample. The large band around 3525 cm⁻¹ and 2929 cm⁻¹ is attributed to the stretching modes of vibration of H₂O molecules and the band corresponds to 1727 cm⁻¹ is due to the deformation of H₂O molecules.

The large band at 1057 cm⁻¹ can be assigned for the presence of NO₃⁻ ions, for the higher concentration of Zirconium and nickel in the strontium hexaferrite 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 [22]. The absorption bands at about 949 cm⁻¹ and 576 cm⁻¹ can be attributing to the metal oxygen stretching vibration of strontium hexaferrite [23].

The slight change in band position is observed due to substitution of zirconium and nickel. The band positions are slightly shifts towards lower frequency with increase in zirconium and nickel substitution in strontium hexaferrite matrix.
Fig. 4.5(a) FT-IR spectra of SrNi$_x$Zr$_x$Fe$_{12-2x}$O$_{19}$ samples.
Fig. 4.5(b) FT-IR spectra of SrNi$_x$Zr$_x$Fe$_{12-2x}$O$_{19}$ samples.
Fig. 4.5(c) FT-IR spectra of SrNi$_x$Zr$_x$Fe$_{12-2x}$O$_{19}$ samples.
4.3.3 ELECTRICAL PROPERTIES

D. C. Electrical resistivity measurements

The resistance (R) was measured using two point probe method within the temperature range of 300-923K and was used to calculate the resistivity (ρ) using the following equation

\[
\rho = \frac{RA}{h}
\]

where, R is the resistance, h is the thickness and A (= \( \pi r^2 \)) is the area of the pellet. The variation of D.C. electrical resistivity with reciprocal of temperature (1000/T) is as shown in Fig. 4.6.

![Graph showing the variation of log ρ vs 1000/T for SrNi₃ZrₓFe₁₂₋₂ₓO₁₉](image)

*Fig. 4.6 Variation of Log \( \rho_{\text{d.c.}} \) versus 1000/T for SrNi₃ZrₓFe₁₂₋₂ₓO₁₉*

It is clear from Fig. 4.6 that the resistivity plot exhibit semiconducting behaviour and obeys Arrhenius relation
\[ \rho = \rho_0 \exp \left( \frac{E_a}{k_B T} \right) \]  

where, \( \rho \) is the electrical resistivity at temperature \( T \), \( \rho_0 \) is the resistivity at initial value of temperature, \( E_a \) is the activation energy and \( k_B \) is the Boltzmann's constant.

Further it can be observed from resistivity plots that the curve is divided into two regions high temperature (paramagnetic region) and low temperature (ferrimagnetic region). The activation energy (\( E_a \)) is also calculated from D.C. electrical resistivity data. It was found that the activation energy in paramagnetic region is greater than that of ferromagnetic region. The calculated values for activation energy in both paramagnetic region (\( E_p \)) and ferrimagnetic region (\( E_f \)) are tabulated in Table 4.3.

<table>
<thead>
<tr>
<th>Composition 'x'</th>
<th>Activation energy in (eV)</th>
<th>( \Delta E = E_p - E_f )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.7008</td>
<td>0.2558</td>
</tr>
<tr>
<td>0.2</td>
<td>0.8788</td>
<td>0.3598</td>
</tr>
<tr>
<td>0.4</td>
<td>0.9409</td>
<td>0.3125</td>
</tr>
<tr>
<td>0.6</td>
<td>0.9505</td>
<td>0.2433</td>
</tr>
<tr>
<td>0.8</td>
<td>1.2001</td>
<td>0.3225</td>
</tr>
<tr>
<td>1.0</td>
<td>1.4804</td>
<td>0.5828</td>
</tr>
</tbody>
</table>
It is evident from Table 4.3 that, the activation energy increases as Ni-Zr content ‘x’ increases. The variation of activation energy with Ni-Zr content ‘x’ is as shown in Fig. 4.7.

