Sayings of the Quran

In the Name of Allah, the Most Beneficent, the Most Merciful

(1) Read! In the Name of your Lord, Who has created (all that exists), (2) Has created man from a clot (a piece of thick coagulated blood). (3) Read! And your Lord is the Most Generous, (4) Who has taught (the writing) by the pen (5) Has taught man that which he knew not. (6) Nay! Verily, man does transgress all bounds (in disbelief and evil deed, etc.). (7) Because he considers himself self-sufficient. (8) Surely! Unto your Lord is the return.

(al-alaq, Verses1-8)
Effect on Physical, Electrical and Magnetic Properties of Strontium Hexaferrite Nanomaterial Doped with Binary Mixtures of Various Metal Ions

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Muhammad Naeem Ashiq

DEPARTMENT OF CHEMISTRY
QUAID-I-AZAM UNIVERSITY
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Muhammad Naeem Ashiq
Abstract

Five series of strontium hexaferrite nanomaterials with nominal compositions, SrZr₃NiₓFe₁₂₋₂ₓO₁₉, SrZrₓCuₓFe₁₂₋₂ₓO₁₉, SrZrₓMnₓFe₁₂₋₂ₓO₁₉, SrZrₓZnₓFe₁₂₋₂ₓO₁₉ and SrZrₓAlₓGaₓFe₁₂₋₂ₓO₁₉ (where x = 0.0-0.8) have been synthesized by the chemical co-precipitation method. The structural analysis is carried out by thermogravimetry (TG/DTG), powder X-ray diffraction (XRD) and energy dispersive X-ray fluorescence (ED-XRF) techniques. The DC electrical resistivity (ρ), dielectric constant (ε) and dielectric loss (tanδ) are measured by a two-point probe method and inductance capacitance resistance (LCR) meter, respectively. The magnetic susceptibility (χ) is measured by a magnetic susceptibility and the hysteresis loops, the saturation magnetization (Mₛ), remanence (Mᵣ) and coercivity (Hᶜ) has been determined by the induction method. Thermal analysis reveals that the magnetoplumbite phase begins to form at a temperature of 873 K and is completed at 1193 K which is also complimented by the XRD studies. The average crystallites sizes of the samples of the five series are in the range of 26-62 nm. All the samples consist of pure single phase as confirmed by the magnetic susceptibility and XRD analysis. The nominal theoretical compositions of the samples are experimentally confirmed by the ED-XRF analysis. Except Zr-Mn substituted series all the samples show metal to semiconductor transition (Tₘₛ). The drift mobility (µₐ) and activation energy (Eₐ) are calculated from the electrical resistivity data. The observed variation of electrical resistivity is explained on the basis of the electrons hopping between ferric and ferrous ions. The room temperature electrical resistivity and activation energy are increased by doping with Zr-Ni, Zr-Cu, Zr-Mn and Al-Ga series up to specific concentration but decreases continuously by substitution of Zr-Zn. The dielectric constant (ε) and dielectric loss (tanδ) are calculated in the frequency range of 100 Hz -1MHz and both the parameters decrease with increase in frequency. This behavior is explained on the basis of the Maxwell- Wagner and Koop’s models. The dielectric constant, dielectric loss and drift mobility increase with the increase in the dopant (Zr-Ni, Zr-Cu, Zr-Mn and Al-Ga) contents but increase by the substitution of Zr-Zn. The Curie temperature (Tₑ) is determined from the temperature dependence of magnetic susceptibility (χ) at temperature from 300 to 800 K. the value of Tₑ decreases for all the five series investigated here. The saturation magnetization (Mₛ)
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1.1 Nanoscience

Nanoscience concerns with synthesizing, modifying and characterizing materials having at least one spatial dimension in the size range of 1-100 nm. The field of nanoscience is considered to revolutionize the world and transform into something better. Nanotechnology involves disciplines of science including chemistry, solid state physics, material engineering, medical science and biotechnology.

Developing a new material is to know specifically the size and shape a material must have in order to exhibit a particular property, function and utility. Nanostructured materials have become a very active research field in the area of material chemistry. Nanostructured materials made of nanosize grains or nanoparticles as a building block have a significant fraction of grain boundaries with high degree of disorder of atoms along grain boundaries and a large ratio of surface area to volume. One of the parameters which deviate the properties of nanostructured material from the bulk material is the surface effect which mainly depends upon ratio of surface area to volume [1-2].

Recently attention has been drawn toward the ferrites nanomaterials because of their great scientific and technological importance. Fine particles of strontium hexaferrites are suitable for use in the high density magnetic recording media. One factor that limits the performance of high density recording media is the media noise which results from coupling between the magnetic grains. It is generally believed that the grains interaction should become less significant with small grain size. In high density recording media, magnetic grains <50 nm are desirable for obtaining a suitable signal-to-noise ratio [3]. The low sintered and fine particles of ferrites are also required for multilayer chip inductor [4].

Ferrites are iron containing complex oxides with technically interesting magnetic and electrical properties. The first attempt to prepare various types of ferrites and to industrialize them was not made until the beginning of this century. The commercial ferrites did not get world wide attention because their magnetic properties were considerably inferior to those of the ferromagnetic alloys [5]. Development of new ferrites, enhancement of existing ferrites characteristics and
improvement of the ferrites manufacturing process began in 1950’s because at that time new applications such as radio, television, carrier telephony, computer circuitry and microwave devices were rapidly expanding. There are mainly two types of ferrites called soft and hard ferrites.

Soft ferrites are the magnetic materials that do not retain their magnetism after being magnetized. They have narrow hysteresis loops possessing high saturation magnetization but very small coercive force typically from 0.5 to 4 Oe [6]. These types of materials include cobalt, nickel, zinc, manganese and magnesium ferrites with spinel structure. They are extensively used in the cores of switched-mode power supply (SMPS) and transformers where they must respond to a rapidly oscillating field [7].

Hard ferrites are permanent magnets because they can retain their magnetism after being magnetized. For hard ferrites the loop is broad having coercivity greater than 10 kAm\(^{-1}\). These materials are commonly used in radios and as permanent magnets [6-7]. The examples of hard ferrites are the M-type hexaferrites. The hexaferrite are classified into six main types depending on the chemical composition [8].

1.2 Chemical Composition of Hexaferrites

The chemical composition of the hexagonal compounds is shown in figure 1.1 as a part of ternary phase diagram for the BaO-MeO-Fe\(_2\)O\(_3\) system.

![Figure 1.1 Compositional diagram for the ferrimagnetic ferrites [9].](image-url)
where $\text{Me}$ represents a divalent ion among the first transition elements. The structure of hexaferrites with the primitive repeating unit of crystal structure is built up from three basic sub-units namely S, R and T. The $S^*$, $R^*$ and $T^*$ are the rotational symmetry of S, R, and T at $180^\circ$ around the hexagonal c-axis. The repeating unit ‘S’ has composition of either $[\text{Me}_2^{2+}\text{Fe}_4^{3+}\text{O}_8]^0$ ($S^0$) or $[\text{Fe}_6^{3+}\text{O}_8]^{2+}$ ($S^{2+}$) with neutral or uncompensated charge of +2 per subunit, respectively. The ‘R’ sub-unit has the composition $[\text{Me}^{2+}\text{Fe}_6^{3+}\text{O}_{11}]^{2-}$ whereas the ‘T’ unit is $[\text{Ba}_2^{2+}\text{Fe}_8^{3+}\text{O}_{14}]^0$. The sub-unit ‘R’ combines with ‘$S^{2+}$’ to give the neutral block (RS), with the total composition $\text{MeFe}_{12}\text{O}_{19}$ (M-phase). Similarly, ‘T’ sub-unit combines with the $S^0$ to give the neutral block (TS), with the total composition $\text{Ba}_2\text{Me}_2\text{Fe}_{12}\text{O}_{22}$ (Y-phase). Other stacking sequences of cubic and hexagonal basic units leading to different compositions such as W, X, Y, Z and U-types hexaferrites are also known as shown in table 1.1 [10].

### Table 1.1 Ferrimagnetic oxides in BaO–MeO–Fe$_2$O$_3$ ternary phase [11]

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Composition</th>
<th>Crystallographic build up</th>
<th>No. of molecules /unit cell</th>
<th>c-axis (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M</td>
<td>BaFe$<em>{12}$O$</em>{19}$</td>
<td>$\text{RSR}^<em>\text{S}^</em>$ ($\text{MM}^*$)</td>
<td>$2\text{M}$</td>
<td>23.2</td>
</tr>
<tr>
<td>X</td>
<td>$\text{Ba}<em>2\text{Me}<em>2\text{Fe}</em>{28}\text{O}</em>{46}$</td>
<td>$\text{MM}^*\text{S}$</td>
<td>$3\text{MeX}$</td>
<td>84.0</td>
</tr>
<tr>
<td>W</td>
<td>$\text{Ba}<em>2\text{Me}<em>2\text{Fe}</em>{16}\text{O}</em>{27}$</td>
<td>$\text{MM}^<em>\text{S}^</em>$</td>
<td>$2\text{MeW}$</td>
<td>32.8</td>
</tr>
<tr>
<td>U</td>
<td>$\text{Ba}<em>2\text{Me}<em>2\text{Fe}</em>{36}\text{O}</em>{60}$</td>
<td>$\text{MM}^<em>\text{Y}^</em>$</td>
<td>$\text{MeU}$</td>
<td>38.1</td>
</tr>
<tr>
<td>Z</td>
<td>$\text{Ba}<em>2\text{Me}<em>2\text{Fe}</em>{24}\text{O}</em>{41}$</td>
<td>MYMY</td>
<td>$2\text{MeZ}$</td>
<td>52.3</td>
</tr>
<tr>
<td>Y</td>
<td>$\text{Ba}<em>2\text{Me}<em>2\text{Fe}</em>{12}\text{O}</em>{22}$</td>
<td>3TS</td>
<td>$3\text{MeY}$</td>
<td>43.5</td>
</tr>
</tbody>
</table>

However, one of the major constituent blocks of compounds are referred to as M-compounds, which have the chemical formulae of BaO.6Fe$_2$O$_3$ (BaM), SrO.6Fe$_2$O$_3$ (SrM) and PbO.6Fe$_2$O$_3$ (PbM) were developed in the initial stages by Went et al [12], Ahlenbrach and Heister [13] as a typical hexagonal ferromagnetic oxide. M-type hexagonal ferrites had and still have a prominent position in the permanent magnet market, due to their unique combination of acceptable magnetic performance and low cost.
1.3 Structure of M-type Hexaferrite

The hexagonal elementary cell consists of 10 oxygen layers and the length of c-axis corresponding to this is 23.2 Å while that of a-axis is 5.88 Å. A schematic representation of M-type hexagonal structure is given in figure 1.2. The arrows indicate the spin orientations and the drawn vertical line are axis of three fold symmetry. A cross indicates the center of symmetry and all layers containing barium are mirror planes and are denoted by ‘m’ in the figure. In an elementary cell each layer contains four large ions. There are always four oxygen ions in four successive layers but each fifth layer contains three oxygen ions and one barium ion.

Figure 1.2 Unit cell of the M-type hexaferrite [9].
The magnetoplumbite structure can be built up from spinel blocks of two oxygen layers being blocks \( S \) and \( S^* \) which are connected by a block \( R \) containing barium or strontium ion. The blocks \( S^* \) and \( R^* \) are obtained from block \( S \) and \( R \), respectively, by rotation over 180° around the \( c \)-axis. The layer containing the barium is hexagonally packed with respect to two oxygen layers at each side. The four oxygen layers between those containing the barium ion are cubically packed. The basal plane containing the barium ion is a mirror plane of \( R \) block and consequently the block preceding and succeeding the \( R \) block must be rotated over 180° with respect to each other. Five oxygen layers make one molecule and two molecules make one unit cell. The crystallographic structure can be described as \( RSR^*S^* \) as given by Braun [14]. The space group is denoted as \( P6_3/mmc \) \((D_{4h}^6)\).

The M-type hexaferrite crystallizes in a hexagonal structure with 64 ions per unit cell on 11 different symmetry sites [15]. The unit cell contain contains 38 oxygen ions, 24 ferric ions and 2 M ions (\( M = Ba^{+2}, Sr^{+2}, Pb^{+2} \) and \( La^{+3} \)). The 24 ferric ions are distributed over five distinct sites i.e. \( 2a, 2b, 4f_1, 4f_2 \) and \( 12k \). Out of these five, \( 2a, 4f_2 \) and \( 12k \) are octahedral, \( 4f_1 \) is tetrahedral and the last in which the ferric ion is surrounded by five oxygen atoms forming a trigonal bipyramid \((2b)\) site [16]. The oxygen ions occupy \( 4e, 4f, 6h \), and \( 12k \) sites form a closed pack lattice [17]. The \( M \) ions (\( M = Ba, Sr, Pb \) and \( La \)) occupy \( 2d \) sites [18]. The 12 \( Fe^{+3} \) are arranged as: 6 \( Fe^{+3} \) are in \( 12k \) site having the spin up, 2 ions in \( 4f_2 \) and \( 4f_1 \) having spin down and 1 ion in \( 2a \) and \( 2b \) site having spin up. So the 8 \( Fe^{+3} \) are in the upward direction and 4 in the downward direction. So 4 upward and downward cancel each other and the net moments is obtained of 4 \( Fe^{+3} \) per formula units. 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 5\( \mu B \) and the total moment is 20 \( \mu B \) per formula unit.

Table 1.2 Number of \( Fe^{+3} \) ions in sublattices of hexaferrites and their spin [19]

<table>
<thead>
<tr>
<th>Site</th>
<th>Geometry</th>
<th>No. of ( Fe^{+3} ) ions</th>
<th>Spin</th>
</tr>
</thead>
<tbody>
<tr>
<td>12K</td>
<td>Octahedral</td>
<td>6</td>
<td>Up</td>
</tr>
<tr>
<td>2a</td>
<td>Octahedral</td>
<td>1</td>
<td>Up</td>
</tr>
<tr>
<td>4f_1</td>
<td>Tetrahedral</td>
<td>2</td>
<td>Down</td>
</tr>
<tr>
<td>4f_2</td>
<td>Octahedral</td>
<td>2</td>
<td>Down</td>
</tr>
<tr>
<td>2b</td>
<td>Trigonal bipyramidal</td>
<td>1</td>
<td>Up</td>
</tr>
</tbody>
</table>
1.4 Magnetism in Ferrites Materials

The origin of magnetism lies in the orbital and spin motion of electrons and how the electrons interact with each other. Atoms have magnetic moments (\(\mu\)) which are produced for electron spin and also for the rotation of electrons around the nucleus. The nucleus has a small magnetic moment which nevertheless is negligible as compared to the one of the electron. Electron can be imagined as a tiny circuit that is carrying a tiny magnetic moment. They responds to external magnetic field and give rise to magnetization (M) that is defined as the net magnetic dipole moment per unit volume (\(v\)) in the material [20-22]:

\[
M = \frac{\mu_{\text{total}}}{v} \quad (1.1)
\]

The total magnetic field inside the material (magnetic induction ‘B’) is a function of the applied external field and the magnetization.

\[
B = B_{\text{ext}} + \mu_0 M \quad (1.2)
\]

where \(B_{\text{ext}}\) is the strength of external magnetic field and \(\mu_0\) is the permeability of free space. The magnetic field strength ‘\(H\)’ depends only on the strength of external magnetic field:

\[
H = \frac{B_{\text{ext}}}{\mu_0} \quad (1.3)
\]

Putting the value of ‘\(B_{\text{ext}}\)’ in equation 1.2

\[
B = \mu_0 (H + M) \quad (1.4)
\]

The relationship between magnetization ‘\(M\)’ and the applied field ‘\(H\)’ is defined as

\[
\chi = \frac{M}{H} \quad (1.5)
\]
where ‘\( \chi \)’ is the magnetic susceptibility of the material which is a measure of the increase in magnetic moment caused by external field.

1.4.1 Classification of Magnetic Materials

The magnetic materials can be classified on the basis of their response to an external applied magnetic field and in the variation of the magnetization ‘M’. These materials are classified in different types such as diamagnetism, paramagnetism, ferromagnetism, ferrimagnetism and antiferromagnetism.

![Diagram of magnetic moments in different types of magnetic materials](image)

**Figure 1.3** Magnetic moment ordering in (a) diamagnetics (b) paramagnetics (c) ferromagnetics (d) antiferromagnetics and (e) ferrimagnetics.

The materials in which the net magnetic moment is zero are known as diamagnetic. When diamagnetic materials are placed in a strong magnetic field, the magnetic dipole moment appears oppositely to the direction of the applied magnetic field as shown in figure 1.3a. The susceptibility for such materials is negative and small, for this reason diamagnetism sometimes is called as negative magnetism. The electrons shells in these materials are completely filled and have no unpaired electrons [23-24].
The materials in which there is no cancellation of the moments of electrons and have a net magnetic moment in the atom are called paramagnetic as shown in figure 1.3b. In the absence of the magnetic field the dipole moments are randomly arranged but when an external field is applied, the atomic moments tend to align by rotation towards the direction of the applied field and the material acquires a net magnetization. Such materials possess a small positive susceptibility. These materials are magnetic as long as the external field is present and when the magnetic field is removed the magnetization is lost. These materials obey Curie’s law which predicts that magnetization is inversely proportional to the temperature

\[ M = C_m \frac{B_{ext}}{T} \]  

(1.6)

where \( C_m \) is a constant depends on the materials, \( T \) the temperature and \( B_{ext} \) is the applied magnetic field. All other forms of magnetic materials have a critical temperature or Curie temperature above which the material behaves as a paramagnetic as a result of thermal agitation.

Ferromagnetic materials possess a permanent magnetic moment even in the absence of magnetic field and a very large permanent magnetization. This permanent magnetic moment is due to the cooperative interactions of large number of atomic spins in domains, where all spins are aligned in the same direction (figure 1.3c). At or above Curie temperature, the spins in ferromagnetic materials are aligned randomly and behave as paramagnetic material. The strontium hexaferrites are also ferromagnetic materials. The antiferromagnetic materials have spin antiparallel to one another (figure 1.3d). This type of configuration is expected to give zero magnetization but not always. These materials may have a net magnetic moment due to spin canting and lattice defects. On the other hand, in ferrimagnetic materials the magnetic ordering is antiparallel but of unequal magnitude which results in lower permanent magnets (figure 1.3e).

### 1.4.2 Influence of Temperature on Magnetic Behaviour

Temperature can affect the magnetic characteristics of the magnetic materials. It is well known that the increase in temperature of a solid result in an increase in the magnitude of the thermal vibrations of the atoms. As a result the atomic magnetic moments are free to rotate which tends to randomize the direction of any moment that may be aligned. When the temperature of ferromagnetic, antiferromagnetic and
ferromagnetic materials increased the atomic thermal motions contract the coupling forces between the adjacent atomic dipole moments, causing some dipole misalignment. This result in the reduction of the saturation magnetization of these materials and show maximum saturation magnetization at temperature of 0 K because at this temperature the thermal motions are minimum. As the temperature increase the saturation magnetization decrease gradually and then abruptly drop to zero at a specific temperature which is known as Curie temperature ($T_c$). The magnitude of the Curie temperature varies from material to material e.g. Iron, Cobalt and Nickel has 1041, 1393 and 608 K, respectively. The antiferromagnetic materials vanishes this character and change into paramagnetic one at certain temperature which is known as Neel temperature [25].

1.4.3 Magnetic Hysteresis

The ferromagnetic or ferrimagnetic materials composed of small volume region in which all the magnetic dipole moments are mutually aligned in the same direction is known as domain. The domains are separated from each other by domain boundaries or walls across which the direction of the magnetization gradually changed. Normally, domains are microscopic in size and for polycrystalline materials each grain may consist of more than one domain. So in a macroscopic piece of material there will be large number of domain and each have different magnetization orientation. The magnitude of the magnetization ($M$) of the entire material is the vector sum of magnetization of all the domains. The hysteresis is simply the sum of the magnetization of all domains. When a ferromagnetic or ferrimagnetic material is subjected to the action of an external magnetic field ($H$) then the dipoles tends to align themselves in the direction of the external applied field. As the applied field increases the magnetization also increase reaching maximum at its saturation point. If the applied field ($H$) gradually decreased then disoriented domains formed again and the magnetization decrease but some of the orientation remained permanent in the material as residual internal magnetic field. The typical hysteresis loops for the Sr-hexaferrite is shown in figure 1.4 and the different parameters such as saturation magnetization ($M_s$), remanence ($M_r$) and coercivity ($H_c$) of the hysteresos loop are also labeled.
1.5 Properties of Strontium Hexaferrite

Strontium hexaferrite (SrFe$_{12}$O$_{19}$) powders have been a subject of continuous interest and intensive study for several decades. SrFe$_{12}$O$_{19}$ powders with a narrow size distribution are promising materials for industrial applications due to their good magnetic, electrical, mechanical and magneto-optical properties and also perfect thermal and chemical stability.

1.5.1 Magnetic Properties of Sr-hexaferrite

The magnetic properties such as saturation magnetization ($M_s$), remanence ($M_r$) and coercivity ($H_c$) are determined from the hysteresis loop. The shape and width of the hysteresis loop of a ferrite depend not only on the chemical composition but also on various factors such as porosity, size and shape of the pores and of the crystals. Strontium hexaferrite is required to have low coercivity and moderate saturation magnetization and remanence for its use in magnetic recording media. Saturation magnetization is a state in magnetic materials when it can not absorb a stronger magnetic field, such that an increase of magnetization force produces no significant changes in the magnetic flux density or at a stronger magnetic field the magnetization becomes constant at its saturation value (figure 1.4). The behavior of magnetic flux density and the magnetization under the action of applied magnetic field is an important factor in the actual use of permanent magnets.