![Graph showing variation of activation energy with composition 'x'](image)

**Fig. 4.7 Variation of activation energy (eV) with Ni-Zr content ‘x’ of the series SrNi$_x$Zr$_{12-x}$Fe$_{2x}$O$_{19}$**

The room temperature values of resistivity were found to increase with increase in Ni-Zr content ‘x’. The D.C. electrical resistivity data is used to calculate the drift mobility ($\mu_d$) using the following equation

$$\mu_d = \frac{1}{ne\rho} \tag{4.9}$$

where, e is the charge of electron, $\rho$ is the electrical resistivity and n is charge carrier concentration calculated using following equation

$$n = \frac{N_A d_p P_{Fe}}{M} \tag{4.10}$$

where, $N_A$ is the Avogadro’s number, M is the molecular mass of the
sample, $P_{Fe}$ is the number of iron atoms in the chemical formula of ferrite samples and $d_b$ is the bulk density.

It was found that the D.C. electrical resistivity increases whereas the drift mobility decreases. The conduction mechanism operating at these two levels can be explained on the basis of electron hopping between Fe$^{2+}$ and Fe$^{3+}$ at octahedral sites. Ni$^{2+}$ ions occupy the 12k (octahedral) site and Zr$^{4+}$ ions occupy the 4f1 (tetrahedral) as well as the 2b (trigonal bypyramidal) sites. When Ni$^{2+}$ ions replaces iron ions at octahedral sites, the number of iron ion decreases at that site and as a result the number of hopping electron decreases, causing the D.C. electrical resistivity to increase and drift mobility to decrease \[14\]. The variation of drift mobility ($\mu_d$) with reciprocal of temperature ($1000/T$) is as shown in Fig. 4.8.

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**Fig. 4.8** Variation of drift mobility ($\mu_d$) versus $1000/T$ for the series SrNi$_x$Zr$_{x}$Fe$_{12-2x}$O$_{19}$
Dielectric measurements

The dielectric constant ($\varepsilon'$) was calculated using the equation

$$\varepsilon' = \frac{Cd}{\varepsilon_0 A}$$

where, C is the capacitance in Farad, d is the thickness of the pellet in meter, A is the cross sectional area of the flat surface of the pellet and $\varepsilon_0$ is the permittivity of the free space.

The variation of dielectric constant ($\varepsilon'$) with logarithm of frequency is as shown in Fig. 4.9.

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**Fig. 4.9 Variation of dielectric constant ($\varepsilon'$) Vs Log F.**

The dielectric structure of ferrite consists of 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 [25]. 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. The variation dielectric loss tangent (\(\tan \delta\)) with logarithm of frequency is as shown in Fig. 4.10.

![Graph showing variation of dielectric loss tangent (\(\tan \delta\)) vs Log F.](image)

**Fig. 4.10 Variation of dielectric loss tangent (\(\tan \delta\)) Vs Log F.**

From Fig. 4.9 and 4.10 it is clear that both the dielectric constant (\(\varepsilon'\)) and dielectric loss tangent (\(\tan \delta\)) decreases as the frequency increases. The decrease in dielectric constant (\(\varepsilon'\)) with increase in frequency is due to the charge polarization. The charge polarization takes place by hopping of electron between Fe\(^{2+}\) and Fe\(^{3+}\) ions. As the frequency of applied electric field increases it becomes more difficult for the electron to hop from Fe\(^{2+}\) and Fe\(^{3+}\) ions with the alternating frequency, the net displacement of charge in one direction decreases and hence dielectric constant (\(\varepsilon'\))
decreases [26]. Due to moisture, voids, dislocation, density and impurities, it is observed that at relatively lower frequencies the value of dielectric constant ($\varepsilon'$) is high as compared to that of higher frequencies.

The dielectric loss factor ($\varepsilon''$) was calculated using the equation

$$\varepsilon'' = \varepsilon' \tan \delta$$

The variation of dielectric loss factor ($\varepsilon''$) with frequency is shown in Fig. 4.11.

![Graph showing variation of dielectric loss factor ($\varepsilon''$) vs log F](image)

**Fig. 4.11 Variation of dielectric loss factor ($\varepsilon''$) Vs Log F.**

It is evident from Fig. 4.11 that the dielectric loss factor decreases with increase in frequency and at higher frequency it remains almost constant in similar manner to that of dielectric constant ($\varepsilon'$). According to Hudson [27], high values for dielectric loss factor ($\varepsilon''$) at lower frequencies are observed due to impurities, crystal defects and moisture.
4.3.4 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. Using M-H plots, the saturation magnetization (Ms), corecivity (Hc), remanance magnetization (Mr), remanance ratio (Mr/Ms) were calculated. The hysteresis loops for Ni^{2+} and Zr^{4+} substituted strontium hexaferrite samples are depicted in Fig. 4.12.