The pure strontium hexaferrite has the total magnetic moment of 20µ$_B$. The saturation magnetization of Sr-hexaferrite depends on the electronic configuration and the distribution of the substituted ions at different sites in the crystal structure. Ferric ions are distributed among five different lattice sites with upward and downward spin (table 1.2). According to Angeles [26] the ions with electronic configuration d$^1$, d$^2$, d$^3$ and d$^4$ prefer tetrahedral coordination while the ions with d$^6$, d$^7$, d$^8$, d$^9$ tend to occupy the octahedral position. On the other hand, the ions with d$^0$, d$^5$ and d$^{10}$ have no site preference. If an ion having unpaired electrons less than that of ferric ion replaces the Fe$^{3+}$ from the site having downward spin (4f$_1$ and 4f$_2$) then the total number of unpaired electrons in the upward spin are increased which increases the total magnetic moment and as a result the saturation magnetization will also increase. The desirable material for its application in the magnetic recording media requires the saturation magnetization as high as possible.
Figure 1.4. Typical magnetization curve and hysteresis loop showing saturation magnetization ($M_s$), remanence ($M_r$) and coercivity ($H_c$).

Coercivity ($H_c$) of a ferromagnetic material is the intensity of the applied magnetic field required to reduce the magnetization of that material to zero after magnetization has been driven to saturation (figure 1.4). The coercivity of M-type hexaferrites (SrM, BaM and PbM) depends on the particle size, porosity and the magnetocrystalline anisotropy. The material having smaller particle size in single domain and large magnetocrystalline anisotropy has high value of coercive force and vice versa. According to Li et al [27] the longitudinal magnetic recording media which is the general type of recording media used in industries requires high enough coercivity (above 600 Oe). If the coercivity is too high (above 1200 Oe) the material can be used for perpendicular recording media which is a developing new technology in the magnetic recording materials.

Remanence ($M_r$) is the magnetization left behind in a medium after an external field is removed (figure 1.4). In order to keep the recording informations for a longer time, magnetic recording media depends upon its remanence. The performance of the recording media also depends upon the remanence. If the remanence value is high then the recording media keep the information for longer time and vice versa. The researchers are also investigating how to increase the remanence to increase the storage time of the data.
1.5.2 Electrical and Dielectric Properties

The resistivity of ferrites at room temperature can vary between $10^{-2}$-$10^{11}$ ohm cm depending on the chemical composition, annealing time and temperature and also on particle size and porosity. According to Verwey model [28] the conduction in ferrites in due to the electron hopping between Fe$^{2+}$ and Fe$^{3+}$ ions at octahedral sites. So the resistivity in ferrites depends on the number of ferrous and ferric ions in the material. The low resistivity in ferrites is due to the simultaneous presence of ferrous and ferric ions at octahedral sites. It is often important to make ferrites with high resistivity at room temperature. Therefore, it is then necessary to ensure that no or very few ferrous ions are present in the synthesized material.

Ferrites are semiconductors and their resistivity decrease with increasing the temperature. The activation energy can be calculated from temperature dependent resistivity data. The activation energy is the energy required to release an electron from the ion for a jump to the neighboring ion. The influence of temperature on the resistivity is that it changes the mobility of electrons or holes. Zaveta [29] determined the electrical conductivity of BaM and PbM and also calculated the activation energy from temperature dependence of conductivity. He also finally concluded that electron hopping mechanism between Fe$^{2+}$ and Fe$^{3+}$ might reasonably be assumed and so the resistivity is related to the presence of Fe$^{2+}$ ions. The drift mobility of electrons can also be calculated from the resistivity data.

Dielectrics are the substances that do not possess free electric charges under ordinary circumstances. They can modify the electric field into which they are introduced. The most important property of dielectrics material is that when an electric field is applied they become polarized. Under the applied external field the positive particles are moved toward the direction of field while the negative particles in the opposite direction from their equilibrium position. Hence dipoles are developed and they produced a field of their own. The process of producing electric dipoles out of neutral atom and molecules is referred as polarization [30].

When a dielectric material is subjected to an alternating field the orientation of dipoles and hence the polarization will tend to reverse every time the polarity of the field changes. As long as the frequency remains low ($< 10^6$ Hz) the polarization follow the alternations of the field without any significant lag. When the frequency increased the dipole will no longer be able to rotate sufficiently rapidly so that their oscillation will begin to lag behind those of the field. As the frequency is further
raised the permanent dipoles, if present in the medium, will be completely unable to follow the field and the contribution to the orientation polarization would be ceased. This usually occurs in the radio frequency range \((10^6-10^{11})\) of the electromagnetic spectrum. At still higher frequencies in the infra-red \((10^{11}-10^{14})\) the atomic or ionic polarization is ceased and only the electronic polarization remains.

The strontium hexaferrite is a dielectric material. The high electrical resistivity of hexaferrites coupled with their low magnetic losses is critical in maintaining low insertion loss in microwave devices. The dielectric behavior offers some valuable information about the localized electric charge carrier which in turn helps to elucidate the mechanisms responsible for charge transport phenomena.

### 1.5.3 Thermal and Mechanical Properties

The thermal properties such as linear thermal expansion coefficient of hexaferrite are of great interest in practice, firstly due to the relationship with cracks formation as a result of thermal shock and secondly due to the necessity to combine various materials in magnetic system exposed to the specific temperature range. When hexaferrite magnets are connected to the metal component it is recommended to use an elastic binding to compensate for the different amount of thermal expansion. The linear thermal coefficient for strontium hexaferrite was found to be \(14.0 \times 10^6\) and \(10.0 \times 10^6\) K\(^{-1}\) for the sample placed parallel and perpendicular to the c-axis, respectively [31]. The other thermal properties are thermal conductivity, thermal diffusivity and specific heat capacity. These properties mainly are affected in ferrites by impurities, composition, temperature, pressure, density, lattice imperfection and porosity. The values of thermal conductivity, thermal diffusivity and heat capacity per unit volume of strontium hexaferrite at room temperature are 2.69 Wm\(^{-1}\) K\(^{-1}\), 1.132 mm\(^2\) S\(^{-1}\) and 2.73 MJ m\(^{-3}\) K\(^{-1}\), respectively as reported by Hussain and Maqsood [32]. The thermal conductivity and thermal diffusivity increase with temperature while the heat capacity per unit volume decreases. The standard molar heat capacity of SrFe\(_{12}\)O\(_{19}\) was also determined by Rakshi et al [33] and was found 683.5 J K\(^{-1}\) mol\(^{-1}\).

Fundamental studies on the mechanical properties of Sr-hexaferrite are quite few. The mechanical properties include hardness, tensile and flexural strength. The critical stress-intensity factor \((K_{IC})\) can also be determined in connection with studies on crack formation and grindability. It is a very sensitive parameter which changes with the operation conditions and give reliable informations about the degree and type
of sintering of hexaferrites. The flexural strength was found to be $86.3 \pm 7.8$ N mm$^{-2}$ [34] for the strontium hexaferrite sample placed perpendicular to the c-axis and that of critical stress-intensity factor was found to be $2.73 \pm 0.24$ MN m$^{-3/2}$. The hardness value for strontium hexaferrite was found to be $8.6$ kN mm$^{-2}$ [35].

1.5.4 Chemical Stability

In addition to the above mentioned properties of M-type hexaferrites they have a good chemical stability. These materials are rather stable in week acids (CH$_3$COOH, Citric acid and phenol solutions), alkalis (NH$_3$, NaOH, NaCl, KOH) and other chemicals but unstable in strong acids (HF, HCl, HNO$_3$, H$_2$SO$_4$ and H$_3$PO$_4$). It is found that they are completely dissolved in hydrofluoric acid and hydrochloric acid after 14 days.

1.6 Applications of M-type Hexaferrites

The potential use of any material for a specific purpose depends on a number of physical and economic factors. Since the discovery around 1950 hexaferrites have enjoyed bigger sale than any other permanent magnetic material. They are still widely used whenever the product cost is the major consideration. The price per unit of magnetic energy is much lower for hexaferrite than for other magnetic materials. The hexaferrites have higher resistivity ($>10^6$ ohm cm) than other technologically useful permanent magnetic materials ($10^{-5}$ ohm cm) such as metal alloys (AlNiCo alloy). The permanent magnetic materials other than hexaferrites with low electrical resistivity have tendency to allow induced current to flow within the materials themselves that produces heat, which is wastage of energy. Therefore, these materials become inefficient for use at high frequency e.g. as inductor cores in TV circuits. However, hexaferrites can perform much better at high frequencies because they have high DC electrical resistivity.

In comparison with spinel ferrite (MeFe$_2$O$_4$), M-type hexaferrites have working frequency of electromagnetic wave limited up to ~ 1 GHz, though the bandwidth of absorption is wide. On the other hand, hexaferrites, because of their strong field of anisotropy can be used as absorbers beyond several GHz, though the bandwidth of absorption is narrow [36]. Strontium hexaferrite (SrFe$_{12}$O$_{19}$) has received a wide attention as a permanent magnet material than barium hexaferrite.
(BaFe$_{12}$O$_{19}$). Although both are relatively close in magnetic properties yet strontium hexaferrite is superior due to unsuccessful production of barium ferrite powder in a good form [37].

The M-type hexaferrites are widely used in the recording media due its large saturation magnetization and has already been discussed in detail in section 1.5. The permanent magnetic materials are also used in loudspeakers, permanent magnetic motors and moving-coil instruments such as galvanometers, ammeters and voltmeters. This is the operating principle for such instruments. In large number of motors the necessary magnetic field is supplied by electromagnet. For small dc motors there has been an increasing preference for a permanent magnet as a field source rather than an electromagnet. The result is a cheaper, more compact and lighter motor. The preferred material for such motors is M-type hexaferrite and these motors have many applications in automobiles (windshield-wipers, heater fans etc) and in homes (electric carving knives, electric toothbrushes etc). The permanent magnetic materials have also applications in microphones. The M-type Sr-hexaferrites are also used in magneto-optical devices. The measurement of DC electrical resistivity is very useful to judge the applications of Sr-hexaferrite in the microwave devices. If the material shows high values of DC resistivity then it is beneficial for its use in microwave device [38]. The researchers are also interested to fabricate the Sr-hexaferrite with high resistivity.

Microwave in the higher gigahertz range are being increasingly utilized in wireless communication, radar, local area network, secret system, satellites communication, precise guidance system and remote sensing techniques. Electromagnetic interface (EMI) is also becoming a serious problem and a matter of crucial concern in higher gigahertz range along with the development of higher gigahertz electronics and the trend towards miniature circuitry [39-40]. The reduction of electromagnetic backscattering using the microwave absorbing materials therefore has important implications in the field of electromagnetic compatibility [41]. Microwave absorbers are also in high demand for defense use. Application of microwave absorbing coating on the exterior surface of military aircraft and vehicles helps avoid detection by radar. The M-type hexaferrites due to their large tunable anisotropy field are extensively exploited in the recent years in higher gigahertz range [42-43].
1.7 Literature Review

Choji et al [44] synthesized the fine particles of strontium hexaferrite by the hydrolysis of refluxed ethanol solution of Fe$^{3+}$ and Sr$^{2+}$ acetylacetonates. The precipitates were then annealed to obtain a single magnetoplumbite phase and their magnetic properties were studied. The average particle size of the sample annealed at 1173 K was found to be in the range of 50-60 nm and coercivity of 6700 Oe.

Kulkarni et al [45] followed the chemical Co-precipitation and conventional ceramic method to synthesize the ultrafine particles of strontium hexaferrite. Thermal (DTA/DTG/TG) studies were carried out to understand the ferritization reaction leading to the formation of hexagonal strontium ferrite. Simultaneous DTA/DTG/TG plots clearly exhibit the onset of the exothermic ferritization reaction at $T \approx 730 \, ^\circ \text{C}$, with activation energy of 43.872 kcal mol$^{-1}$ for the precursors derived from the co-precipitation route. On the other hand, the temperature required for the reaction with the ceramic route precursors was greater than 900 °C without any accompanying energy change.

Osamu et al [46] prepared the ultrafine particles of Sr-hexaferrites with high value of coercive force i.e. 6700 Oe. The sample was synthesized by the citrate process with different concentration of Fe$^{3+}$ ion ranging from 10.8 – 12.0. The pure iron metal and strontium carbonate were dissolved into nitric acid to convert them into nitrates. The nitrates salts of strontium and iron were not used directly due to their hygroscopic nature. The samples were annealed at 1000 °C for one hour and obtain a pure phase of strontium hexaferrite. The samples were characterized by TG/DTG and XRD. The magnetic properties as well as the BET surface area were also measured.

Surig et al [47] used the chemical sol-gel route to prepare undoped and doped barium and strontium hexaferrites. They carried out the crystallographic, magnetic and ferromagnetic resonance experiments to analyze the formation of the hexaferrite phase and to determine the anisotropy field strength. Specific saturation magnetization, coercive and anisotropy field strength were determined and were found to be depending on the heat treatment of the gel and the ion-ratio in the starting sol. The special preparation conditions and the magnetic properties of sol-gel derived $[\text{Ba, Sr}]\text{Me}_x^{2+}\text{Ti}_x^{4+}\text{Fe}_{12-2x}\text{O}_{19}$ with Me$^{2+} = \text{Zn}^{2+}, \text{Co}^{2+}$ and $x = 0.0 - 1.0$ were also
discussed. The morphology of the synthesized powders was underlined by TEM-
photographs.

Choy et al [48] prepared the magnetoplumbite-type strontium ferrite
(SrFe\textsubscript{12}O\textsubscript{19}) powders from metal citrate complexes and their magnetic properties were
studied. The optimum pH condition (≈ 6.5) for the formation of metal citrate
complexes was predicted through the theoretical consideration of thermodynamic
equilibrium constants of the corresponding metal salts in an aqueous solution.
Nanometer-sized ferrite particles (≈ 50 nm) were obtained through the thermal
decomposition of polymeric citrate precursor at relatively low temperature of 850 °C.
A large coercive force of 6500 Oe was obtained.

Ataie et al [49] synthesized the fine particles of strontium hexaferrite,
SrFe\textsubscript{12}O\textsubscript{19}, with a narrow size distribution from mixed aqueous solutions of iron and
strontium nitrates by hydrothermal method under different synthesis conditions. The
relationship between the synthesis variables such as temperature, time and alkali
molar ratio was investigated. The results showed that as the synthesis temperature was
increased the saturation magnetization of the particles increased and the coercivity
decreased. As the alkali molar ratio was increased, the coercivity decreased while the
saturation magnetization increased. Increasing the annealing time from 2 to 5h had no
significant effect on the saturation magnetization, but resulted in a decrease in the
coercivity.

Rashmi et al [50] investigated the magnetism, microstructure, and phase
formation of strontium hexaferrite nanoparticles prepared by the pulsed excimer laser
ablation and cold condensation technique using vibrating sample magnetometry
(VSM), scanning electron microscopy (SEM), and X-ray diffraction (XRD)
techniques. The as-condensed powders did not exhibit the same magnetic properties
as the target material. The samples showed very high coercivity of 6665 Oe after
annealing at 850 °C for 3 hours.

Ataie et al [51] annealed the strontium hexaferrite powder in nitrogen,
hydrogen and carbon atmospheres. The results showed that the phase composition,
morphology and the magnetic properties of the strontium hexaferrite were affected
significantly by these gas/vapor treatments. The coercivity was decreased to below
0.8 kOe and the magnetization at 14 kOe was increased significantly when strontium
hexaferrite powder had been treated in a nitrogen, hydrogen or carbon atmosphere.
The particle/grain sizes of the calcined samples were also significantly smaller than
those of the non-treated samples and it was believed that they were single domain particles/grains.

Dung et al [52] investigated the influence of La substitution on the structural, magnetic and electrical properties of Sr hexaferrite in isotropic and anisotropic samples. High quality hard ferrite was obtained with high coercivity.

Gajbhiye and Vijayalakshmi [53] synthesized the ultrafine particles of SrFe$_{12}$O$_{19}$ by citrate precursor technique. Solid state reactivity studies of citrate precursor led to the formation of fine particles of SrFe$_{12}$O$_{19}$ below 823 K. The size and morphology of these particles were studied by SEM. The surface area measured by BET method for 5.2 nm crystallite was found to be 27.45$\text{m}^2\text{g}^{-1}$ having particle size of 42 nm. Ultrafine particles of SrFe$_{12}$O$_{19}$ showed interesting magnetic properties measured by vibrating sample magnetometer VSM. The intrinsic coercive force of 6500 Oe and TC of 830 K was observed. Mossbauer spectroscopy was explored to study these fine particles for non-collinear spin structure predominantly at the surface compared to the core of the particle.

Ding et al [54] prepared the nanocrystalline hexaferrite (BaFe$_{12}$O$_{19}$ and SrFe$_{12}$O$_{19}$) and mixed Fe,Co-ferrite ($\text{Fe}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ with ($x = 0.0 - 1.0$) materials by mechanical alloying and subsequent annealing. High coercivities were obtained in these nanocrystalline materials, 6–7 kOe for hexaferrite and ~ 3 kOe for Co-ferrite. Hexaferrite powders prepared by mechanical alloying were used as the starting material for high-coercivity bonded magnets. Hot-pressed anisotropic hexaferrite magnets were produced with high values of coercivity and remanence.

Calleja et al [55] synthesized the fine strontium hexaferrite particles by lyophilization (known as freeze-drying) and co-precipitation of nitrates and chloride salts. The resulting powders were calcined at different temperatures between 700 °C and 1100 °C. They concluded that the freeze-dried hexaferrite showed better magnetic characteristics than co-precipitated samples. The coercivity values were found to be 5690 and 1300 Oe for the samples synthesized by freeze-dried and co-precipitated methods, respectively.

Fang et al [56] prepared the fine strontium ferrite powder with high coercivity by forming hydroxide precursor particles in the continuous ethanol-based phase of a microemulsion consisting of iso-octane, NP9 and an ethanol solution containing Sr$^{2+}$ and Fe$^{3+}$ cations at a molar ratio of 1:12. The microemulsion-derived hydroxide precursor was calcined at various temperatures ranging from 600 to 1100 °C to
develop the hexagonal strontium ferrite phase. X-ray diffractometry and infrared characterizations revealed that the formation mechanisms of strontium ferrite in the microemulsion-derived precursor differed from those of the precursor derived by conventional co-precipitation. The strontium ferrite samples synthesized by microemulsion method were of finer particle size and better magnetic properties than those prepared by the conventional co-precipitated method. The microemulsion-derived strontium ferrite exhibited an intrinsic coercivity of 6195 Oe and a saturation magnetization of 58.28 emu g\(^{-1}\) when calcined at 900 °C. The saturation magnetization increased further to 69.75 emu g\(^{-1}\) when the precursor was calcined at 1100 °C.

Fang et al [57] investigated the effect of heat treatment on the magnetic properties of strontium hexaferrite nanoparticles prepared by the chemical sol–gel route. Specific saturation magnetization \(\sigma_s\) and coercive field strength \(H_c\) were found to be dependent on the heat treatment of the gel and iron/strontium ratio in the starting solution. These ultrafine powders with single-domain behavior had specific saturation magnetization of \(\sigma_s = 74\) emu g\(^{-1}\) and coercive field strength of \(H_c = 6.4\) kOe. Experimental results showed that it was necessary to preheat the gel between 400 and 500 °C for several hours. It can prevent the formation of intermediate \(\gamma\)-Fe\(_2\)O\(_3\) and help to obtain ultrafine strontium ferrite single phase with narrow size distribution at a low annealing temperature. They also studied the effect of substitution of Zn\(^{2+}\), Ti\(^{4+}\) and Ir\(^{4+}\) on the magnetic properties of sol–gel derived strontium ferrite. Substitution of strontium ferrite by binary mixture of (Zn, Ti)\(_x\) \(0.0 \leq x \leq 0.6\), showed higher values of both coercive field strength and saturation magnetization than by the substitution of (Zn, Ir)\(_x\).

Ataie and Heshmati [58] synthesized the uniform and ultra-fine particles of strontium hexaferrite, SrFe\(_{12}\)O\(_{19}\), with a particle size range from 0.1 to 0.2 \(\mu\)m by a modified co-precipitation from mixed aqueous solutions of iron and strontium nitrates. They also investigated the effect of calcination temperature on the phase composition, particle size and shape as well as on the magnetic properties of the products. It was found that the coercivity increased rapidly on increasing the calcining temperature from 650 to 750 °C and exhibited a maximum at 850 °C. The results showed that single domain particles of strontium hexaferrite exhibiting a significantly higher coercivity of 444.5 kA m\(^{-1}\) (5.55 kOe) can be produced by hydrothermally
processing NaOH-precipitated precursor nitrate solution at a lower temperature of 130 °C, followed by calcination of the product phase at 850 °C for 45 min in air.

Garcia et al [59] calcined the fine particles of SrFe_{12}O_{19} synthesized by the sol–gel method in oxygen-controlled atmosphere and studied the effect of oxygen-controlled environment on the structural and particle size of the synthesized sample. The effect of the SrCO_3 phase hindering the synthesis of the hexaferrite in air atmosphere at lower temperatures was analyzed. The samples were studied by infrared spectroscopy and X-ray diffraction. The morphology of the samples was analyzed by transmission electron microscope (TEM).

Carp et al [60] obtained small particles of strontium hexaferrite (SrFe_{12}O_{19}) starting from magnetite as source for iron ions. They investigated the influence of the precursor’s history upon the phase composition evolution. A pure strontium hexaferrite with mean crystallite sizes of 320 Å and saturation magnetization of 65.7 emu g\(^{-1}\) was obtained starting from synthesized Fe_3O_4 by a wet method and Sr(NO_3)_2, molar ratio Fe:Sr 10.5:1, using urea as complexing agent after a calcination treatment performed at 800 °C for 4 hours.

Wang et al [61] investigated the effect of annealing temperature and Nd-substitution on the magnetic properties of Sr hexaferrite (Sr_{1-x}Nd_xFe_{12}O_{19}) plate-like particles synthesized by hydrothermal method. The samples were calcined at temperatures ranging from 1100 °C to 1250 °C for 2h in air. The effects of the Nd-Sr ratio and the calcination temperature on the phase stability were also investigated. Nd substitution up to Nd-Sr ratio of 1/8 causes an increase of the coercivity without causing any significant deterioration in either the saturation magnetization or the remanence.

Wang et al [62] synthesized the ultrafine (~80 nm), single domain Sr hexaferrite (SrM) particles with Sm additives by a chemical co-precipitation technique. The effects of the Sm\(^{3+}/\)Sr\(^{2+}\) ratio on the crystallography and magnetic properties of Sm doped SrM ultrafine particles were investigated. A very high coercivity of 528 kA m\(^{-1}\) (6635 Oe) with a magnetization of 63.07 J/T kg at 1100 kA m\(^{-1}\) was obtained for the sample having Sm\(^{3+}/\)Sr\(^{2+}\) = 14 calcined at 850 °C for 2 hours in air.

Ebrahimi [63] studied the effect of heat treatment in nitrogen and hydrogen atmosphere and also in air on the magnetic properties of strontium hexaferrite
powder, prepared conventionally from strontium carbonate and iron oxide. Magnetic measurements after the gas treatment stage indicated a marked decrease of intrinsic coercivity and an increase in saturation magnetization which made the material suitable for magnetically soft applications. During the calcination stage there was a recovery of the magnetic properties. The material exhibited a remanence and saturation magnetization close to those of the starting hexaferrite but a much higher intrinsic coercivity of 5 kOe. The high coercivity was attributed to a much finer grain size. The characteristics of the optimum hydrogen-processed Sr- hexaferrite powder were compared with those of the optimum nitrogen-processed material. The phase constitution, microstructure and magnetic properties of these powders were also investigated.

Fu et al [64] synthesized the strontium hexaferrite powders by a microwave-induced combustion process. The process only took a few minutes to obtain calcined strontium hexaferrite powders. The resultant powders were investigated by XRD, TEM, VSM, TG/DTA, and surface area measurement. The results showed strontium ferrite with a saturation magnetization ($M_s$) of $\approx 38$ emu g$^{-1}$ and an intrinsic coercive force ($H_c$) of 525 Oe. The coercivity was increased to 1950 Oe and saturation magnetization to 62 emu g$^{-1}$ when the sample was annealed at 1000 °C for 2h.

Fang et al [65] fabricated zinc and niobium binary mixture doped strontium hexaferrite nanoparticles, $\text{Sr(Zn}_{0.7}\text{Nb}_{0.3})_{x}\text{Fe}_{12-x}\text{O}_{19}$ ($x = 0.0 – 1.0$), using a sol-gel method for high density magnetic recording. The structure and temperature dependence of magnetic properties were investigated. The experiments showed that strontium hexaferrite with small Zn and Nb substitutions remained a hexagonal magnetoplumbite phase. The coercive force was reduced from 6.7 to about 2.3 kOe, while the values of saturation magnetization increased to 67–74 emu g$^{-1}$ in the substitution range of $x = 0.0 – 1.0$. This indicated that the saturation magnetization and coercivity of strontium hexaferrite nanoparticles can be held over a very wide range by an appropriate amount of Zn and Nb doping contents. It was also found that the doped strontium hexaferrite nanoparticles showed a small positive temperature coefficient of coercivity. This nanoparticle system is considered to be suitable for high-density recording.

Fang et al [66] studied the crystal structure, magnetic properties and temperature coefficient of coercivity of $\text{Sr(Zn}_{0.7}\text{Nb}_{0.3})_{x}\text{Fe}_{12-x}\text{O}_{19}$ strontium hexaferrite nanoparticles prepared using a sol–gel technique for perpendicular magnetic
recording. X-ray diffraction analysis confirmed the hexagonal magnetoplumbite phase. Magnetic measurements revealed that the values of specific saturation magnetization, $M_s$, increased to $67 – 73.3$ emu g$^{-1}$ ($x = 0.0 – 0.8$) and coercivity, $H_c$, was reduced from $6.5$ to about $2.3$ kOe. Temperature measurements exhibited that substitution of Zn–Nb binary mixture can effectively decreased the temperature coefficient of $dH_c/dT$ with the increase in doping, which means that the samples had a perfect thermal stability.

Sivakumar et al [67] synthesized a fine strontium hexaferrite powder successfully by a sonochemical method employing Fe(CO)$_5$ and SrCO$_3$. SrCO$_3$ was first synthesized using strontium nitrate and urea and it was found that applying ultrasound radiation during this process resulted in the uniform formation of SrCO$_3$ hexagonal rods. These rods were then dispersed with in-situ generated amorphous Fe$_2$O$_3$, using Fe(CO)$_5$ as the source. The resultant precursor was then calcined at $900^\circ$C, which is lower than the conventional solid-state reaction of applying $1300^\circ$C to get the strontium hexaferrite fine powder. This sonochemically derived ferrite exhibited an intrinsic coercivity of $\sim 4600$ Oe and a saturation magnetization of $\sim 60$ emu g$^{-1}$ at $20$ K and $\sim 32$ emu g$^{-1}$ at $300$ K.

Gomez et al [68] measured the relaxation of the initial permeability in polycrystalline strontium hexaferrites with the initial composition SrOnFe$_2$O$_3$ ($n = 5.7$, 6.0), prepared by means of standard ceramic techniques in air as well as CO$_2$ sintering atmospheres. The isochronal disaccommodation spectra showed the presence of different relaxation processes, depending on both the sintering atmosphere and especially the initial composition, and associated to ionic reorientations of ferrous cations and lattice vacancies in the different metallic sites within the spinel (S) and hexagonal (R) blocks of the close packed lattice.

Wang et al [69] investigated the effect of La/Sr ratio and calcination temperature on the structure, particle morphology and magnetic properties of La-substituted Sr hexaferrite synthesized by hydrothermal method. The samples were characterized by X-ray diffraction, scanning electron microscopy, vibrating sample magnetometry and a pulsed field magnetometer. It was found that under hydrothermal conditions the La$^{3+}$ additives did not substitute exclusively into the SrM structure but this could be achieved to a greater extent by subsequent calcinations at high temperatures. Compared to the effect of Sm and Nd substitutions by same authors [57,
La substitution slightly increased the coercivity for the samples with initial La/Sr ratios up to 1/8 and for the samples with La/Sr ratios such as 1/4 and 1/2 the coercivity was smaller than that of the sample without La. Most of the La-substituted samples exhibited a similar magnetization to that of SrFe₁₂O₁₉.

Fang et al [19] studied the variation in structural and magnetic properties of the chromium-substituted hexagonal strontium ferrite, SrFe₁₂₋ₓCrₓO₁₉ (x = 0.0 – 1.0), nanoparticles prepared by the chemical sol–gel route for high-density magnetic recording. For suitable doping (x ≤ 0.4), the values of specific saturation magnetization slightly increased but coercivity decreased. This substituted particle is considered to be suitable for high-density magnetic recording. Structural analysis showed that the samples remained a hexagonal magnetoplumbite phase in x = 0.0 – 0.4 and the non-magnetic phase, α-Fe₂O₃, appeared after x = 0.6 and that the change in the main axis (c-axis) in hexaferrite was larger than that of a-axis for the substitution with Cr³⁺ ion.

Fang et al [70] fabricated the SrFe₁₂₋ₓCrₓO₁₉ (x = 0.0 – 1.0) hexaferrite nanoparticles using a sol-gel technique for perpendicular magnetic recording. Experimental results showed that the values of specific saturation magnetization, σₛ, was increased for x ≤ 0.4 as the Cr doping content increased and reach maximum at x = 0.2, while the coercivity, Hₑ, decreased for x < 0.5. This feature is favorable to magnetic recording. It was also found that the α-Fe₂O₃ non-magnetic phase appears after x = 0.6 and remains to be a hexagonal magnetoplumbite phase for x = 0.0 – 0.4. Magnetic measurements have revealed that Cr substitution can decrease the magnetization and increase the peak-widening for Hopkinson peak when doped with Cr³⁺.

Wang et al [71] substituted the Pr in Sr hexaferrite particles prepared by hydrothermal synthesis and subsequent calcinations. The effects of the initial Pr/Sr ratio and the calcination temperature on the structure, particle morphology and magnetic properties of Pr-substituted Sr hexaferrite were investigated by X-ray diffraction, scanning electron microscopy and vibrating sample magnetometry. It was found that under hydrothermal conditions a small amount of Pr³⁺ substituted into the SrM structure at low temperature but this could be achieved to a greater extent by calcinations at high temperatures. Compared to the effect of Sm, Nd and La substitutions, Pr improved the coercivity by 14%, which was smaller than that of Sm substitution but higher than those of Nd and La substitution. It was also observed that
the Pr substitution increased the coercivity without causing any significant deterioration in either the magnetization or the remanence.

Popa [72] synthesized the strontium (SrFe$_{12}$O$_{19}$) and barium (BaFe$_{12}$O$_{19}$) hexaferrite powder, with CaO additive used in magnetic recording by a modified co-precipitation method. According to this method, named self combustion, the reacting substances were metal nitrates and ammonium hydroxide. The CaO additive improves the coercivity of hexaferrites and a better control of the grain growth was achieved.

Topfer et al [73] investigated the effect of simultaneous addition of CaO and SiO$_2$ on the microstructure and magnetic properties of sintered SrO-excess Sr-hexaferrites. Both additives markedly affected the grain growth behavior and the magnetic properties. CaO-additions promote the densification, which resulted to increase the remanence but due to simultaneous grain growth the coercivity dropped to $< 100$ kA m$^{-1}$. Simultaneous additions of CaO and SiO$_2$ were shown to be very beneficial in tailoring a dense microstructure with relatively small grains. The ratio of CaO/SiO$_2$ was found to be optimum at about 1 and magnets with a remanence of 430 mT and a coercivity of 300 kA m$^{-1}$ were obtained. Transmission electron microscopy (TEM) and energy-dispersive X-rays (EDX) studies showed that both CaO and SiO$_2$ are concentrated at grain boundaries and grain junctions forming an amorphous secondary phase.

Fu and Lin [74] used the microwave-induced combustion process for the synthesis of strontium hexaferrite nano-particles. Magnetic properties of strontium ferrite powders with Fe/Sr ratios varying from 11 to 12 and different annealing temperatures range of 850 to 1050 °C were investigated. The resultant powders were characterized by XRD, TEM, SEM, VSM, TG/DTA, and surface area measurement. The optimum magnetic properties of strontium ferrite powders were as follows: the composition with Fe/Sr ratio of 11.6 annealed at 1000 °C for 2 hours possessed a saturation magnetization of 62 emu g$^{-1}$ and an intrinsic coercive force of 1950 Oe. Moreover, the microwave-heated strontium ferrite powders with a Fe/Sr ratio of 11.6 annealed at various temperatures had particle size ranging from 52 to 78 nm. Low-coercivity strontium ferrite powders can be obtained by microwave-induced combustion process without doping with metal elements such as Co–Ti, Co–Sn, Zn–Sn, etc. These low coercive strontium ferrite powders are suitable for magnetic recording applications in hard disks, floppy disks, video tapes, etc.
Zaitsev et al [75] prepared the glasses with nominal compositions SrFe$_{10}$Al$_2$O$_{19}$ + 4(SrB$_2$O$_4$+Sr$_2$B$_2$O$_5$) (1) and SrFe$_9$Al$_3$O$_{19}$+4(SrB$_2$O$_4$+Sr$_2$B$_2$O$_5$) (2) by rapid quenching of melts. Thermal treatment of glass samples at 600 – 900 °C resulted in crystallization of the magnetic phase SrFe$_{12-x}$Al$_x$O$_{19}$ (x = 1.1 ± 0.1) and strontium borates. Platelet hexaferrite particles with average sizes from (250×60) nm$^2$ to (450×140) nm$^2$ were prepared. The coercive force of glass ceramics was 580 and 475 kA m$^{-1}$ for glasses 1 and 2, respectively. The coercive force of 580 kA m$^{-1}$ was the highest known value compared to hexaferrite particles prepared earlier by glass crystallization.

Zhao et al [76] characterized the dried gel of SrFe$_{12}$O$_{19}$ prepared by citrate approach by means of infrared spectroscopy (IR), thermogravimetric analysis (TG), differential scanning calorimetry (DSC), X-ray diffraction (XRD) techniques, energy dispersive spectroscopy (EDS) and transmission electron microscopy (TEM). The decomposition of the strontium M-type hexaferrite took place at about 688.6°C determined by DSC investigation. The strontium M-type hexaferrite nanoparticles were decomposed into SrFeO$_{2.5}$ with an orthorhombic cell and Fe$_2$O$_3$ with a tetragonal cell as well as possible α-Fe$_2$O$_3$. The agglomerated particles with sizes less than 200 nm obtained at 800°C. The thermally stable strontium M-type hexaferrite nanoparticles with sizes less than 100 nm could take place at 900°C. Up to 1000°C, the phase transformation to form strontium M-type hexaferrite was ended, the calcinations with the sizes more than 1 µm were composed of α-Fe$_2$O$_3$ and strontium M-type hexaferrite.

Rezlescu et al [77] prepared the Er-substituted Sr hexaferrite having the composition, SrFe$_{12-x}$Er$_x$O$_{19}$, by sol-gel self combustion. The combusted powders were annealed at 800, 900 and 1000 °C for 5, 10, 20, 40, 80, 160 and 320 min. The influence of annealing temperature and time on the structure and magnetic properties such as specific saturation magnetization $M_s$, specific remanent magnetization $M_r$ and coercivity $H_c$ was studied. The structural characterization was made using X-ray diffraction and scanning electron microscopy and the magnetic measurements were carried out with a vibrating sample magnetometer. During the heat treatments the soft magnetic powder obtained by sol-gel self combustion was changed to a hard magnetic powder. The coercivity increased to a value much greater than its value before annealing. The remarkable increase of $H_c$ was explained by crystallization of the hard magnetic hexaferrite phase and corresponds to a transition from superparamagnetic to
stable single-domain particles. The $H_c$ values of the samples heat treated for longer times (over 80 min) were fairly satisfactory. This means that the particle sizes were well under control to prevent abnormal growth of the particles. It was also found that $M_s$ and $M_r$ are dependent on both annealing temperature and its duration. $M_s$ and $M_r$ began to increase when $H_c$ sharply increased and tend to a constant value with increasing annealing time. Also, $M_s$ and $M_r$ decrease with increasing Er content. This dependence may be ascribed to the lowering of the total magnetic moment when $Er^{3+}$ ions substitute magnetic $Fe^{3+}$ ions in the M-hexagonal structure or to the formation of more non-magnetic phase like hematite, $\alpha$-Fe$_2$O$_3$.

Alamolhoda et al [78] used a novel sol-gel auto-combustion method to synthesize ultrafine particles of strontium hexaferrite. The nitrate citrate gels were prepared from metal nitrates and citric acid with various molar ratios of Fe/Sr. Results showed that the nitrate citrate gel exhibit a self-propagating behavior after ignition in air. The resultant powders with different molar ratios of Fe/Sr were investigated by the differential thermal analysis, thermal gravimetry and X-ray diffraction techniques. The investigations showed that there was an optimum molar ratio for Fe/Sr in which the annealing temperature for obtaining single-phase strontium hexaferrite was a minimum. Scanning electron microscopy was also used to characterize the microstructure of the products. The crystallite size of the resultant powder was about 40 to 50 nm.

Doroftei et al [79] prepared the rare-earth substituted strontium ferrite nanopowders SrFe$_{12-x}$RxO$_{19}$ (R = La, Gd and Er; $x = 0.2$, 0.5 and 1) by sol-gel-auto-combustion method. Structural and magnetic properties of SrFe$_{12-x}$RxO$_{19}$ powders heat treated at 800, 900 and 1000 °C for various times were characterized with an X-ray diffractometer, a vibrating sample magnetometer and a scanning electron microscope. The results of X-ray diffraction measurements showed the formation of M-type hexagonal structure by heat treatments. Magnetic properties, such as specific saturation magnetization $\sigma_s$, specific remanent magnetization $\sigma_r$ and coercivity $H_c$, as well as microstructure depend on the heat treatment conditions (temperature and time). The coercivity $H_c$ exhibited a great increase after a critical heat treatment time. With increasing R content the $\sigma_s$ and $\sigma_r$ decreased due to the dissolution of R ions into the hexaferrite lattice. They believed that by selecting the time and temperature of the heat treatment, microstructure and magnetic properties suitable for magnetic recording media application can be obtained.
Brito et al [80] used the coconut water as a precursor for the preparation of strontium hexaferrite (SrFe\(_{12}\)O\(_{19}\)) powder by the proteic sol-gel process. X-ray diffraction (XRD) measurement showed the formation of SrFe\(_{12}\)O\(_{19}\) with a small amount of the hematite for the sample calcined at 1000 °C with Fe/Sr = 12.0. Riveted refinement disclosed that this sample had 87.56% of the SrFe\(_{12}\)O\(_{19}\) and 12.44% of Fe\(_2\)O\(_3\) and the values for \(R_p\), \(R_wp\) and \(\chi^2\) were 4.28%, 5.93% and 1.71, respectively. The magnetic properties were \(M_s = 64\) emu g\(^{-1}\), \(M_r/M_s = 0.55\) and \(H_c = 1.4\) kOe for a crystallite size of 57 nm.

Alamolhoda et al [81] studied the effect of the surfactant on the crystallite size of ultra-fine strontium hexaferrite synthesized by a novel sol-gel auto-combustion method. The DTA/TGA plot exhibited the formation temperature of hexaferrite. The XRD results showed that adding surfactant to the sol did not change the composition of the combustion product and the surfactant burns completely during the combustion process. The average crystallite size of hexaferrite powders was also measured by the X-ray line broadening technique employing the Scherrer formula. The results showed that adding surfactant to the gel made the particle size of the final product much smaller.

Gravchikova et al [82] prepared the glass of nominal composition Sr\(_{0.6}\)La\(_{0.4}\)Fe\(_{11.6}\)Co\(_{0.4}\)O\(_{19}\) + 12SrB\(_2\)O\(_4\) by rapidly quenching an oxide melt and was then heat-treated at temperatures from 550 to 900 °C to gave glass-ceramics containing fine lanthanum and cobalt-doped strontium hexaferrite particles and microcrystalline SrB\(_2\)O\(_4\). The materials were characterized by X-ray diffraction, scanning electron microscopy and magnetic measurements. The coercivity of the glass-ceramic samples was shown to increase up to 427 kA m\(^{-1}\) with increasing heat-treatment temperature. The saturation magnetization of the samples increased up to 25.0 A m\(^2\) kg\(^{-1}\) as the heat-treatment temperature was raised to 750 °C and decreased slightly at higher temperatures.

Doroftei et al [83] investigated the effect of annealing temperature, time and La substitution on the structural and magnetic properties of the Sr hexaferrites with compositions Sr\(_{La}\)Fe\(_{12-x}\)O\(_{19}\) (\(x = 0, 0.2, 0.5, 1.0\)) prepared by sol-gel self-combustion method. The combusted powders were annealed at different temperatures (800, 900 and 1000 °C) for various annealing times (10, 20, 40, 80,160 and 320 minutes). Experiments showed that \(M_s\) and \(M_r\) increased with the annealing time and annealing temperature but coercivity \(H_c\) exhibited a spectacular variation with annealing time. For longer annealing time \(H_c\) began to decrease. This variation was explained by the
transition from single domain to multidomain particles by increasing annealing time. By manipulating the annealing time, the crystal growth can be controlled to obtain SrLa hexaferrite having properties for special applications.

Wang et al [84] observed that Sm substitution had the largest beneficial effect both on the coercivity and on the inhibition of grain growth at high temperature among the other elements such as La, Nd and Pr. The average grain size of the samples decreased with increasing Sm/Sr ratio. All the magnets with Sm additions exhibited a bigger coercivity and remanence than those of the SrM magnet without Sm. EDX quantitative analysis suggested that the solubility of Sm$^{3+}$ in the SrM-type structure was very small and that the Sm$^{3+}$ preferably formed the SrFeO$_{3-x}$, which was probably located around the SrM grain boundaries. The formation and the distribution of the SrFeO$_{3-x}$ phase around the SrM grain boundaries probably provided the inhibition of SrM grain growth. All these factors would contribute to the improvements of the coercivity of the magnets with Sm additions.

Hasab et al [85] used a sol-gel auto-combustion method in which n-decyldimethylammonium bromide was used as a cationic surfactant to synthesize strontium hexaferrite nanocrystalline powder. The dried nitrate-citrate gel, prepared from a solution of ferric nitrate, strontium nitrate, citric acid, trimethylamine and cationic surfactant exhibited an auto-combustion behavior after ignition in air. The formation reaction temperature, phase identification, crystallites size, particles size distribution and morphology of resultant strontium hexaferrite powder were investigated by DTA/TGA, FTIR, XRD, TEM and SEM techniques. The results showed that in the presence of the cationic surfactant, the combustion intensity was increased and the crystallite size decrease. The crystallite size of strontium hexaferrite powder in sample with surfactant calcined at 800 °C was found to be 27.2 nm.

Hasab et al [86] proposed a sol-gel auto-combustion route to synthesize strontium hexaferrite nanopowder using metal nitrates, ammonia as pH adjusting agent, n-decyldimethylammonium bromide as a cationic surfactant and different fuels such as citric acid, glycine, acetylacetone and oxalic acid. The formation temperature of strontium hexaferrite and its crystallite size in presence of different fuels were compared together. The results showed the lowest formation temperature as well as the smallest crystallite size in the presence of citric acid as 900 °C and 37.3 nm respectively.
Kaur et al. [87] reported the dielectric behavior of flux grown substituted crystals bearing composition \( \text{SrGa}_x\text{In}_y\text{Fe}_{12-(x+y)}\text{O}_{19} \) \( (x = 5, 7, 9; \ y = 0.8, 1.3, 1.0) \). Variation of dielectric constant \( (\varepsilon) \), dielectric loss \( (\tan \delta) \) and ac conductivity \( (\sigma_{ac}) \) with temperature in the range 30–500 °C under the frequency of the applied ac field in the range 1–10\(^4\) kHz for all the varied compositions were analyzed and explained. The effect of swift heavy ion irradiation on these parameters was also investigated. On irradiation the crystals showed changes in the values of dielectric constant \( (\varepsilon) \), dielectric loss \( (\tan \delta) \) and ac conductivity \( (\sigma_{ac}) \). The frequency variation of \( \varepsilon \) and \( \tan \delta \) was explained by Koop's phenomenological theory and hopping frequency of electrons between Fe\(^{2+}\) and Fe\(^{3+}\) on octahedral sites for both irradiated and un-irradiated crystals.