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**Fig. 4.12 Hysteresis plots of SrNi_xZr_xFe_{12-2x}O_{19} samples**

It is clear from Fig. 4.12 that, the saturation magnetization increases up to $x = 0.8$ and then decreases while the remanence magnetization increases up to $x = 0.6$ and then decreases with the increase in Ni-Zr content. This
can be explained on the basis of the Ni$^{2+}$ and Zr$^{4+}$ ions occupying different sites in the Fe$^{3+}$ sub-lattices based on the previous research reports [21, 24]. From this report, Zr$^{4+}$ ions replace Fe$^{3+}$ ions at the 2b site for small substitutions (x = 0.1) and at 4f1 for higher substitutions, while Ni$^{2+}$ ions replace Fe$^{3+}$ ions at the 4f2 site for x = 0.1, and at the 12k site for larger values of substitutions. When a nonmagnetic Zr$^{4+}$ ion replaces a Fe$^{3+}$ ion at the 4f1 site with spin down, then the total number of unpaired electrons with upward spin is increased, causing the saturation magnetization of the samples to increase. The Ni$^{2+}$ ions replace Fe$^{3+}$ at the 12k site with spin up and a magnetic moment of 2 μB, which is also less than that of Fe$^{3+}$ (5 μB), but the total magnetic moment increases by 2 μB due to replacement of ferric ions by a nonmagnetic Zr$^{4+}$ ion at the 4f1 site. The decrease in saturation magnetization above x = 0.8 is due to the larger amount of nonmagnetic ions which are responsible for the weakening of exchange interactions [28].

The coercivity decreases with increasing Zr–Ni content, which is due to the decrease in the magneto-crystalline anisotropy. There are very few reported examples in which the saturation magnetization increases and at the same time the coercivity decreases with substitutions in M-type hexaferrites. Recording media require high enough coercivity above 600 Oe and saturation magnetization as high as possible [21].

The values of saturation magnetization (Ms), corecivity (Hc), remenances magnetization (Mr), remenances ratio (Mr/Ms) are listed in Table 4.4. From Table 4.4, it is clear that the magnetic properties were influenced by Zr$^{4+}$ and Ni$^{2+}$ substitution in the strontium hexaferrite. Our results on magnetic measurements are in good agreement with the reported, for
substituted strontium hexaferrite \cite{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, 12Fe\textsuperscript{3+} ions are distributed at five different sublattices: three
octahedral (12k, 2a, 4f2), one tetrahedral (4f1) and one trigonal
bipyramidal (2b). Out of 12 Fe\textsuperscript{3+} ions four have spin in downward direction
i.e. 2Fe\textsuperscript{3+} ions at 4f1, 2Fe\textsuperscript{3+} ions at 4f2 while other 8Fe\textsuperscript{3+} ions have spin in
upward direction i.e. 6Fe\textsuperscript{3+} at 12k, 1Fe at 2a, 1Fe\textsuperscript{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\textmu B is due to uncompensated
spin of electron in the upward direction \cite{32}.

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**Table 4.4**

Saturation magnetization (Ms), remanent magnetization (Mr),
remenance ratio Mr/Ms, coercivity (Hc) and magneton number (nB)
of Sr\textsubscript{Ni\textsubscript{x}}Zr\textsubscript{2}Fe\textsubscript{12-2x}O\textsubscript{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>Ms (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>Mr (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>Mr/Ms</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>Hc (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>nB (\textmu 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 $\text{Zr}^{4+}$ and $\text{Ni}^{2+}$ substitution due to the replacement of low magnetic moment of $\text{Zr}^{4+}$ and $\text{Ni}^{2+}$ as compared to $\text{Fe}^{3+}$. 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 $\text{SrNi}_x\text{Zr}_x\text{Fe}_{12-2x}\text{O}_{19}$
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 hexaferrite was also determined from D. C. resistivity and Loria technique [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 4.5

<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 (ε’) and dielectric loss tangent (tan δ) 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 (μB) 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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