Shirteliffe et al. [88] prepared aluminium doped barium and strontium hexaferrite nanoparticles \( \text{BaAl}_x\text{Fe}_{12-x}\text{O}_{19} \) and \( \text{SrAl}_x\text{Fe}_{12-x}\text{O}_{19} \) via a sol–gel route using citric acid to complex the ions followed by an auto-combustion reaction. It was found that around half of the iron could be substituted for aluminium in the barium ferrite with structure retention, whereas strontium aluminium ferrites could be produced with any aluminium content including total substitution of the iron. All synthesized materials consisted of particles smaller than 1 µm, which is the size of a single magnetic domain. The materials showed structural and morphological changes as they move from iron to aluminium ferrites.

Hasab et al. [89] investigated the effect of cationic, anionic and nonionic surfactant on the structural and physical properties of Sr-hexaferrite nanopowders synthesized by a sol–gel auto-combustion route. The obtained powders were characterized by FTIR, XRD and SEM techniques and their physical properties were compared. The results showed a decrease in crystallite size of the resultant Sr-hexaferrite powder in presence of cationic and anionic surfactants while there were no significant changes in presence of nonionic one. However, all three types of surfactants resulted in a decrease in the formation temperature of Sr-hexaferrite.

Iqbal et al. [90] synthesized a series of Zr–Ni-substituted strontium hexaferrite materials, \( \text{SrZr}_x\text{Ni}_y\text{Fe}_{12-2x}\text{O}_{19} \) \( (x = 0.0 – 0.8) \), by the co-precipitation method and the crystallite size determined was in the range of 30–47 nm. It was found that the saturation magnetization increased from 72 to 98 kA m\(^{-1}\) while coercivity decreased from 1710 to 428 Oe with Zr–Ni substitution. This improvement in both these properties made these materials suitable for applications in recording media. The
increase in resistivity also suggested that the synthesized materials can be useful for application in microwave devices.

Iqbal and Ashiq [91] compared the two synthesis methods, i.e., the chemical co-precipitation and the sol-gel combustion used for the preparation of strontium hexaferrite $\text{SrZr}_x\text{Mn}_x\text{Fe}_{12-2x}\text{O}_{19}$ ($x = 0.0 – 0.8$) nanoparticles. The co-precipitation was found to be more suitable because samples synthesized by this method have a single phase for $x = 0.0 – 0.8$ and DC resistivity was also improved, whereas samples synthesized by the sol–gel combustion method had single phase only when $x = 0.0 – 0.4$. The dielectric constant and dielectric loss were in excellent agreement with DC electrical resistivity data.

Ghasemi and Morisako [92] synthesized the ultrafine particles of well-crystallized, monophase strontium hexaferrite $\text{SrFe}_9(\text{Mn}_{0.5}\text{Co}_{0.5}\text{Zr})_{3/2}\text{O}_{19}$ doped with Mn, Co and Zr using sol–gel method. The phase analysis was carried out by X-ray diffraction (XRD). Powders of sample show a hexagonal fine platelet structure and narrow particle size distribution. Based on microwave measurement on reflectivity, $\text{SrFe}_9(\text{Mn}_{0.5}\text{Co}_{0.5}\text{Zr})_{3/2}\text{O}_{19}$ was found to be a good candidate for electromagnetic compatibility and other practical applications at high frequency.

Kazin et al [93] formed the submicron-sized $\text{SrFe}_{12-x}\text{Al}_x\text{O}_{19}$ ($x = 1.3$) in glass-ceramic matrix using controlled thermocrystallization of the $\text{SrO–Fe}_2\text{O}_3–\text{Al}_2\text{O}_3–\text{B}_2\text{O}_3$ glass and the hexaferrite powder was obtained by removing the matrix phases. The X-ray diffraction and scanning electron microscopy (SEM) with energy-dispersive X-ray (EDX) analyses were used for structural characterization and Faraday balance magnetometer and SQUID magnetometer were used for magnetization measurements. The glass-ceramic material exhibits very high coercivity value up to 10.18 kOe which approaches a theoretically estimated maximum value for the compound. The powder saturation magnetization value is close to the theoretically estimated one for bulk material. The distribution of Al atoms on Fe sites was also determined. Al atoms occupy 41% of 2a sites and 14% of 12k sites while 4f1 and 4f2 sites are not affected.

Hessien et al [94] used the co-precipitation-calcination route for the synthesis of nanocrystalline strontium hexaferrite ($\text{SrFe}_{12}\text{O}_{19}$) powders. The ferrite precursors were obtained from aqueous mixtures of strontium carbonate and ferric chloride using 5M sodium hydroxide solution as a precipitating agent. Effects of $\text{Fe}^{3+}/\text{Sr}^{2+}$ mole ratio, annealing temperature and pH on the formation, crystallite size, morphology and magnetic properties were systematically studied. The results obtained showed that
the single phase SrFe$_{12}$O$_{19}$ powders were achieved by decreasing the Fe$^{+3}$/Sr$^{+2}$ mole ratio from the stoichiometric value 12 to 9.23 and increasing the annealing temperature up to 900 °C for 2h and pH 10. The maximum saturation magnetization (84.15 emu g$^{-1}$) was achieved when Fe$^{+3}$/Sr$^{+2}$ = 9.23 and at the annealing temperature of 1000 °C, annealing time 2h and pH 10.

Rezlescu et al [95] prepared the rare-earth substituted strontium ferrite nanopowders SrFe$_{12-x}$RxO$_{19}$ (R = La, Gd and Er; x = 0.2, 0.5 and 1.0) using sol–gel autocombustion method. The results of X-ray diffraction measurements showed a single magnetoplumbite hexagonal phase. The coercivity $H_c$ exhibits a great increase after a critical heat-treatment time. This jump of $H_c$ was explained by a transition from the superparamagnetic state to normal state of the single domain nanoparticles. The saturation magnetization and the remanence decrease with the increase in ‘R’ contents.

Iqbal and Ashiq [96] investigated the magnetic and electrical behavior of SrZr$_x$Cu$_x$Fe$_{12-2x}$O$_{19}$ (where x = 0.0 – 0.8) hexaferrite nanoparticles synthesized by the chemical co-precipitation method. The FTIR spectrum and XRD pattern of the samples showed that the synthesized materials were of a single phase. The particle size was in the range 26–37 nm as estimated by Scherrer formula, which is comparable with the values estimated from SEM (40–80 nm) and TEM (30–60 nm) analyses. The Curie temperature ($T_C$) decreases on substitution of Zr–Cu. A significant increase in the room temperature resistivity is observed with the addition of Zr–Cu. The variation of the dielectric constant ($\varepsilon$) and the dielectric loss (tan $\delta$) with frequency in the range 80 Hz – 1 MHz and composition of the sample is observed.

Iqbal et al [97] used a simple co-precipitation method to obtain nanocrystallite and single phase of Al–Ga substituted strontium hexaferrite. The XRD analysis assures the single magnetoplumbite phase. The room temperature DC electrical resistivity and activation energy increase while the dielectric constant and dielectric loss decrease with the increase in Al–Ga concentration. The improvement in the electrical resistivity and decrease in both the dielectric loss factor and the dielectric constant make the synthesized materials suitable for application in microwave devices because a high resistivity material is required for the applications in microwave devices. The maximum values of magnetic parameters, i.e. saturation magnetization, remanence and coercivity, are obtained for the sample annealed at 1020 °C.
1.8 Methods of Synthesis

The synthesis of pure, homogenous and nano sized hexaferrite has been a challenging job for many researchers since last few years. Different methods have been adopted for the fabrication of hexaferrite nanoparticles. These include sol-gel, microemulsion, hydrothermal, sonochemical and the co-precipitation methods.

The sol-gel process refers to the hydrolysis and condensation of alkoxide based precursor. This method involves the transition of a system from a liquid “sol” into a solid “gel” phase which is then converted into the required product after annealing. This process involves a series of distinct steps. The size of the sol particles depends on the solution composition, pH and temperature [98]. Various chelating agent in the sol-gel process have been used such as stearic acid, poly vinyl alcohol (PVA) and ethylene glycol by various researchers for the synthesis of various materials [95, 99-105]. The advantage of this method is its lower annealing temperature but the disadvantage of this method is its longer time. As it takes 20 hours to dry the gel and also the annealing time and temperature is higher [104]. There is possibility of impurities due to the presence of chelating agent.

Microemulsion is defined as a thermodynamically stable dispersion of two immiscible liquids consisting of microdomains of one or both liquids stabilized by an interfacial film of surface active molecules [106]. Hoar and Schulman observed that certain combinations of water, oil, surfactant and alcohol or amine based cosurfactant make clear, seemingly homogeneous solution that termed as microemulsions [107]. The selection of surfactant for the synthesis of nanomaterials is very important. A number of factors are advisable while selecting a surfactant i.e. the starting materials and the reaction conditions. The water-in-oil microemulsion technique has been employed for the synthesis of various nanoparticles including metals [108-110], halides [111] and oxides [112-113]. A variety of surfactants such as cetyltrimethylammonium chloride (CTAC), sodium dodecyl sulfate (SDS), Igepal Co-520, polyvinylpyrrolidone (PVP), Brij-97, tween 20 and triton X-100 has been used by various researchers for the synthesis of M-type hexaferrites [98, 105, 106, 114-116]. This method is very costly and also it required higher annealing time of about 12 hours [117].

The basic principle of hydrothermal method is that in a sealed vessel i.e. bomb or autoclave the solvents are brought to temperatures above their boiling points by
increasing the pressure resulting from heating. When a chemical is performed under such conditions is referred as solvothermal process. The reaction can be carried out in water or in any other solvent. When water is used as a solvent then the process is known as hydrothermal process. The critical point for water lies at a temperature of 647 K and 218 atmospheric pressure. Above this temperature and pressure, water is said to supercritical and such fluids have characteristics of liquid as well gas. The interface of solids and supercritical liquids lack surface tension so it can easily dissolve the chemical compounds that would otherwise show very low solubility under normal conditions. Many inorganic materials can be synthesized by method such as TiO₂ [118], BaTiO₂ [119], CoFe₂O₄ [120], ZnFe₂O₄ [121] and SrFe₁₂O₁₉ [69] prepared. The main disadvantage of this method is slow reaction rate at any given temperature. In order to increase the kinetics of crystallization one must introduce the microwave, electric or ultrasonic fields in the hydrothermal system and these are termed as microwave-hydrothermal, electrochemical-hydrothermal and ultrasonic-hydrothermal, respectively [122-126] which contributing to make this method costly and time consuming.

Sonochemical method was initially proposed for the synthesis of iron nanoparticles but nowadays it is used to synthesize different metal oxides nanoparticles [127]. A number of theories have been developed to explain how 20 KHz sonic radiations can break chemical bonds. They all agree that the main event in sonochemistry is the creation, growth and the collapse of bubble that is formed in liquid. A very high temperature (5000-25000 K) is obtained by the collapsing of liquid bubbles which is responsible for the breakage of chemical bonds [128]. In most cases, the end product is amorphous and highly aggregated making it difficult to characterize individual particles [129]. The main disadvantage is that it requires costly machinery.

### 1.8.1 Co-precipitation Method

Co-precipitation reactions [130] involve the simultaneous occurrence of nucleation, growth, coarsening and agglomeration process. When precipitation begins, numerous small crystallites initially form (nucleation) but they tend to quickly aggregate together to form larger, more thermodynamically stable particles (growth). Coarsening is the phenomenon by which smaller particles are essentially consumed by larger particles during the growth process. To produce nanoparticles, the
nucleation process must be relatively faster as compared to the growth process. The formation of particles with a narrow size distribution further requires that the nuclei of all species present form simultaneously and without subsequent nucleation of smaller particles [131]. Reaction for synthesis of oxide can generally be broken into two categories: those that produce an oxide directly and those that produce a precursor that must be subjected to further processing (drying, calcinations). The corresponding metal hydroxides or carbonates usually form and precipitate in water on addition of a precipitating agent such as NaOH, NH₄OH or Na₂CO₃ solution. The resulting chlorides, nitrates or acetates are washed away and the hydroxide is annealed after filtration and washing to obtain the final oxide powder [132].

In present work, the chemical co-precipitation method has been used for the synthesis of strontium hexaferrite because this method ensures proper distribution of various metal ions resulting into stoichiometric and smaller particles size product compared to some of the others. In microemulsion method there is also possibility that the surfactant adsorbed on the surface of nanoparticles and may appear as impurity in the sample [133]. The yield in this method is also very low but it uses large amount of liquids [131]. It is very difficult to control the process in the hydrothermal method. The other disadvantage of this method is the problem of reliability and reproducibility [134]. The chemical co-precipitation has advantage of smaller annealing time (1 hour) and temperature (1193 K) to get single phase as compared to others. It is also simpler and cheaper than microemulsion, sol-gel, sonochemical, spray pyrolysis and hydrothermal methods. The product yield is also high by chemical co-precipitation method as compared to the other methods and it also has advantages of reliability and reproducibility.
1.9 Objectives and Plan of Work

One of the aims of this work is to synthesize the nanoparticles of the strontium hexaferrite by a simple and economic method of preparation. After going through the literature survey, it becomes evident that strontium hexaferrite nanoparticle has been studied extensively due to interest in its magnetic and electrical properties. The physical, electrical and magnetic properties of these materials depend upon the synthesis methods, chemical composition, annealing temperature, annealing time and distribution of ions at different sites. Various researchers used different methods for the synthesis of strontium hexaferrite nanoparticles including the sol-gel, microemulsions, spray pyrolysis, hydrothermal, sonochemical and co-precipitation methods. In the present work, the chemical co-precipitation method for the synthesis of strontium hexaferrite nanomaterials is preferred over other methods for the reason that the sol-gel method requires 10-15 hours for drying of the gel and higher annealing temperature of ~ 1100 °C to obtain single phase. The microemulsion method needs the surfactant and co-surfactant which are costly. The other methods require complex and expensive equipments for synthesis. The co-precipitation method is cheaper and it only requires approximately an hour for obtaining single phase of magnetoplumbite hexagonal structure. It also ensures the proper mixing of the metals and homogeneity in the synthesized sample. The particles obtained by this method are also smaller in size.

The second aim is to increase the saturation magnetization and to decrease the coercivity simultaneously. Many researchers have used different substituents doped at Fe$^{3+}$ as well as at Sr$^{2+}$ sites. Most of the research was focused on the magnetic properties of the strontium hexaferrite and to control the coercivity by substituting different cations at iron sites. In doing so saturation magnetization was notably decreased limiting the application of these materials for recording media [57, 69, 135-137]. There are very few examples in the literature in which the coercivity decreases and simultaneously the saturation magnetization increases on doping at iron sites [65].

The third aim of this work is to increase the DC electrical resistivity and to reduce the dielectric constant and dielectric loss so that the material becomes suitable for application in the microwave devices. The increase in the resistivity is the challenging job for the researchers working in the field of ferrites. Highly resistive materials are required for applications in microwave devices [38]. Few examples have
been reported on the electric and dielectric properties of the strontium hexaferrite nanoparticles. The study of the dielectric parameters and DC electrical resistivity offer valuable information about the behavior of localized and free electrical charge carriers. This leads to a better understanding of the mechanism of electric conduction.

In order to achieve the specific properties as described above it was planned to dope Sr-hexaferrite with a tetravalent Zr$^{4+}$ ion along with divalent Ni$^{2+}$, Cu$^{2+}$, Zn$^{2+}$ and Mn$^{2+}$ ions and trivalent Ga$^{3+}$-Al$^{3+}$ ions at Fe sites. In the reported literature, Ti$^{4+}$ has been doped at iron since Ti$^{4+}$ prefers to occupy the 4f$_2$ site in the hexagonal structure [138-139]. As Zr$^{4+}$ has the same configuration as that of Ti$^{4+}$ and also is in the same group of the periodic table, it is also expected to replace the iron from 4f$_2$ (spin in downward direction). It also has been reported in some papers that Zr$^{4+}$ replaces the iron at 4f$_1$ site (spin in downward direction) [140]. Whether Zr$^{4+}$ nonmagnetic ion replaces iron from 4f$_2$ or 4f$_1$ the net magnetic moment would be increased. It is therefore, expected that the magnetic properties i.e. saturation magnetization would be improved by doping with zirconium ion since the spin down states contribute negatively to the total magnetization. The Ni$^{2+}$, Mn$^{2+}$ and Cu$^{2+}$ are well known to have a preference for the octahedral sites [140, 141] so that their substitution in Sr-hexaferrite could improve the electrical resistivity and to reduce the magnetocrystalline anisotropy constant. It is also expected that the coercivity of the materials will decrease which is good for their use in the magnetic recording media. The other purpose of substituting divalent cations along with tetravalent is to maintain the overall electroneutrality in the samples. The Al$^{3+}$ and Ga$^{3+}$ both have preference to occupy the octahedral 12k site and are expected to increase the electrical resistivity for their applications in the microwave devices [142].

The ionic radii of Zr$^{4+}$, Al$^{3+}$, Ga$^{3+}$ and Fe$^{3+}$ are 0.80, 0.53, 0.62 and 0.64 Å, respectively and those of the divalent cations i.e. Zn$^{2+}$, Ni$^{2+}$ and Mn$^{2+}$ are 0.74, 0.72 and 0.80 Å, respectively. Therefore they can easily replace the iron Fe$^{3+}$ (0.64 Å) with minor distortion of the lattice parameters resulting into single phase of hexaferrite.
2.1 Chemicals Used

The chemicals used at various stages of the synthesis of samples were of high purity compounds procured from well known suppliers. The details of the chemicals are listed as follows:

Table 2.1 Specification of the chemicals used

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Compound</th>
<th>Chemical Formula</th>
<th>Molar Mass</th>
<th>Purity</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ferric nitrate nonahydrate</td>
<td>Fe(NO₃)₃.9H₂O</td>
<td>404.00</td>
<td>98.0%</td>
<td>Sigma, Aldrich</td>
</tr>
<tr>
<td>2</td>
<td>Strontium nitrate</td>
<td>Sr(NO₃)₂</td>
<td>211.63</td>
<td>99.0%</td>
<td>Fluka</td>
</tr>
<tr>
<td>3</td>
<td>Nickel acetate tetrahydrate</td>
<td>Ni(CH₃COOH)₂.4H₂O</td>
<td>248.86</td>
<td>99.0%</td>
<td>Merck</td>
</tr>
<tr>
<td></td>
<td>Zirconyl chloride tetrahydrate</td>
<td>ZrOCl₂.4H₂O</td>
<td>322.25</td>
<td>≥96.0%</td>
<td></td>
</tr>
<tr>
<td>BDH</td>
<td>5 Copper acetate monohydrate</td>
<td>Cu(CH₃COOH)₂·H₂O</td>
<td>195.65</td>
<td>99.0%</td>
<td>Merck</td>
</tr>
</tbody>
</table>
acetate
tetrahydrate Mn(CH$_3$COOH)$_2$.4H$_2$O 245.09 98.0% Merck 7 Aluminium
nitrate nonahydrate Al(NO$_3$)$_3$.9H$_2$O 375.13 95.0% Merck 8 Gallium
nitrate Ga(NO$_3$)$_3$ 255.74 99.9% Aldrich 9 Zinc
chloride ZnCl$_2$ 136.28 98% Aldrich 10 Sodium
hydroxide NaOH 40.00 $\geq$97% Fluka

All the chemicals were used as supplied without further purification.

**Procedure for Sample Preparation**

The strontium hexaferrite having nominal composition SrFe$_{12}$O$_{19}$ was prepared by a chemical co-precipitation method [143]. The required molarities of the metallic salts i.e. Fe(NO$_3$)$_3$.9H$_2$O and Sr(NO$_3$)$_2$ were dissolved in distilled water and mixed in a beaker. This solution mixture was heated up to 343 K with continuous stirring on a hot plate. As the temperature reached to 343 K, the 2M NaOH was added drop wise to form the precipitate and the pH of the solution was kept at 12.5-13. All the samples were stirred for 3 hours in order to control the crystallite size and the homogeneity of the samples. The precipitates were washed with distilled water, dried at 373 K in an oven for 5 hours and annealed at temperature of 1193 K for one hour in a temperature programmed tube furnace at a heating rate of 5 K min$^{-1}$. The flow sheet diagram for the chemical co-precipitation method is shown in figure 2.1.
Figure 2.1 Schematic diagram for the preparation of strontium hexaferrite by the chemical co-precipitation method.

All the series of Sr-hexaferrite samples doped with $\text{Al}^{3+}$-$\text{Ga}^{3+}$ and $\text{Zr}^{4+}$-$\text{M}$ (where $\text{M} = \text{Ni}, \text{Mn}, \text{Cu}$ and $\text{Zn}$) were synthesized using the same method as mentioned above by the addition of the aqueous solution of salts of required molarities of the dopants. The chemicals used for the synthesis of the substituted samples are given in section 2.1. The schematic diagram of the chemical co-precipitation method is as follows.

2.3 Optimization of Synthesis Conditions

Strontium hexaferrite ($\text{SrFe}_{12}\text{O}_{19}$) is synthesized by the chemical co-precipitation method and optimized the Fe/Sr ratio, annealing temperature and annealing time. The energy dispersive X-ray fluorescence (ED-XRF) analysis is performed in order to optimize the Fe/Sr ratio in the sample $\text{SrFe}_{12}\text{O}_{19}$. The theoretical ratio of Fe/Sr = 12.0 is obtained when the Fe/Sr ratio is kept 11.0 as shown in table.
2.2 and therefore the same ratio i.e. Fe/Sr = 11 is kept to synthesize all other samples. This is due to the higher solubility of Fe than that of Sr and it is necessary to keep the concentration of strontium slightly higher. A single hexagonal phase is found when Fe/Sr = 11 whereas the samples, in which the Fe/Sr molar ratio is above 11, an additional nonmagnetic \( \alpha \)-Fe\(_2\)O\(_3\) phase is also appeared along with hexagonal phase. It is also observed that as the Fe/Sr molar ratio is decreased from 12 to 11, the percentage of the M-type phase is increased while that of \( \alpha \)-Fe\(_2\)O\(_3\) decreased.

**Table 2.2** ED-XRF of the samples having different Fe/Sr ratio and the observed phases.

<table>
<thead>
<tr>
<th>Fe/Sr ratio added</th>
<th>Experimental ratio by ED-XRF</th>
<th>Phases observed</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.00</td>
<td>12.80</td>
<td>M-type, ( \alpha )-Fe(_2)O(_3)</td>
</tr>
<tr>
<td>11.80</td>
<td>12.74</td>
<td>M-type, ( \alpha )-Fe(_2)O(_3)</td>
</tr>
<tr>
<td>11.60</td>
<td>12.51</td>
<td>M-type, ( \alpha )-Fe(_2)O(_3)</td>
</tr>
<tr>
<td>11.40</td>
<td>12.36</td>
<td>M-type, ( \alpha )-Fe(_2)O(_3)</td>
</tr>
<tr>
<td>11.20</td>
<td>12.17</td>
<td>M-type, ( \alpha )-Fe(_2)O(_3)</td>
</tr>
<tr>
<td>11.00</td>
<td>11.96</td>
<td>M-type</td>
</tr>
</tbody>
</table>

Sr-hexaferrite (SrFe\(_{12}\)O\(_{19}\)) nanoparticles having the Fe/Sr molar ratio 11 are annealed at different temperatures (873-1193 K) for one hour and the hexagonal phase formation is observed by X-ray diffraction (XRD) analysis as shown in figure 2.2. It is observed that the unannealed sample is amorphous and shows no crystallinity (figure 2.2a) and it is necessary to anneal the sample at higher temperature to develop the crystallinity. The formation of M-type hexagonal phase is started to appear at 873 K but the major phase is observed for \( \alpha \)-Fe\(_2\)O\(_3\) and the M-type hexagonal phase is in low percentage. As the annealing temperature is increased from 873 to 1193 K, the concentration of the \( \alpha \)-Fe\(_2\)O\(_3\) phase decreased gradually and a pure magnetoplumbite phase having no \( \alpha \)-Fe\(_2\)O\(_3\) phase is obtained at 1193 K (figure 2.2). Therefore, all other synthesized samples are annealed at this temperature of 1193 K. The samples are also annealed at different time (15-75 minutes) and it is observed that the pure magnetoplumbite phase is obtained for the sample annealed for one hour. So this annealing time is kept for all other synthesized series.
Initially, the strontium hexaferrite (SrFe$_{12}$O$_{19}$) is synthesized by three different methods namely, the chemical co-precipitation, the sol-gel auto-combustion and the microemulsion methods. It is noted that the sol-gel auto-combustion method requires annealing temperature of 1223 K and time of 5 hours to obtain the single phase. It also requires several hours for the formation of gel. The density of the synthesized material is very low and also high temperature is required for the densification of the material. In the microemulsion method the annealing temperature (1173 K) is slightly low but the single phase is attained at the annealing time of 8 hours. The surfactant and co-surfactant used for the synthesis process are very costly. The sample synthesized by the chemical co-precipitation method is observed to form the single phase at 1193 K and the time required is only 1 hour but the particle size (30 nm) is observed same in all three methods. The sol-gel auto-combustion and microemulsion methods are time consuming as well as higher annealing temperature and time is required to obtain the single magnetoplumbite phase. The microemulsion method is also very costly as well. The chemical co-precipitation method is very simple, cheaper and also less time consuming. So the chemical co-precipitation method is used for the synthesis of all other series.
Figure 2.2 XRD patterns of SrFe$_{12}$O$_{19}$ annealed at different temperatures (a = 100 °C, b = 600 °C, c = 700 °C, d = 800 °C, and e = 920 °C) * = α-Fe$_2$O$_3$. 
2.4 Characterization Techniques

The synthesized samples were characterized by thermogravimetric analysis (TGA), powder X-rays diffraction (XRD), energy dispersive X-ray fluorescence (ED-XRF), DC electrical resistivity, dielectric constant and dielectric loss, low field ac magnetic susceptibility and hysteresis loop measurements. X-ray diffraction (XRD), thermogravimetric analysis (TGA) and energy dispersive X-ray fluorescence (ED-XRF) give the structural information such as lattice constants, cell volume, X-ray density, crystallite size, phase transformation temperature, particle size and composition of the samples, respectively. Electrical resistivity measurement, dielectric constant and dielectric loss give informations about the conduction mechanism. Hysteresis loops provide informations about the saturation magnetization \(M_s\), remanence \(M_r\) and coercivity \(H_c\). The instruments used for characterization are described as follows

2.4.1 Thermogravimetric Analyzer

Thermal analysis is the measurement of physical and chemical properties of materials as a function of temperature. There are many applications of thermal analysis in solid state science including the thermodynamics and kinetics of solid state reactions, thermal decomposition and phase transformation, etc. Thermal analysis includes two main techniques which are thermogravimetry (TG) and differential scanning calorimetry (DSC). Thermogravimetry is a technique in which the change in weight of the material is monitored as a function of time or temperature. The derivative thermogravimetric (DTG) is a plot of the rate of mass change with time \((\text{dm/dt})\). The thermogravimetric analyzer consists of three main parts: microbalance, furnace and controller.

The electronic microbalance (B) is a light ray balance that consists of an arm articulated on a torsion thread that is balanced by the weight of the sample in one of its end and by a counterbalance in the other which is necessary whenever the weight of the sample surpasses the rank of automatic tare of the thermobalance. The weight of the samples used was about 200 mg in the form of cylindrical pellet. The furnace (F) in this system is a cylindrical shape which is formed by a graphite heating system in an argon atmosphere to avoid its oxidation. It is protected by a tube of alumina in its inner part and by water cooled steel case in the outer part. The temperature of the
furnace is detected by a thermocouple (TC) (Pt Rh 6%-Pt Rh 30%) located very near to the sample and the temperature controller is used to control the temperature. The system also allows to modify the composition of the atmosphere during the sintering by using different gases (A). To avoid the oxidation of the sample an inert gas (C) is circulated inside the furnace and it also help to drag all the gases outside that are produced during the reaction. The flow diagram of this system is shown in figure 2.3.

**Figure 2.3 Thermogravimetric equipment**

SETARAM TG-92 (figure 2.3) with computer interface was used to investigate the changes occur on heating the sample in the present investigations. The sample used was in the cylindrical shape having 10 mm length and 2 mm thickness. The instrument was operated at the heating rate of 5 K min\(^{-1}\) and the weight loss with temperature was recorded. In order to measure the phase transitions temperatures accurately a low heating rate of 5 K min\(^{-1}\) was chosen which is normal in such analysis. The typical TG/DTG curve is shown in figure 3.1.
2.4.2 X-ray Diffractometer

X-ray diffraction (XRD) is the most useful, nondestructive and least ambiguous technique to identify the structure and crystallinity in the material. This technique requires no specific sample preparation [144-146]. It provides informations on the structures, phases and other structural parameters such as lattice constant, cell volume, crystallite size and X-ray density. The basic principle of X-ray diffraction is that when a beam of x-ray applies on a material it is scattered in various directions by the electron clouds and if the wavelength of X-ray is comparable to the separation between the atoms then interference can occur.

Three different methods for the determination of crystal structure by X-ray diffraction can be adopted. All these routes are based on Bragg’s law. These include Laue, rotating-crystal and powder methods. The powder method [144] can be used by two different techniques namely Debye-Scherrer camera and diffractometer method [145].

When X-ray strikes a powder sample, the layers of crystals of the sample act like mirrors that “reflect” the X-ray beams. Constructive interference takes place only between those scattered rays which obey the Bragg’s law, \( n\lambda = 2dsin\theta \) (\( n = 1, 2, 3, \ldots \)), where \( n \) is the order of interference, \( \lambda \) is the wavelength of the incident X-ray beam, \( d \) is the distance between atomic layers in the crystal, and \( \theta \) is the angle of incidence.

The X-ray diffractometer consists of different part i.e. X-ray tube (T), filters (F), beam slits (BS), beam masks (BM), X-ray mirror (A), monochromator (M), detector (D) and sample holder (S). The X-ray tube (T) consists of an evacuated envelope containing an anode, a cathode, a focusing cylinder and exit window. The X-ray tube used in most cases is Cu LFF with maximum transmission of 94% of Cu K\(_\alpha\) X-ray radiations. A beta filter (F) is used to suppress the K\(_\beta\) radiations and to pass the K\(_\alpha\) radiations as much as possible. The divergence slits are fitted in the incident beam path to control the equatorial divergence of the incident beam. There are two types of slits i.e. fixed divergence slit (FDS) and programmable divergence slit (PDS). The beam masks (BM) are also fitted in the incident beam path to control the axial width of the incident beam [144].

To improve the peak shape and the resolution of the 2\(\theta\)-type scan especially at low scattering angles the soller slits are used. The X-ray mirror (A) is used to diffract the characteristics K\(_\alpha\) radiations. The K\(_\beta\) radiations are suppressed to a level below
0.5% of its original level. In the analyses where the resolution is of high importance the incident beam monochromator is an important tool. The monochromator (M) is placed in the incident beam path between the X-ray tube and the sample. Anti-scatter slits (AS) are fitted into the diffracted beam path to control the amount of the diffracted X-ray that is accepted by the detector. The detector (D) is used to count the number of photons i.e. the intensity of the diffracted beam at a certain 2θ position. The detector consists of a chamber filled with xenon/methane gas mixture [144]. The last part of the diffractometer is the sample holder (S) made up of the aluminium having volume of 15mm + 20mm + 1.8mm. The X-ray pattern is observed by the display unit (B). The schematic diagram for X-ray diffractometer is shown in figure 2.4.

![Figure 2.4 Flow sheet diagram for the X-ray diffractometer.](image)

X-ray diffraction analysis was performed to confirm the purity and phase formation of hexaferrites using Philips X’Pert PRO 3040/60 diffractometer which uses Cu-Kα as a radiation source. The XRD pattern recorded by the above mentioned X-ray diffractometer is shown in figure 2.5.
Various parameters were calculated from XRD data such as crystallite size, lattice constants, cell volume, and X-ray density. The peak broadening of the experimental diffraction peak gave information about the diameter of the crystallite size ($D$). The crystallite size was calculated from the Scherrer’s formula, using the full width at half maximum (FWHM) values of indexed peaks in the X-ray patterns [144, 147-148].

$$D = \frac{K\lambda}{\beta \cos \theta}$$  \hspace{1cm} (2.1)

where ‘$\lambda$’ is the X-ray wavelength and is equal to 1.542 Å, ‘$\beta$’ the half-peak width, ‘$\theta$’ the Bragg angle and $K$ is the constant and its value is 0.89 [144, 149-150].

The lattice constants ($a$ & $c$) and cell volume ($V_l$) were calculated from the following equations using XRD data.

$$\frac{1}{d^2} = \frac{4}{3}(\frac{h^2 +hk +k^2}{a^2}) + \frac{l^2}{c^2}$$  \hspace{1cm} (2.2)

$$V = 0.8666 \ a^2c$$  \hspace{1cm} (2.3)

The X-ray density ($\rho_{\text{x-ray}}$), bulk density ($\rho_m$) and porosity ($P$) were also calculated using following formulae [151-152].

$$\rho_{\text{x-ray}} = \frac{ZM}{N_A V}$$  \hspace{1cm} (2.4)
\[ \rho'_m = \frac{m}{m^2 h} \]  \hspace{1cm} (2.5)

\[ P = 1 - \frac{\rho'_m}{\rho_{x-ray}} \]  \hspace{1cm} (2.6)

where ‘\(Z\)’ is the number of formula units in a unit cell which is 2 for M-type hexaferrite ‘M’ the molecular mass of the sample, ‘\(N_A\)’ the Avogadro’s number, ‘\(m\)’ is the mass of the pellet, ‘\(h\)’ the height of the pellet and ‘\(r\)’ is the radius of the pellet.

### 2.4.3 Energy Dispersive X-ray Fluorescence (ED-XRF)

It is a fact that there is a rapidly growing need of the precise elemental analysis of various materials in various fields such as steel, ceramics, nanomaterials, and food. X-ray fluorescence (XRF) is a simple and nondestructive technique with high speed qualitative and quantitative analysis of many kinds of elements in a wide range of concentration. XRF systems are further divided into two major systems which are wave length dispersive X-ray fluorescence (WD-XRF) and energy dispersive X-ray fluorescence (ED-XRF).

In WD-XRF analyzers, the X-rays are irradiated from the X-ray tube (T) toward the sample (S) in a vacuum and the generated characteristic X-rays are separated into each component by the monochromator. The elements in the sample are detected by the proportional counter. The main disadvantage of this technique is that there must be separate analysis for individual element. On the other hand, in ED-XRF analyzer the generated characteristic X-rays are directly guided to a semiconductor x-ray detector where the energy levels are separated, so many elements in the sample can be analyzed simultaneously [153]. The WD-XRF analyzer is highly sensitive and requires handling expertise. On the other hand ED-XRF analyzer is easy to handle and is used as a versatile multi-element analyzer.

The analyzer has capability of analyzing components in solids, liquids and powders at high speed rate and without damaging the sample. This also requires no standard sample. It consists of an analyzing unit, a data processing unit, a vacuum pump and a computer. The analyzer unit consists of a power supply for X-ray tube (T) and a high precision current and voltage control circuit for the power supply which give the X-rays radiations which are controlled by X-ray controller (C) to the sample (S). The data processing unit (P) is composed of a high rate pulse processing circuit which measures the detector (D) signals [153]. The computer (R) is preinstalled with
a Window operating system and software. This software provides easy access to spectrum analysis, automatic qualitative and quantitative analysis of the sample. The block diagram of the energy dispersive X-ray fluorescence (ED-XRF) is given in figure 2.6. The ED-XRF (Horiba MESA-500) spectrometer was used to know the qualitative and quantitative composition of the hexaferrite nanoparticles. The characteristics X-rays from the source fall on the sample and then enter to Si (Li) detector which is connected to the data processing units. It is necessary to cool the detector to liquid nitrogen temperature in order to reduce the electronic noise and to ensure optimum resolution. The detector acts as a transducer which convert the X-rays photon to charge. The charge produce is directly proportional to the energy of the X-rays which enter the detector. The signals enter to the data processing unit that uses the computer software and the recorder which record the spectra.

Figure 2.6 Block diagram for energy dispersive X-ray fluorescence (ED-XRF).

2.4.4 DC Electrical Resistivity Measurement

Two methods namely two-point and four-point probe methods are reported for the measurement of DC electrical resistivity of the materials. The two-point probe method was used for the measurement of resistivity of hexaferrites materials in the temperature range of 300-675 K. 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 [97]. The use of four-point probe method is also not suitable at high temperature due to unstability of silver paste used for connections.
While the two point probe method is suitable for the samples having high resistivity and at high temperature.

A resistivity measuring apparatus was developed to measure the electrical properties such as resistivity, conductivity, mobility and activation energy at high temperature range (300-675 K). An element heater (H) was used to heat the sample which is clamped inside a hollow ceramic pot. The maximum temperature of 773 K can be attained from this heater. A thermocouple was connected with a UT-55 multimeter to read the temperature which can measure the temperature in the range 73 to 1473 K. A triac control (B) was introduced in series with the heater to heat the sample at a slow rate. The sample holder was made according to the requirement of two-probe method. Two metal strips (P1 and P2) were used for this purpose. The upper strip (P1) was connected to the lower strip (P2) at the ends and ceramic beads were inserted between them to avoid the short circuiting (D). There were two holes in the middle of the strips and two screws were used to hold the sample as shown in Figure 2.7. The constant voltage was applied by a Keithley source meter-2400 to the sample (S) and the change in current (A) as a function of temperature was measured keeping the voltage (V) constant by the same Keithley source meter.

![Figure 2.7 Block diagram representing the resistivity apparatus.](image)

The electrical resistivity was measured with sample pellet of 2.0mm thickness and 13mm diameter. The resistivity of the samples was calculated by following equation [148]
\[ \rho = \frac{RA}{L} \quad (2.7) \]

where ‘R’ is the resistance of the sample, ‘A’ the area of the pellet and ‘L’ is the length of the sample pellet. The drift mobility and activation energy of all the samples were also calculated from the DC electrical resistivity data. The variation of electrical resistivity with temperature measured by the above mentioned apparatus is shown in figure 2.8.

![Temperature dependence of electrical resistivity measured by the apparatus described in section 2.4.4.](image)

**Figure 2.8** Temperature dependence of electrical resistivity measured by the apparatus described in section 2.4.4.

The drift mobility ‘\( \mu_d \)’ of all the hexaferrite samples was calculated using the relation [154].

\[ \mu_d = \frac{1}{nep\rho} \quad (2.8) \]

where ‘e’ is the charge of electron, ‘\( \rho \)’ the DC electrical resistivity at given temperature and ‘n’ is the concentration of charge carriers and can be calculated from the relation

\[ n = \frac{N_A\rho_mP_{Fe}}{M} \quad (2.9) \]
where \( N_A \) is the Avogadro’s number, \( \rho_m \) the bulk density, \( M \) the molecular weight of the sample and \( p_{Fe} \) is the number of iron atom in the chemical formula of the samples. The electrical resistivity of the ferrite materials decreases with increasing temperature obeying the Arrhenius type equation [148]

\[
\rho = \rho_0 \exp\left(\frac{\Delta E}{kT}\right)
\]

where \( k \) is the Boltzmann constant, \( T \) the temperature expressed in Kelvin and \( \Delta E \) is the activation energy, which is the energy needed for the hopping of electron from an ion to the neighboring ion, so give rise to the electrical conductivity. Using equation 2.10 we are able to calculate the activation energy.

### 2.4.5 Inductance, Capacitance, Resistance (LCR) Meter

The inductance, capacitance and resistance (LCR) meter provides economical, fast and accurate testing of any passive material up to several frequency ranges. One can automatically measure the inductance (L), capacitance (C) and resistance (R) as well as other parameters such as quality factor, impedance, AC resistance, conductance and dissipation factor. The dielectric constant (\( \varepsilon \)) and dielectric loss (\( \tan\delta \)) are calculated from inductance, capacitance and resistance data. It consists of a power supply (PS) to generate the ac voltage. The frequency and the amplitude of the power supply can be set according to the requirements. The voltage is applied to the sample (S) through source resistance ‘\( R_S \)’ (B) which varies according to the measurement range. The current flows through resistance \( R_R \) to the operational amplifiers (A₁ and A₂). The output of the operational amplifier provides a signal proportional to the current \( IR_R \). The voltage across the sample is measures by a separate signal path providing a four wire Kelvin connection. Out of these four wires Kelvin, two wires use to carry the test current and two independent wires to sense the voltage across the sample. The real and imaginary signals are obtained by multiplying the voltage and current signals with a reference signal in phase with power supply voltage and other shifted 90° from power supply voltage. These signals are read by a microprocessor (M). This prevents the voltage drop in the current carrying wires from affecting the voltage measurement. The LCR meters are controlled by a high speed microcontroller that operates the display, keypad, general purpose interface bus (GPIB) computer interfaces and handler interface. The schematic diagram of LCR meter is shown in figure 2.9.
Polycrystalline ferrites are very good dielectric materials and have many technological applications ranging from microwave to radio frequencies. Hence, it is important to study their dielectric behavior at different frequencies. The dielectric properties of ferrites are dependent on several factors, including the method of preparation, concentration of impurities added and temperature. In any dielectric materials there will be some power loss because of the work done to overcome the frictional damping forces encountered by the dipole during their rotation. A capacitor when charged under an ac voltage will have some loss current due to ohmic resistance or impedance by heat absorption.

**Figure 2.9** Schematic diagram of LCR meter.

Dielectric constant is a measure of the degree to which a medium can resist the flow of charge which is calculated using equation 2.11. LCR meter (Wayne Kerr LCR 4275) was used to calculate the dielectric constant and dielectric loss in the frequency range of 80 Hz – 1MHz. The samples were of the same dimensions as were used for the electrical resistivity measurement i.e. pellet of 13mm diameter and 2.0mm thickness [91].

\[
\varepsilon' = \frac{Cd}{\varepsilon_o A} \tag{2.11}
\]

where ‘C’ is the capacitance of the pellet in farad, ‘d’ the thickness of the pellet in meter, ‘A’ the cross-sectional area of the flat surface of the pellet and ‘\(\varepsilon_o\)’ is the permittivity constant of free space. The dielectric loss (\(\tan\delta\)) is calculated by following equation
where \( \delta \) is the loss angle, \( f \) the frequency, \( R_p \) the equivalent parallel resistance and \( C_p \) is the equivalent parallel capacitance.

### 2.4.6 AC Magnetic Susceptibility Measurement

The magnetic materials are classified on the basis of their response to an applied magnetic field and this response is characterized by the ac magnetic susceptibility. Ac magnetic susceptibility (\( \chi \)) is a measure of how easy it is to magnetically polarize the substance [155] which is given in equation 1.5. The AC magnetic susceptibility as a function of temperature of strontium hexaferrite nanomaterials is measured by primary and secondary coil set up operated at the frequency of 273Hz and is built up in the surface and solid state chemistry laboratory, department of chemistry quaid-i-azam university Islamabad, Pakistan.

An AC susceptometer was constructed for the measurement of AC magnetic susceptibility as a function of temperature in the temperature range of 300-800 K, based upon the principle of mutual inductance for measuring the temperature dependence of the ferrite nanoparticles. The coil assembly consists of a pair of co-axial coils, the primary (\( C_1 \)) and the secondary (\( C_2 \)) which are wound over a non-magnetic Teflon core having hole of diameter 27mm and length 85mm as shown in figure 2.10. The secondary coil (\( C_2 \)) is divided into two equal halves wound in opposite directions to make the total induced voltage of coil equal to zero. The wire used for winding was swg 34 which is high-purity copper wire having the diameter 0.3mm. The DC power supply (PS) having model (Topward 33010D) was used to provide the current to the heater (H). The power supply (PS) has the maximum capacity of 30 A current. An element heater (H) was placed inside the coil to heat the sample. The diameter of the heater was about 10 mm and the resistance of the heater wire was reduced to 5\( \Omega \). A thick cylindrical shaped glass tube was placed between the heater and the coil to avoid the heating of the coil because as the sample is heated the Teflon coil was also heated. Moreover air gap was employed between the coil and the glass tube. Also an exhaust fan (F) was mounted at the backside of the coil. The fan was mounted at some distance to avoid the signal produced by the motor of the fan. A pt-100 thermocouple (TC) was used as a temperature sensor and the resistance value was read by a Keithley 2000 multimeter (M) which is converted to temperature.
coil assembly was fixed on a wooden table with the help of screws. To measure the output signal from the secondary coil a Lock-in Amplifier (LA) (Stanford SR830 DSP) was used and the frequency was kept 273 Hz.

The apparatus was calibrated by pure nickel and a graph was plotted between temperature and inverse of the susceptibility to determine the Curie temperature which is the temperature at which the ferromagnetic or ferrimagnetic materials change into paramagnetic one. The Curie temperature for pure Ni measurement is found to be \(633 \pm 5\) K and is in excellent agreement with the reported value \(631\pm2\) K [155] for pure Ni. The magnetic susceptibility was measured using the above mentioned apparatus. The sample (S) used for this purpose was cylindrical in shape of 10 mm length and 3 mm thickness. The graphs were plotted between temperature and reverse of the susceptibility and the Curie temperature was determined from these plots. The typical plot between \(1/\chi\) and temperature is shown in figure 2.11.

**Figure 2.10** Flow sheet diagram for the high temperature susceptibility measurement apparatus.

\[\text{Figure 2.10 Flow sheet diagram for the high temperature susceptibility measurement apparatus.}\]
2.4.7 Hysteresis Loops Measurement System

The measurement of hysteresis loops gives information about the saturation magnetization, remanence and coercivity of the magnetic materials. A standard AC induction method was used for the measurement of hysteresis loops, in which the magnetic field $H$ and the magnetic induction $B$ are both measured through two coils placed near the sample. The system is composed of several subsystems.

It is made up of a silicon iron laminated core and two excitation coils connected to the mains supply through a variable transformer. The core has two identical gaps in which the sensor coils are placed. The magnetic field at the gaps can be controlled by varying the applied voltage applied to the excitation coils. The excitation coils can also be connected to the output of a waveform generator through a power amplifier in order to generate fields of variable frequency. In this setup, the maximum allowable field is limited by the maximum output power of the amplifier.

There are two identical flat and square sensor coils (SC) placed at the core gaps $L_1$ and $L_2$ as shown in figure 2.12. The coil $L_1$ is empty while $L_2$ is filled with the powdered sample. The core ($A$) is used to cover both $L_1$ and $L_2$ coils. The coils are wired in series and connected to the input of a digital oscilloscope (OS) (Tektronix TDS 210). The voltage induced in $L_1$ ($e_1$) is applied to the channel 1 (CH1) while the difference between $e_1$ and $e_2$ ($B$) (where $e_2$ is the voltage induced by the coil filled

![Figure 2.11](image)

**Figure 2.11** Plot of temperature versus $1/\chi$ for Sr-hexaferrite measured by the apparatus given in section 2.4.6.
with the powdered sample L2) is applied to channel 2 (CH2) of the oscilloscope as shown in figure 2.13.

![Diagram of sensor coils and oscilloscope connection](image)

**Figure 2.12** The sensor coils used in the hysteresis loops measurement system.

**Figure 2.13** The sensor coil connection with the oscilloscope.

The waveform data acquired by the oscilloscope is transferred to the control computer via the general purpose interface bus (GPIB) of the oscilloscope to USB bridge. The computer performs all the data manipulation need to extract the relevant data from the digitized waveforms. The computer program is written in Agilent VEE graphical language, using Agilent I/O libraries.
The magnetic flux in the L1 coil can be written as

\[ \phi_1 = nA_1 \mu_0 H \]  

(2.13)

where \( n \) is the number of turns and \( A_1 \) is the effective surface area of both coils.

The magnetic flux in L2, taking into account the sample placed inside, can also be written as

\[ \phi_2 = nA_2 \mu_0 (AH + A_s M) \]  

(2.14)

where \( A_s \) is the sample area and \( M \) is its magnetization.

The voltage at the CH1 input will be

\[ e_1 = -\frac{d\phi_1}{dt} = -nA_1 \mu_0 \frac{dH}{dt} \]  

(2.15)

and the voltage at the CH2 input

\[ e_1 - e_2 = -\frac{d(\phi_1 - \phi_2)}{dt} = -nA_2 \mu_0 \frac{dM}{dt} \]  

(2.16)

It is to be noted that the CH2 voltage is not dependent on the coil area it only depends on the sample area. The coil area \( A \) is calculated in the calibration process using an accurate gaussmeter to measure magnetic field in the gaps. The computer performs the numerical integration of these values to obtain M-H loop for each sample, saves the data and plots the resulting curve. The hysteresis loop measured by the above mentioned system for the Sr-hexaferrite is shown in figure 2.14.

Figure 2.14 A typical hysteresis loop of Sr-hexaferrite measured by the system mentioned in section 2.4.7.
The magnetic moment ($n_B$) can also be calculated from the saturation magnetization data using the following formula [90].

$$n_B = \frac{M \times M_s}{5.585 \times d_b}$$  \hspace{1cm} (2.17)

where ‘$M$’ the molecular weight of the samples, ‘$M_s$’ the saturation magnetization and ‘$d_b$’ is the measured density of the samples.
3.1 Structural Properties

The structural analyses of the synthesized samples are carried out using thermogravimetric analysis (TGA), X-ray diffraction (XRD) and energy dispersive X-ray fluorescence (ED-XRF).

3.1.1 TG/DTG Analysis

The TG/DTG analysis of the synthesized series with nominal compositions i.e., SrZr$_x$Ni$_x$Fe$_{12-2x}$O$_{19}$, SrZr$_x$Cu$_x$Fe$_{12-2x}$O$_{19}$, SrZr$_x$Mn$_x$Fe$_{12-2x}$O$_{19}$, SrZr$_x$Zn$_x$Fe$_{12-2x}$O$_{19}$ and SrZr$_x$Al$_x$Ga$_x$Fe$_{12-2x}$O$_{19}$ is carried out to evaluate the mechanism of strontium hexaferrite phase formation process and to observe the effect of heating on the structural changes. The TG/DTG analysis is carried out by the SETARAM TG-92 thermogravimetric analyzer at the heating rate of 5 K min$^{-1}$ as discussed in section 2.4.1.

![Figure 3.1 TG/DTG curve for an unannealed and undoped SrFe$_{12}$O$_{19}$ sample.](image)

Figure 3.1 TG/DTG curve for an unannealed and undoped SrFe$_{12}$O$_{19}$ sample.

Figure 3.1 shows the TG/DTG curve for an unannealed sample of pure strontium hexaferrite. The weight loss at 375 and 598 K are attributed to the loss of water and the formation of oxides from the hydroxides of the metals, respectively [156]. The third peak at round about 873 K is due to the formation of strontium...
monohexaferrite and strontium hexaferrite which is also complimented by the XRD analysis as discussed previously (Figure 2.8). The crystalline hexaferrite phase starts to form at or above 873 K but at this temperature the other impurities, such as SrO\(\text{Fe}_2\text{O}_3\) and \(\alpha\text{-Fe}_2\text{O}_3\) are also present. Therefore it is necessary to anneal it at higher temperature in order to get the pure phase. The TG analysis shows that the hexaferrite phase is formed at relatively low temperature for the sample synthesized by the co-precipitation method as compared to other methods [67, 81, 157-159].

The TG/DTG curves for samples of the series doped with Zr-Ni, Zr-Cu, Zr-Mn and Zr-Zn are shown in figures 3.2-3.5. Samples with \(x = 0.4\) from each of the five series are selected. The observed weight loss (10%) at \(\sim 373\) corresponds to loss of water from the samples and the weight loss at \(\sim 573\) K shows the formation of oxides from the hydroxides i.e. \(\text{Sr} \cdot \text{Fe(OH)}_n \rightarrow \text{SrO} \cdot \text{Fe}_2\text{O}_3\) [156]. A slightly higher temperature is required for the formation of hexaferrite phase which begins to form at 973 K for the Zr-Ni, Zr-Cu, Zr-Mn and Zr-Zn doped samples of Sr-hexaferrite in contrast to a temperature of 873 K in undoped strontium hexaferrite (figure 3.1). It has already been reported [160-162] that the substitution of Ti-Ni, Ti-Cu and Ti-Co increase the annealing temperature to 1373 K and it is expected that doping with Zr-M (where M = Ni, Cu, Mn and Zn) may also increase the phase formation temperature because zirconium and titanium are in the same group of the periodic table and have a similar electronic configuration. But, in the present case, the phase formation temperature has only just increased from 873 to 973 K which is much lower than those reported for the substitution of Ti-M (M = Ni, Cu and Co) [160-162]. The DTG curve for Zr-Mn doped material is slightly different which may be due to that some the water trapped in the sample which was in the form of pellet. As the temperature increase to some higher value then trapped water also evaporate from the sample and a second peak near the first one appeared.

The TG/DTG curve for the Al-Ga substituted sample is shown in figure 3.6. The DTG curve for the Al-Ga substituted sample with nominal composition \(\text{Sr}_{0.4}\text{Ga}_{0.4}\text{Fe}_{11.2}\text{O}_{19}\) has an additional peak at 923 K before the phase transition temperature which may be due to the evaporation of aluminium from the sample because it has lower melting point of 933 K. The TG/DTG curve shows that the crystalline hexaferrite phase is formed from 1073 K to 1193 K.
Figure 3.2 TG/DTG curve for the unannealed Zr$_{0.4}$Ni$_{0.4}$doepd Sr-hexaferrite.

Figure 3.3 TG/DTG curve for the unannealed Zr$_{0.4}$Cu$_{0.4}$ doped Sr-hexaferrite.
Figure 3.4 TG/DTG curve for the unannealed Zr_{0.4}Mn_{0.4} doped Sr-hexaferrite.

Figure 3.5 TG/DTG curve for the unannealed Zr_{0.4}Zn_{0.4} doped Sr-hexaferrite.
3.1.2 X-ray Diffraction (XRD) Studies

The X-ray diffraction analysis (XRD) is carried out in order to determine the sample purity, the lattice constants (a & c), cell volume (V), crystallite size (D) and X-ray density (ρ\textsubscript{x-ray}) are calculated using the XRD data. The XRD patterns for the Zr-Ni substituted series are shown in figure 3.7. This pattern is matched with the standard Inorganic Crystal Structure Database with reference code (ICSD-00-051-1879) and it is observed that all the peaks match perfectly with the ICSD pattern and no extra peak was observed, confirming the single magnetoplumbite phase formation in the samples synthesized here.

The crystallite size of the different samples is calculated using Scherrer formula (equation 2.1) and their values are given in table 3.1. The observed crystallite sizes are found in the range of 30-47 nm are much smaller as compared to those reported earlier 83, 151-200, 70-100 and 60-300 nm for the M-type hexaferrites [79, 163-165]. In high density recording media, magnetic grain size of <50 nm is desirable for the purpose of obtaining a suitably low signal-to-noise ratio [3]. Therefore, Zr-Ni substituted Sr-hexaferrites are suitable for use in the recording media.

Figure 3.6 TG/DTG curve for the unannealed Al\textsubscript{0.4}Ga\textsubscript{0.4} doped Sr-hexaferrite.
Figure 3.7. The indexed XRD patterns of Sr-hexaferrite doped with Zr$_x$Ni$_{1-x}$ (a) $x = 0.0$, (b) $x = 0.2$, (c) $x = 0.4$, (d) $x = 0.6$ and (e) $x = 0.8$. 

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Other parameters such as lattice constants (a & c), cell volume (V) and X-ray density (\(\rho_{x	ext{-ray}}\)) are calculated by the relations (equations 2.2-2.4) as described in the previous chapter and their values are tabulated in table 3.1. The lattice constant ‘a’ remains almost constant while the constant ‘c’ increases from 23.06 to 23.28 Å and the cell volume (V) from 688 to 699 Å³ with increase in the concentration of Zr-Ni. The increase in the cell volume and lattice constant ‘c’ may be due to the larger ionic radii of Zr⁴⁺ (0.80 Å) and Ni²⁺ (0.69 Å) as compared to the ionic radius of Fe³⁺ (0.64 Å). The X-ray densities of the substituted materials are also increased with the increase in the concentration of substituents as given in table 3.1. The increase in X-ray density on substitution of Zr-Ni is due to the larger molar masses of the substituted samples according to equation 2.4. The bulk density (\(\rho_m\)) and the porosity (P) are also calculated using the equation 2.5 and 2.6, respectively. The porosity decreases while the bulk density increases for Zr-Ni content of \(x = 0.0\) to \(x = 0.6\).

Table 3.1 Crystallite size (D), lattice constants (a and c), cell volume (V), X-ray density (\(\rho_x\)), bulk density (\(\rho_m\)) and porosity (P) for the samples with nominal composition ZrxNi₁₂₋₂xO₁₉.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>ZrxNi₁₂₋₂xO₁₉ content, x</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystallite sizes (D) nm ± 5</td>
<td>0.0  0.2  0.4  0.6  0.8</td>
</tr>
<tr>
<td>Lattice constant (a) Å ± 0.01</td>
<td>5.87  5.88  5.89  5.89  5.89</td>
</tr>
<tr>
<td>Lattice constant (c) Å ± 0.01</td>
<td>23.06 23.06 23.08 23.12 23.28</td>
</tr>
<tr>
<td>Cell volume (v) Å³ ± 0.1</td>
<td>688  690  693  695  699</td>
</tr>
<tr>
<td>Bulk density ((\rho_m))  g cm⁻³ ± 0.01</td>
<td>2.36  2.80  2.86  2.90  2.52</td>
</tr>
<tr>
<td>X-ray density ((\rho_{x	ext{-ray}})) g cm⁻³ ± 0.01</td>
<td>5.13  5.15  5.16  5.18  5.19</td>
</tr>
<tr>
<td>Porosity (P) % ± 0.01</td>
<td>0.54  0.46  0.45  0.44  0.51</td>
</tr>
</tbody>
</table>

The XRD patterns for the series doped with ZrxCuₓ, ZrxMnx, ZrxZnx and AlₓGaₓ where \(x = 0.0 - 0.8\) are shown in figures 3.8-3.11. All the peaks match with the standard ICSD pattern showing the single phase of the synthesized materials. The
XRD patterns also show some noisy peaks which may be due to two reasons. Firstly, the crystallites size is very small so and due to amorphousity these noisy peaks may appear. Secondly, it may be due to instrumental error. The crystallite sizes are in the range of 30-40, 30-37, 30-47 and 30-62 nm for the Zr-Mn, Zr-Cu, Zr-Zn and Al-Ga series, respectively (tables 3.2-3.5). All the crystallite sizes are small enough to obtain the suitable signal to noise ratio used in the high density recording media. The cell volumes ‘V’ and the lattice constant ‘c’ for the Zr-M substituted series increase with the increase in Zr-M contents but both these parameters decrease for the Al-Ga substituted samples. However the values of lattice constant ‘a’ remain constant in each case since ionic radii of the substituted cations are 0.80, 0.73, 0.80, 0.74, 0.52 and 0.62 Å for Zr⁴⁺, Cu²⁺, Mn²⁺, Zn²⁺, Al³⁺ and Ga³⁺, respectively. These values being higher than that of the Fe³⁺ increase the cell volume as well as the lattice constant ‘c’.

The values of the bulk density (ρₘ), X-ray density (ρₓ-ray) and the porosity (P) of the synthesized series as calculated from relevant equations described in section 2.4 are also given in tables 3.2-3.5. The X-ray density increases for Zr-M substituted series while it decreases for the Al-Ga substituted series. The molar masses of the Zr-M doped samples are larger while that of the Al-Ga doped is smaller than that of the pure strontium hexaferrite nanoparticles. The bulk density shows the irregular behavior but up to certain concentration of the substituents its value increases for all the series investigated here, indicating that the doped samples are denser than the undoped. The X-ray density is higher than the bulk density (ρₘ) which indicates the presence of pores in the synthesized samples. The porosity decrease for the samples in which the bulk density increase up to a specific concentration of the substitutions.

It has been observed that the bulk density for the samples doped with Zr-Ni (table 3.1), Zr-Cu (table 3.2) and Zr-Mn (table 3.3) increase up to a certain concentration level and then decrease while that of for Zr-Zn (table 3.4). The increase in bulk density is due to the decrease in porosity up to the same doping concentration range. From tables 3.1-3.5 it is clear that the data of porosity is in agreement with that of the bulk density i.e. the sample having smaller value of porosity has high value of bulk density and vice versa. The inconsistency in the cell volume for the few samples such as SrZr₀.₈Cu₀.₈Fe₁₀₆O₁₉ (table 3.2), SrZr₀.₆Mn₀.₄Fe₁₀₆O₁₉ (table 3.3) and SrAl₀.₈Ga₀.₈Fe₁₀₆O₁₉ may be due to different solubilities because the inconsistency is observed only at high doping level and the solubility of the doped ions may decrease and cause to decrease the cell volume.
Figure 3.8 The indexed XRD patterns of Sr-hexaferrite doped with Zr$_x$Cu$_x$ (a) $x = 0.0$, (b) $x = 0.2$, (c) $x = 0.4$, (d) $x = 0.6$ and (e) $x = 0.8$. 
Figure 3.9 The indexed XRD patterns of Sr-hexaferrite doped with Zr$_x$Mn$_{1-x}$ (a) $x = 0.0$, (b) $x = 0.2$, (c) $x = 0.4$, (d) $x = 0.6$ and (e) $x = 0.8$. 
Figure 3.10 The indexed XRD patterns of Sr-hexaferrite doped with $\text{Zr}_x\text{Zn}_x$ (a) $x = 0.0$, (b) $x = 0.2$, (c) $x = 0.4$, (d) $x = 0.6$ and (e) $x = 0.8$. 
Figure 3.11 The indexed XRD patterns of Sr-hexaferrite doped with Al$_x$Ga$_{1-x}$ (a) $x = 0.0$, (b) $x = 0.2$, (c) $x = 0.4$, (d) $x = 0.6$ and (e) $x = 0.8$. 

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Table 3.2 Crystallite size (D), lattice constants (a and c), cell volume (V), X-ray density ($\rho_x$), bulk density ($\rho_m$) and porosity (P) for Zr$_x$Cu$_x$ doped SrFe$_{12-2x}$O$_{19}$.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>0.0</th>
<th>0.2</th>
<th>0.4</th>
<th>0.6</th>
<th>0.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystallite sizes (D) nm ± 5</td>
<td>30.0</td>
<td>37.0</td>
<td>33.0</td>
<td>26.0</td>
<td>37.0</td>
</tr>
<tr>
<td>Lattice constant (a) Å ± 0.01</td>
<td>5.87</td>
<td>5.88</td>
<td>5.88</td>
<td>5.88</td>
<td>5.87</td>
</tr>
<tr>
<td>Lattice constant (c) Å ± 0.01</td>
<td>23.06</td>
<td>23.16</td>
<td>23.17</td>
<td>23.20</td>
<td>23.21</td>
</tr>
<tr>
<td>Cell volume (V) Å$^3$ ± 0.1</td>
<td>688</td>
<td>693</td>
<td>694</td>
<td>695</td>
<td>693</td>
</tr>
<tr>
<td>Bulk density ($\rho_m$) g cm$^{-3}$ ± 0.01</td>
<td>2.36</td>
<td>3.15</td>
<td>3.47</td>
<td>3.45</td>
<td>3.24</td>
</tr>
<tr>
<td>X-ray density ($\rho_{\text{x-ray}}$) g cm$^{-3}$ ± 0.01</td>
<td>5.13</td>
<td>5.13</td>
<td>5.16</td>
<td>5.20</td>
<td>5.26</td>
</tr>
<tr>
<td>Porosity (P) % ±0.01</td>
<td>0.54</td>
<td>0.39</td>
<td>0.33</td>
<td>0.34</td>
<td>0.38</td>
</tr>
</tbody>
</table>

Table 3.3 Crystallite size (D), lattice constants (a and c), cell volume (V), X-ray density ($\rho_x$), bulk density ($\rho_m$) and porosity (P) for Zr$_x$Mn$_x$ doped SrFe$_{12-2x}$O$_{19}$.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>0.0</th>
<th>0.2</th>
<th>0.4</th>
<th>0.6</th>
<th>0.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystallite sizes (D) nm ± 5</td>
<td>30.0</td>
<td>40.0</td>
<td>34.0</td>
<td>39.0</td>
<td>31.0</td>
</tr>
<tr>
<td>Lattice constant (a) Å ± 0.01</td>
<td>5.87</td>
<td>5.87</td>
<td>5.88</td>
<td>5.87</td>
<td>5.88</td>
</tr>
<tr>
<td>Lattice constant (c) Å ± 0.01</td>
<td>23.06</td>
<td>23.12</td>
<td>23.19</td>
<td>23.20</td>
<td>23.27</td>
</tr>
<tr>
<td>Cell volume (V) Å$^3$ ± 0.1</td>
<td>688.1</td>
<td>690.0</td>
<td>695.2</td>
<td>693.4</td>
<td>696.1</td>
</tr>
<tr>
<td>Bulk density ($\rho_m$) g cm$^{-3}$ ± 0.01</td>
<td>2.36</td>
<td>2.38</td>
<td>2.56</td>
<td>2.52</td>
<td>2.46</td>
</tr>
<tr>
<td>X-ray density ($\rho_{\text{x-ray}}$) g cm$^{-3}$ ± 0.01</td>
<td>5.11</td>
<td>5.12</td>
<td>5.13</td>
<td>5.13</td>
<td>5.14</td>
</tr>
<tr>
<td>Porosity (P) % ± 0.01</td>
<td>0.54</td>
<td>0.54</td>
<td>0.50</td>
<td>0.51</td>
<td>0.50</td>
</tr>
</tbody>
</table>

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### Table 3.4 Crystallite size (D), lattice constants (a and c), cell volume (V), X-ray density ($\rho_x$), bulk density ($\rho_m$) and porosity (P) for Zr$_x$Zn$_{1-x}$ doped SrFe$_{12-2x}$O$_{19}$.

<table>
<thead>
<tr>
<th>Parameters</th>
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<th>0.4</th>
<th>0.6</th>
<th>0.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystallite sizes (D) nm ± 5</td>
<td>30.0</td>
<td>47.0</td>
<td>43.0</td>
<td>33.0</td>
<td>30.0</td>
</tr>
<tr>
<td>Lattice constant (a) Å ± 0.01</td>
<td>5.87</td>
<td>5.89</td>
<td>5.89</td>
<td>5.89</td>
<td>5.90</td>
</tr>
<tr>
<td>Lattice constant (c) Å ± 0.01</td>
<td>23.06</td>
<td>23.09</td>
<td>23.20</td>
<td>23.22</td>
<td>23.27</td>
</tr>
<tr>
<td>Cell volume (v) Å$^3$ ± 0.1</td>
<td>688</td>
<td>694</td>
<td>697</td>
<td>697</td>
<td>701</td>
</tr>
<tr>
<td>Bulk density ($\rho_m$) g cm$^{-3}$ ± 0.01</td>
<td>2.36</td>
<td>2.47</td>
<td>2.56</td>
<td>2.59</td>
<td>2.73</td>
</tr>
<tr>
<td>X-ray density ($\rho_{x-ray}$) g cm$^{-3}$ ± 0.01</td>
<td>5.13</td>
<td>5.13</td>
<td>5.14</td>
<td>5.19</td>
<td>5.20</td>
</tr>
<tr>
<td>Porosity (P) % ± 0.01</td>
<td>0.54</td>
<td>0.52</td>
<td>0.50</td>
<td>0.50</td>
<td>0.47</td>
</tr>
</tbody>
</table>

### Table 3.5 Crystallite size (D), lattice constants (a and c), cell volume (V), X-ray density ($\rho_x$), bulk density ($\rho_m$) and porosity (P) for Al$_x$Ga$_{1-x}$ doped SrFe$_{12-2x}$O$_{19}$.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>0.0</th>
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<th>0.4</th>
<th>0.6</th>
<th>0.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystallite sizes (D) nm ± 5</td>
<td>30.0</td>
<td>60.0</td>
<td>62.0</td>
<td>51.0</td>
<td>47.0</td>
</tr>
<tr>
<td>Lattice constant (c) Å ± 0.01</td>
<td>23.06</td>
<td>23.05</td>
<td>23.03</td>
<td>22.95</td>
<td>22.91</td>
</tr>
<tr>
<td>Lattice constant (a) Å ± 0.01</td>
<td>5.87</td>
<td>5.87</td>
<td>5.86</td>
<td>5.86</td>
<td>5.87</td>
</tr>
<tr>
<td>Cell volume (v) Å$^3$ ± 0.1</td>
<td>688.1</td>
<td>688.1</td>
<td>684.9</td>
<td>682.5</td>
<td>683.6</td>
</tr>
<tr>
<td>Bulk density ($\rho_m$) g cm$^{-3}$ ± 0.01</td>
<td>2.36</td>
<td>2.43</td>
<td>2.48</td>
<td>2.46</td>
<td>2.51</td>
</tr>
<tr>
<td>X-ray density ($\rho_{x-ray}$) g cm$^{-3}$ ± 0.01</td>
<td>5.13</td>
<td>5.10</td>
<td>5.11</td>
<td>5.12</td>
<td>5.09</td>
</tr>
<tr>
<td>Porosity (P) % ± 0.01</td>
<td>0.54</td>
<td>0.42</td>
<td>0.40</td>
<td>0.42</td>
<td>0.41</td>
</tr>
</tbody>
</table>
3.1.3 Energy Dispersive X-ray Fluorescence (ED-XRF) Analysis

The energy dispersive X-ray fluorescence (ED-XRF) is carried for the qualitative and quantitative analysis of the synthesized samples. The experimental values of elemental composition of Zr-Ni, Zr-Cu, Zr-Mn and Zr-Zn doped samples are in good agreement with the nominal composition as shown in table 3.6. The molar concentration of strontium is kept slightly higher i.e. 1.10 in the hexaferrite matrix due to its lower solubility as compared to that of the iron and therefore it has been optimized as discussed in section 2.5.

The experimental composition of aluminum and gallium doped materials is lower than the actual amount added to the system. Although, the oxides of Al and Ga have high melting points of 2327 and 2173 K, respectively, yet, conversion of hydroxides to crystalline oxides during annealing, some of the Al and Ga may have evaporated resulting in some loss in the contents of these elements. The melting points of Al (933.37 K) and Ga (302.79 K) are much smaller than the annealing temperature of 1193 K. The extra peak in the DTG curve for this series is also observed at 923 K before the phase transition temperature (figure 3.6) which may be an indication of the evaporation of aluminum from the system as it has its melting point in this temperature range. The molarities of Sr and Fe are almost in agreement with the nominal composition in Al-Ga series.

In conclusion, the hexaferrite phase begins to form at 873 K and completes at 1193 K as evidenced by the TG/DTG and XRD analysis. Doping of different cations has no significant effect of the lattice constant ‘a’ but the lattice constant ‘c’, cell volume (V) and X-ray density (ρ_x-ray) increase with the doping of Zr-Ni, Zr-Cu, Zr-Mn and Zr-Zn but in contrast, these parameters decrease on doping with Al-Ga. The crystallite size (D) is in the range of 26-62 nm. The experimental compositions of the samples are found in good agreement with the nominal composition as investigated by ED-XRF studies.
Table 3.6 The elemental composition of the samples of series determined by the ED-XRF analysis.

<table>
<thead>
<tr>
<th>Series</th>
<th>Elements (Mol)</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>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe</td>
<td>11.9</td>
<td>11.6</td>
<td>11.1</td>
<td>10.7</td>
<td>10.3</td>
</tr>
<tr>
<td><strong>Zr-Ni Series</strong></td>
<td>Sr</td>
<td>1.10</td>
<td>1.20</td>
<td>1.16</td>
<td>1.10</td>
<td>1.12</td>
</tr>
<tr>
<td></td>
<td>Zr</td>
<td>-</td>
<td>0.23</td>
<td>0.45</td>
<td>0.65</td>
<td>0.84</td>
</tr>
<tr>
<td></td>
<td>Ni</td>
<td>-</td>
<td>0.18</td>
<td>0.38</td>
<td>0.63</td>
<td>0.81</td>
</tr>
<tr>
<td></td>
<td>Fe</td>
<td>11.9</td>
<td>11.5</td>
<td>11.1</td>
<td>10.7</td>
<td>10.3</td>
</tr>
<tr>
<td><strong>Zr-Cu series</strong></td>
<td>Sr</td>
<td>1.10</td>
<td>1.08</td>
<td>1.05</td>
<td>1.10</td>
<td>1.06</td>
</tr>
<tr>
<td></td>
<td>Zr</td>
<td>-</td>
<td>0.18</td>
<td>0.39</td>
<td>0.62</td>
<td>0.81</td>
</tr>
<tr>
<td></td>
<td>Cu</td>
<td>-</td>
<td>0.21</td>
<td>0.43</td>
<td>0.56</td>
<td>0.75</td>
</tr>
<tr>
<td></td>
<td>Fe</td>
<td>11.9</td>
<td>11.6</td>
<td>11.2</td>
<td>10.7</td>
<td>10.3</td>
</tr>
<tr>
<td><strong>Zr-Mn series</strong></td>
<td>Sr</td>
<td>1.10</td>
<td>1.13</td>
<td>1.10</td>
<td>1.14</td>
<td>1.12</td>
</tr>
<tr>
<td></td>
<td>Zr</td>
<td>-</td>
<td>0.19</td>
<td>0.41</td>
<td>0.58</td>
<td>0.83</td>
</tr>
<tr>
<td></td>
<td>Mn</td>
<td>-</td>
<td>0.21</td>
<td>0.38</td>
<td>0.63</td>
<td>0.81</td>
</tr>
<tr>
<td></td>
<td>Fe</td>
<td>11.9</td>
<td>11.6</td>
<td>11.1</td>
<td>10.7</td>
<td>10.3</td>
</tr>
<tr>
<td><strong>Zr-Zn series</strong></td>
<td>Sr</td>
<td>1.10</td>
<td>1.10</td>
<td>1.17</td>
<td>1.30</td>
<td>1.13</td>
</tr>
<tr>
<td></td>
<td>Zr</td>
<td>-</td>
<td>0.23</td>
<td>0.42</td>
<td>0.55</td>
<td>0.86</td>
</tr>
<tr>
<td></td>
<td>Zn</td>
<td>-</td>
<td>0.18</td>
<td>0.35</td>
<td>0.62</td>
<td>0.75</td>
</tr>
<tr>
<td></td>
<td>Fe</td>
<td>11.9</td>
<td>11.7</td>
<td>11.3</td>
<td>10.9</td>
<td>10.5</td>
</tr>
<tr>
<td><strong>Al-Ga series</strong></td>
<td>Sr</td>
<td>1.10</td>
<td>1.09</td>
<td>1.22</td>
<td>1.21</td>
<td>1.20</td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>-</td>
<td>0.14</td>
<td>0.27</td>
<td>0.51</td>
<td>0.68</td>
</tr>
<tr>
<td></td>
<td>Ga</td>
<td>-</td>
<td>0.12</td>
<td>0.28</td>
<td>0.43</td>
<td>0.61</td>
</tr>
</tbody>
</table>
3.2 Electrical Properties

The DC electrical resistivity of the synthesized materials is measured by the two-point probe method as discussed in section 2.6.

Figure 3.12 shows the temperature dependence of electrical resistivity of SrZr$_x$Ni$_y$Fe$_{12-2x}$O$_{19}$ in the temperature range of 300-675 K. The electrical resistivity decreases with the increase in temperature for the undoped strontium hexaferrite as it is a semiconductor but as Zr-Ni is doped at the iron site the resistivity increases with the increase in temperature at the beginning showing metallic behavior. After attaining a maximum value, it decreases with further increase in temperature showing semiconducting behavior as is expected in case of ferrites (figure 3.12).

The temperature at which maximum value of electrical resistivity ($\rho$) is observed is known as metal to semiconductor transition temperature ($T_{M-S}$). Such behavior has been also observed by Chhaya et al for the Al-Cr substituted spinel ferrites [166]. The value of $T_{M-S}$ increases with the increase in Zr-Ni concentration up to $x = 0.6$ and then decreased as shown in table 3.7. Such kind of temperature dependence of resistivity is mainly due to the occurrence of phase transition, cation migration, cations re-ordering, the presence of impurities and magneto-transport effect [167-168]. In the present case, the presence of impurities can be ruled out because the XRD studies shows the presence of only a single magnetoplumbite phase and no other impurity was observed. There is also no real possibility of phase transition at such low temperature (353-458 K) and the cation migration is not also so fast at such low temperatures to give rise to the observed behavior of electrical resistivity nevertheless such trend can not be totally ruled out. The other possibility is the spin canting [166] because with increase in substitution and temperature the spin canting angle change and this may be responsible for such behavior of resistivity.

The drift mobility ($\mu_d$) is calculated by equations 2.8 and 2.9. Variation of the drift mobility ($\mu_d$) as a function of temperature is shown in figure 3.13. The drift mobility decreases below $T_{M-S}$ but increases above this temperature. The decrease in drift mobility below $T_{M-S}$ is due to the increase in resistivity and decrease in the charge carrier mobility while the increase is due to the increase in the mobility of charge carriers from one site to another above $T_{M-S}$. 
Table 3.7 Curie (T_c) and transition (T_{M-S}) temperatures, drift mobility (\mu_d), dielectric constant (\epsilon), dielectric loss (\tan\delta) and magnetic moment (n_B) for Zr-Ni doped strontium hexaferrite.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>0.0</th>
<th>0.2</th>
<th>0.4</th>
<th>x = 0.6</th>
<th>x = 0.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Curie temperature (T_c) K ± 5</td>
<td>748</td>
<td>703</td>
<td>685</td>
<td>600</td>
<td>549</td>
</tr>
<tr>
<td>Transition Temperature (T_{M-S}) K ± 2</td>
<td>-</td>
<td>353</td>
<td>368</td>
<td>458</td>
<td>393</td>
</tr>
<tr>
<td>Drift mobility (\mu_d) \times 10^{-11} cm²V⁻¹S⁻¹ at 573K ± 0.01</td>
<td>6.76</td>
<td>4.51</td>
<td>2.14</td>
<td>1.32</td>
<td>6.03</td>
</tr>
<tr>
<td>Dielectric constant (\epsilon) at 600 kHz</td>
<td>221</td>
<td>152</td>
<td>144</td>
<td>118</td>
<td>189</td>
</tr>
<tr>
<td>Dielectric constant (\epsilon) at 1000kHz</td>
<td>183</td>
<td>139</td>
<td>132</td>
<td>111</td>
<td>168</td>
</tr>
<tr>
<td>Dielectric loss (\tan\delta) at 600 kHz</td>
<td>0.39</td>
<td>0.27</td>
<td>0.22</td>
<td>0.17</td>
<td>0.33</td>
</tr>
<tr>
<td>Dielectric loss (\tan\delta) at 1000kHz</td>
<td>0.35</td>
<td>0.22</td>
<td>0.14</td>
<td>0.13</td>
<td>0.20</td>
</tr>
<tr>
<td>Magnetic moment (n_B)</td>
<td>11.2</td>
<td>11.5</td>
<td>11.8</td>
<td>14.0</td>
<td>12.5</td>
</tr>
</tbody>
</table>

The variation of room temperature DC electrical resistivity with the substitution of Zr-Ni content is shown in figure 3.14. It is clear from the figure that the resistivity is increased from a value of 2.04\times10^8 to 35.5\times10^8 ohm cm while the drift mobility decrease from 6.76\times10^{11} to 1.32\times10^{11} ohm cm at 573 K (table 3.7) by increasing Zr-Ni content. The value of resistivity reaches a maximum value but the drift mobility attains a minimum values at Zr-Ni content of x \leq 0.6. It however decreases for x > 0.6 while the drift mobility increases. The conduction mechanism operating in these two concentration levels can be explained on the basis of hopping of electrons between Fe^{2+} and Fe^{3+} at octahedral sites. It has been reported in the literature [17] that in ferrites the conductivity is due to hopping of electrons between ferrous and ferric ions at octahedral sites. Since it has also been reported that Ni^{2+} ions occupy the 12k (octahedral) site and Zr^{4+} ions occupy the 4f₁ (tetrahedral) as well as 2b (trigonal bipyramidal) sites when it is in small amount [169]. When Ni^{2+} ions replaces the iron ions at the octahedral sites, the number of iron ions decreased at that
site and as a result the number of hopping electrons decreases causing the electrical resistivity ($\rho$) to increase and drift mobility to decrease. It has been suggested that $\text{Ni}^{3+}$ could be formed during annealing process and the exchange interaction of the type shown below becomes possible:

$$\text{Fe}^{3+} + \text{Ni}^{2+} \rightleftharpoons \text{Fe}^{2+} + \text{Ni}^{3+}$$  \hspace{1cm} (3.1)

The conductivity is now due to hopping of electrons between the ferrous and ferric ions as well as due to transfer of holes between $\text{Ni}^{2+}$ and $\text{Ni}^{3+}$. Since electron transfer is easier than the holes exchange, the resistivity of the material is expected to increase and the decrease in the value of drift mobility. Moreover, $\text{Zr}^{4+}$ is a tetravalent ion which forms the stable bond with $\text{Fe}^{2+}$ ions which are formed during the sintering process [170]. This localizes the $\text{Fe}^{2+}$ ions and hence the hopping between $\text{Fe}^{2+}$ and $\text{Fe}^{3+}$ also hindered which results in the increase in resistivity.

![Image](image_url)

**Figure 3.12** Effect of temperature on the electrical resistivity of $\text{SrZr}_x\text{Ni}_x\text{Fe}_{12-2x}\text{O}_{19}$ substituted strontium hexaferrite.
Figure 3.13 Variation of drift mobility with temperature of SrZrxNiFe12-2xO19.

Figure 3.14 Room temperature DC electrical resistivity and activation energy as a function of Zr-Ni content.
The activation energy \( (E_a) \) for the semiconductor region is calculated from the temperature dependence resistivity data using equation 2.10 (figure 3.15) and the variation of activation energy with Zr-Ni content is shown in figure 3.14. One representative plot for the calculation of activation energy is shown in figure 3.23. The activation energy \( (E_a) \) increases by increasing the concentration of Zr-Ni as dopant and reaches a maximum value at \( x \leq 0.6 \). Activation energy then decrease for \( x > 0.6 \). The behavior of activation energy is similar to that of both the electrical resistivity and drift mobility. Such behavior of activation energy was expected due to the decrease in drift mobility up to the same concentration. The sample having low drift mobility and high electrical resistivity will have high value of activation energy and vice versa. The increase in electrical resistivity and activation energy suggest that the Zr-Ni substituted samples can be used for the application in the microwave devices.

The variation of electrical resistivity for Zr-M (where M = Cu\(^{2+}\), Mn\(^{2+}\) and Zn\(^{2+}\)) and Al-Ga doped series with temperature are shown in figures 3.15-3.18. All the series show almost similar behavior of electrical resistivity with temperature to that of Zr-Ni doped strontium hexaferrite as discussed above (figure 3.12) except for the Zr-Mn doped samples (Figure 3.16). The Zr-Mn substituted strontium hexaferrite series shows the semiconducting behavior i.e. the resistivity of the samples decreases temperature through out the dopant concentration range i.e. \( x = 0.0 - 0.8 \) as shown in figure 3.16. The appearance of \( T_{\text{M-S}} \) is due to the spin canting in all series as discussed above in case of Zr-Ni substituted samples except for Zr-Mn.

This may be explained on the basis of the electronic configuration of the substituted cations at iron sites. The Mn\(^{2+}\) (\( d^5 \)) and Fe\(^{3+}\) (\( d^5 \)) both have five number of unpaired electrons in their outer most shell but all others, i.e. Cu\(^{2+}\) (1), Ni\(^{2+}\) (2) and Zn\(^{2+}\) (0) have different unpaired electrons from that of the Fe\(^{3+}\). Since the possibility of the change in the spin angle of electrons in case of Zr-Mn doped samples is remote due to having the same number of unpaired electrons the samples behave as the undoped strontium hexaferrite. The values of transition temperature (tables 3.8-3.9) are increased up to a specific concentration in each series i.e. from \( x = 0.0 - 0.4 \) for the Zr-Cu and Zr-Zn doped samples but its value increases continuously for the Al-Ga doped samples in the whole concentration range of the dopant.
Figure 3.15 Effect of temperature on the electrical resistivity of SrZr\textsubscript{x}Cu\textsubscript{y}Fe\textsubscript{12-2x}O\textsubscript{19} substituted strontium hexaferrite.

Figure 3.16 Effect of temperature on the electrical resistivity of SrZr\textsubscript{x}Mn\textsubscript{y}Fe\textsubscript{12-2x}O\textsubscript{19} substituted strontium hexaferrite.
Figure 3.17 Effect of temperature on the electrical resistivity of SrZrxZnxFe12-2xO19 strontium hexaferrite.

Figure 3.18 Effect of temperature on the electrical resistivity of SrAlxGaxFe12-2xO19 strontium hexaferrite.
Table 3.8 Curie ($T_c$) and transition ($T_{M-S}$) temperatures, drift mobility ($\mu_d$), dielectric constant ($\varepsilon$), dielectric loss ($\tan\delta$) and magnetic moment ($n_B$) for Zr$_x$Cu$_{1-x}$ doped strontium hexaferrite.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Zr$<em>x$Cu$</em>{1-x}$ content, x</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.0</td>
</tr>
<tr>
<td>Curie temperature ($T_c$) K ± 5</td>
<td>748</td>
</tr>
<tr>
<td>Transition Temperature ($T_{M-S}$) K ± 2</td>
<td>-</td>
</tr>
<tr>
<td>Drift mobility ($\mu_d$)×10$^{11}$ cm$^2$V$^{-1}$S$^{-1}$ at 573K ± 0.01</td>
<td>6.76</td>
</tr>
<tr>
<td>Dielectric constant ($\varepsilon$) at 600 kHz</td>
<td>221</td>
</tr>
<tr>
<td>Dielectric constant ($\varepsilon$) at 1000 kHz</td>
<td>183</td>
</tr>
<tr>
<td>Dielectric loss ($\tan\delta$) at 600 kHz</td>
<td>0.39</td>
</tr>
<tr>
<td>Dielectric loss ($\tan\delta$) at 1000 kHz</td>
<td>0.35</td>
</tr>
<tr>
<td>Magnetic moment ($n_B$)</td>
<td>11.2</td>
</tr>
</tbody>
</table>

Table 3.9 Curie ($T_c$) and transition ($T_{M-S}$) temperatures, drift mobility ($\mu_d$), dielectric constant ($\varepsilon$), dielectric loss ($\tan\delta$) and magnetic moment ($n_B$) for Zr$_x$Mn$_{1-x}$ doped strontium hexaferrite.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Zr$<em>x$Mn$</em>{1-x}$ content, x</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.0</td>
</tr>
<tr>
<td>Curie temperature ($T_c$) K ± 5</td>
<td>748</td>
</tr>
<tr>
<td>Drift mobility ($\mu_d$)×10$^{11}$ cm$^2$V$^{-1}$S$^{-1}$ at 573K ± 0.01</td>
<td>6.76</td>
</tr>
<tr>
<td>Dielectric constant ($\varepsilon$) at 600 kHz</td>
<td>221</td>
</tr>
<tr>
<td>Dielectric constant ($\varepsilon$) at 1000 kHz</td>
<td>183</td>
</tr>
<tr>
<td>Dielectric loss ($\tan\delta$) at 600 kHz</td>
<td>0.39</td>
</tr>
<tr>
<td>Dielectric loss ($\tan\delta$) at 1000 kHz</td>
<td>0.35</td>
</tr>
<tr>
<td>Magnetic moment ($n_B$)</td>
<td>11.2</td>
</tr>
</tbody>
</table>
Table 3.10 Curie ($T_c$) and transition ($T_{M-S}$) temperatures, drift mobility ($\mu_d$), dielectric constant ($\varepsilon$), dielectric loss (tan$\delta$) and magnetic moment ($n_B$) for Zr$_x$Zn$_x$ doped strontium hexaferrite.

<table>
<thead>
<tr>
<th>Parameters</th>
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<th>0.4</th>
<th>0.6</th>
<th>0.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Curie temperature ($T_c$) K ± 5</td>
<td>748</td>
<td>675</td>
<td>607</td>
<td>579</td>
<td>512</td>
</tr>
<tr>
<td>Transition Temperature (T$_{M-S}$) K ± 2</td>
<td>-</td>
<td>388</td>
<td>423</td>
<td>408</td>
<td>383</td>
</tr>
<tr>
<td>Drift Mobility ($\mu_d$) 10$^{-11}$ cm$^2$ V$^{-1}$ sec$^{-1}$ at 573K ± 0.01</td>
<td>6.76</td>
<td>8.36</td>
<td>13.81</td>
<td>21.57</td>
<td>26.23</td>
</tr>
<tr>
<td>Dielectric constant ($\varepsilon$) at 600 kHz</td>
<td>221</td>
<td>227</td>
<td>277</td>
<td>289</td>
<td>298</td>
</tr>
<tr>
<td>Dielectric constant ($\varepsilon$) at 1000 kHz</td>
<td>183</td>
<td>186</td>
<td>196</td>
<td>217</td>
<td>254</td>
</tr>
<tr>
<td>Loss factor (tan$\delta$) at 600 kHz</td>
<td>0.39</td>
<td>0.47</td>
<td>0.72</td>
<td>0.80</td>
<td>0.83</td>
</tr>
<tr>
<td>Loss factor (tan$\delta$) at 1000 kHz</td>
<td>0.35</td>
<td>0.39</td>
<td>0.53</td>
<td>0.66</td>
<td>0.73</td>
</tr>
<tr>
<td>Magnetic moment ($n_B$)</td>
<td>11.2</td>
<td>12.1</td>
<td>13.6</td>
<td>11.6</td>
<td>9.2</td>
</tr>
</tbody>
</table>

Table 3.11 Curie ($T_c$) and transition ($T_{M-S}$) temperatures, drift mobility ($\mu_d$), dielectric constant ($\varepsilon$), dielectric loss factor (tan$\delta$) and magnetic moment ($n_B$) for Al$_x$Ga$_x$ doped strontium hexaferrite.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>0.0</th>
<th>0.2</th>
<th>0.4</th>
<th>0.6</th>
<th>0.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Curie temperature ($T_c$) K ± 5</td>
<td>748</td>
<td>695</td>
<td>653</td>
<td>620</td>
<td>568</td>
</tr>
<tr>
<td>Transition Temperature (T$_{M-S}$) K ± 2</td>
<td>-</td>
<td>398</td>
<td>408</td>
<td>423</td>
<td>468</td>
</tr>
<tr>
<td>Drift Mobility ($\mu_d$) 10$^{-11}$ cm$^2$ V$^{-1}$ sec$^{-1}$ at 573K ± 0.01</td>
<td>6.76</td>
<td>6.03</td>
<td>5.61</td>
<td>4.23</td>
<td>3.40</td>
</tr>
<tr>
<td>Dielectric constant ($\varepsilon$) at 600 kHz</td>
<td>220</td>
<td>212</td>
<td>196</td>
<td>179</td>
<td>146</td>
</tr>
<tr>
<td>Dielectric constant ($\varepsilon$) at 1000 kHz</td>
<td>183</td>
<td>178</td>
<td>164</td>
<td>143</td>
<td>129</td>
</tr>
<tr>
<td>Dielectric Loss (tan$\delta$) at 600 kHz</td>
<td>1.09</td>
<td>0.99</td>
<td>0.74</td>
<td>0.65</td>
<td>0.32</td>
</tr>
<tr>
<td>Dielectric Loss (tan$\delta$) at 1000 kHz</td>
<td>0.98</td>
<td>0.87</td>
<td>0.62</td>
<td>0.55</td>
<td>0.26</td>
</tr>
<tr>
<td>Magnetic moment ($n_B$)</td>
<td>11.2</td>
<td>10.7</td>
<td>10.0</td>
<td>9.1</td>
<td>7.3</td>
</tr>
</tbody>
</table>
The drift mobility of all the synthesized series are calculated from the electrical resistivity data using equations 2.8 and 2.9. The variation of drift mobility with the temperature is shown for Zr-Cu (figure 3.19), Zr-Mn (figure 3.20), Zr-Zn (figure 3.21) and Al-Ga (figure 3.22) doped strontium hexaferrite nanoparticles. The Zr-Cu, Zr-Zn and Al-Ga doped strontium hexaferrite samples show a curvature at a specific temperature i.e. the drift mobility decrease with the increase in temperature and above the metal-to-semiconductor transition temperature ($T_{M-S}$) the drift mobility starts to decrease with the temperature.

![Graph showing variation of drift mobility ($\mu_d$) with temperature of SrFe$_{12}$O$_{19}$ doped with Zr$_x$Cu$_x$.](image)

**Figure 3.19** Variation of drift mobility ($\mu_d$) with temperature of SrFe$_{12}$O$_{19}$ doped with Zr$_x$Cu$_x$.

These results can be explained on the basis of the electrical resistivity data of these series. As discussed above, that the electrical resistivity initially increases with the rise in temperature below $T_{M-S}$ and above $T_{M-S}$ resistivity decreases for Zr-Cu, Zr-Zn and Al-Ga doped samples as shown in figures 3.15, 3.17 and 3.18, respectively. The initial decrease in the drift mobility with temperature is due to the increase in the electrical resistivity in this temperature range which causes to decrease the mobility of the charge carriers. The increase in drift mobility above $T_{M-S}$ is due to the fact that the electrical resistivity decreases above this temperature and as a result the mobility of
the charge carriers increases. In case of Zr-Mn substituted samples the increase in drift mobility in the whole temperature range is due to the same behavior of resistivity (figure 3.20).

**Figure 3.20** Variation of drift mobility ($\mu_d$) with temperature of SrFe$_{12}$O$_{19}$ doped with Zr$_x$Mn$_{1-x}$.

**Figure 3.21** Variation of drift mobility ($\mu_d$) with temperature of SrFe$_{12}$O$_{19}$ doped with Zr$_x$Zn$_{1-x}$.
Figure 3.22 Variation of drift mobility ($\mu_d$) with temperature of SrFe$_{12}$O$_{19}$ doped with Al$_x$Ga$_{1-x}$.

The compositional dependence of electrical resistivity of strontium hexaferrite doped with Zr-Cu, Zr-Mn, Zr-Zn and Al-Ga is shown in figures 3.23, 3.24, 3.25 and 3.26, respectively. Figure 3.23 indicates that the electrical resistivity initially increases with the addition of Zr-Cu content up to $x \leq 0.4$ and then decreases. Cu$^{2+}$ ions are known to occupy octahedral sites [171] and the conduction mechanism is explained by the number of hopping of electrons between Fe$^{2+}$ and Fe$^{3+}$ at the octahedral sites [172]. When Cu$^{2+}$ replaces the iron ions at the octahedral sites the number of hopping charge carriers decrease and the resistivity increases. Secondly, when Cu$^{2+}$ enters into the octahedral lattice interstitials, it distorts the lattice and generates internal stress [173]. All this will reduce the movement of iron ions on the octahedral and tetrahedral interstices, confining the hopping of electron between ferric and ferrous ions. The substitution of Cu$^{2+}$ ions also reduces the Fe$^{2+}$ generation to a result decrease of the electrical resistivity. Thirdly, it is also known that Cu$^{2+}$ can be changed into Cu$^{1+}$ producing holes which can contribute positively to the resistivity since hopping of holes is difficult as compared to that of electrons. As discussed earlier, Zr$^{4+}$ ions have a preference for the trigonal bipyramidal and tetrahedral sites. However due to a small amount of Zr$^{4+}$ ($x \leq 0.4$) the migration of Fe$^{3+}$ ions to the octahedral sites may not be
affected considerably. Whereas, on increasing the substitution to \( x > 0.4 \), \( \text{Zr}^{4+} \) ions force some of the iron ions at tetrahedral sites to migrate gradually to octahedral sites resulting a decrease in the resistivity.

The electrical resistivity also increases with the substitution of \( \text{Zr-Mn and Al-Ga} \) up to \( x \leq 0.3 \) (figure 3.24) and \( x \leq 0.8 \) (figure 3.26), respectively, whereas it decreases in the case of \( \text{Zr-Zn} \) doped samples \( x = 0.0-0.8 \) (figure 3.26). These results can be explained on the basis of the occupation of the substituted cations at different sites. It is known that \( \text{Mn}^{2+} \) ions occupy the octahedral sites (12k and 2a) and thus reduce the number of iron ions. This also reduces the numbers of hopping electrons and consequently decreases the conductivity of the samples [174]. However, the hopping of electrons between \( \text{Mn}^{2+} \) and \( \text{Mn}^{3+} \) can also take place but the hopping energy between \( \text{Mn}^{3+} \) and \( \text{Mn}^{2+} \) is greater than that between \( \text{Fe}^{2+} \) and \( \text{Fe}^{3+} \). The \( \text{Al}^{3+} \) and \( \text{Ga}^{3+} \) both occupy the 12k (octahedral site) and the resistivity is expected to increase with the doping of these cations [175-176]. The main purpose of this substitution was to increase the electrical resistivity and make the materials suitable for the application in the microwave devices.

The electrical resistivity for the \( \text{Zr-Zn} \) substituted samples is found to decrease continuously (figure 3.25) with the increase in the substitution level. \( \text{Zn}^{2+} \) ions occupy the tetrahedral (4f1) site [177] and \( \text{Zr}^{4+} \) ions occupy at tetrahedral (4f1) and trigonal bipyramidal (2b) sites. As both of the substituted ions replace the iron ions from the tetrahedral sites, the possibility of migration of some of the \( \text{Fe}^{3+} \) ions from the tetrahedral to the octahedral site exists. As a result, the hopping of electrons is increased at the octahedral sites. Consequently, the conductivity of the samples is increased.

The variation of activation energy calculated from the Arrhenius type plot (one representative plot is shown in figure 3.23) and the drift mobility as a function of substituents content is shown in figures 3.24-3.27 and tables 3.8-3.11, respectively. It is clear (figures 3.24, 3.25 and 3.27) that the activation energy increases with the doping of \( \text{Zr-Cu, Zr-Mn and Al-Ga} \) to a certain substitution level but its values decrease for the substitution of \( \text{Zr-Zn} \) in the whole range of doping concentration (Figure 3.26). Similarly, the drift mobility for the \( \text{Zr-Cu, Zr-Mn and Al-Ga} \) substituted strontium hexaferrite decrease (tables 3.8, 3.9 and 3.11) while in case of substitution of \( \text{Zr-Zn} \) its value increases (table 3.10). The increase in activation energy and decrease in drift mobility up to a certain concentration level is due to the increase in
the electrical resistivity of these samples in the same concentration range. On further addition of the aforementioned dopants, the increase in drift mobility and decrease in the activation energy is due to the decrease in electrical resistivity as discussed in case of Zr-Ni substituted series. The decrease in the activation energy and increase in the charge carriers concentration in the case of Zr-Zn doped samples is due to the decrease in electrical resistivity in the whole concentration range of the substitution as shown in figure 3.26 and table 3.10. The data of electrical resistivity is in agreement with the drift mobility and activation energy.

![Figure 3.23](image.png)

**Figure 3.23** Arrhenius type plots for resistivity of strontium hexaferrite doped with Zr$_x$Mn$_x$. 

**Figure 3.24** Room temperature resistivity and activation energy as a function of Zr-Cu content.

**Figure 3.25** Room temperature resistivity and activation energy as a function of Zr-Mn content.
Figure 3.26 Room temperature resistivity and activation energy as a function of Zr-Zn content.

Figure 3.27 Room temperature resistivity and activation energy as a function of Al-Ga content.
A few studies on the electrical properties of the bulk and nanomaterials of M-type hexaferrite have been reported in the literature. The electrical, magnetic and physical properties of M-type hexaferrites depend upon the particle size. In comparison with the bulk materials, the porosity of the samples is very low. Shahid and Maqsood [178] synthesized undoped strontium hexaferrite (bulk) by solid state reaction method and reported that the porosity is about 12% which decreases with the addition of Si and Ca contents. But, in the present work, the porosity of pure strontium hexaferrite is determined as 0.54% which indeed is very low as compared to that of the bulk material (12%). The lower porosity reflects the homogeneity in the synthesized samples. The room temperature electrical resistivity for the SrFe_{12}O_{19} bulk material is reported as $1.67 \times 10^6$ ohm cm [178] but the sample in the present work with exactly the same composition has a much higher resistivity value of $2.04 \times 10^8$ ohm cm (figure 3.24). This suggests that the nanomaterials are more suitable for applications in the microwave devices as compared to the bulk material because high resistivity materials are preferred for this purpose. The higher resistivity in the strontium hexaferrite nanoparticle can be explained on the basis of their grain size.

It is well known that in the bulk materials the number of atoms, molecules or ions is smaller at the surface as compared to the bulk but in nanomaterials the number of atoms, molecules or ions is greater at the surface than the bulk. The ferrite conductivity is due to hopping of electrons between ferric and ferrous ions. When the material is in bulk, the number of the ferric and ferrous ions is greater and the hopping between Fe$^{3+}$ and Fe$^{2+}$ is easier but for nano ferrites the number of ferrous and ferric ions is greater at the surface than in the bulk causing the hopping of electrons to cease. As a result, the strontium hexaferrite nanomaterials have greater resistivity than that of the bulk materials.

As reported earlier the activation energy for the undoped bulk strontium hexaferrite is 0.21 eV [178] and 0.31 eV [179] which is lower than 0.49 eV calculated in the present work for undoped nanosized strontium hexaferrite (figure 3.24). The drift mobility is greater for the bulk Sr-hexaferrite than that of the nano Sr-hexaferrite. This is due to higher resistivity of the synthesized materials in the present study as compared to the bulk material as discussed above. The resistivity variations with temperature are similar in case of both the bulk and the nanosized Sr-hexaferrites i.e. resistivity decreases with the increase in temperature (figure 3.12). The doped bulk
materials also show the semiconducting behavior but in the present study the substituted samples show the transition between semiconducting to metallic behavior.

The undoped sample is semiconductor but a metal-to-semiconductor transition takes place at a temperature \( T_{M-S} \) in the samples doped with the binary mixture of various metal ions except in the case of Zr-Mn doped samples. The resistivity of the Sr-hexaferrites can be increased by doping it with different contents of Zr-Ni, Zr-Cu, Zr-Mn and Al-Ga but can be decreased by Zr-Zn doping. The drift mobility \( \mu_d \) decreases below transition temperature \( T_{M-S} \) but increases above \( T_{M-S} \) while in case of Zr-Mn doping samples it increases with temperature. The drift mobility of Sr-hexaferrite doped with Zr-Ni, Zr-Cu, Zr-Mn and Al-Ga can be lowered up to a certain doping level but for the samples doped with Zr-Zn the \( \mu_d \) increases. The data of activation energy \( (E_a) \), drift mobility \( (\mu_d) \) and electrical resistivity \( (\rho) \) are in good agreement with each other.

### 3.3 Dielectric Properties

The dielectric constant \( (\varepsilon) \) is calculated using equation 2.11. Dielectric constant is the property of dielectrics which determines the electrostatic energy stored per unit volume for unit potential gradient. It describes the material capacity to store charge when it is used as a capacitor dielectric. The study of the dielectric parameters such as dielectric constant and dielectric loss offer valuable informations about the behavior of localized and free electrical charge carriers.

The variation of dielectric constant and dielectric loss factor are carried out in the frequency range of 100Hz to 1MHz for the Zr-Ni substituted strontium hexaferrite nanoparticles is shown in figures 3.28. The dielectric constant decreases with increasing frequency. This is a normal behavior of ferrites observed by various researchers [180-185] which is be due to the interfacial polarization as predicted by Maxwell-Wagner [186] and is in agreement with the Koops phenomenological theory [187]. According to these models, the dielectric structure of a ferrite material is assumed to be made up of two layers. First layer being a conducting layer consists of large ferrite grains and the other being the grain boundaries that are poor conductors. By electron exchange between Fe\(^{2+}\) and Fe\(^{3+}\), the local displacement of electrons in the direction of the applied field occurs and these electrons determine the polarization. The polarization decreases with increasing frequency and then reaches a constant
value due to the fact that beyond a certain frequency of external field, the electron exchange between Fe\(^{2+}\) and Fe\(^{3+}\) cannot follow the alternating field. The large value of ‘\(\varepsilon\)’ at lower frequency is due to the presence of Fe\(^{2+}\) ions, interfacial dislocations, oxygen vacancies, grain boundary defects, etc [188]. The decrease in ‘\(\varepsilon\)’ with increase in frequency is natural because any species contributing to polarization lag behind the applied field at higher frequencies.

The variation of dielectric loss (\(\tan \delta\)) with frequency at room temperature is shown in figure 3.29. It is observed that \(\tan \delta\) decreases continuously with increasing frequency for all the samples. In the low frequency region, which corresponds to high resistivity (due to grain boundary), more energy is required for electron exchange between Fe\(^{2+}\) and Fe\(^{3+}\) ions. Thus the energy loss is high. On the other hand, the high-frequency range, corresponding to low resistivity (due to grains), a small energy is needed for electron transfer between Fe\(^{2+}\) and Fe\(^{3+}\) in the grains and hence the energy loss is small.

The variations of dielectric constant and dielectric loss as a function of Zr-Ni contents are shown in table 3.7 at two different frequencies i.e. 600 and 1000 kHz. It is evident from the table that the values of both dielectric constant and dielectric loss decrease with the increase in Zr-Ni contents but when the concentration of substituents increases up to \(x = 0.6\) both the parameters start to decrease. Iwauchi [189] reported that there is a strong relationship between the conduction mechanism and the polarization mechanism. The space charge polarization occurs due to the electron displacement when electric field is applied to the sample. The subsequent charge build up at the insulating grain boundary acts as a major contributor to the dielectric constant in ferrites. Therefore, by increasing the number of Fe\(^{2+}\) ions at the octahedral site the space charge polarization is expected to be enhanced. As a result, the dielectric constant would have higher values.

As discussed earlier, in the discussion of electrical resistivity, that Ni\(^{2+}\) ions replace the iron ions from octahedral site thus reducing the number of Fe\(^{3+}\) ions as well as the charge transfer between Fe\(^{2+}\) and Fe\(^{3+}\) which cause in the reduction of the charge polarization. The \(\tan \delta\) and \(\varepsilon\) therefore would be expected to decrease by increasing Zr-Ni concentration as it has also been proved experimentally. The increase in dielectric constant and dielectric loss above Zr-Ni content of \(x = 0.6\) may be due to migration of some of the Fe\(^{3+}\) ions from tetrahedral to the octahedral site owing to large amount of Zr\(^{4+}\) ions at the tetrahedral site. The increase in resistivity
and decrease in dielectric constant with the substitution of Zr-Ni make them suitable for the applications in microwave devices [38].

**Figure 3.28** Variation of dielectric constant with frequency for strontium hexaferrite doped with Zr$_x$Ni$_x$.

**Figure 3.29** Variation of dielectric loss with frequency for strontium hexaferrite doped with Zr$_x$Ni$_x$. 
The dependence of dielectric constant and dielectric loss on the frequency of strontium hexaferrite doped with Zr-Cu, Zr-Mn, Zr-Zn and Al-Ga are shown in figures 3.30-3.37. It is clear from the figures that values of both i.e. dielectric constant and dielectric loss decrease with the increase in frequency. The decrease in the values of both the parameters is rapid at lower frequencies and become almost constant at higher frequencies. The reason for this is the same as discussed in case of Zr-Ni doped strontium hexaferrite and can be explained on the basis of the Maxwell-Wagner and Koops models i.e. an alternating electric field applied to a dielectric material causes loss and a delay response of the exchange of electrons between Fe$^{2+}$ and Fe$^{3+}$ to the electric field. As a result, the dielectric constant and dielectric loss decrease with the frequency.

![Graph showing frequency dependence of dielectric constants of strontium hexaferrite doped with Zr$_x$Cu$_x$.](image)

**Figure 3.30** Frequency dependence of dielectric constants of strontium hexaferrite doped with Zr$_x$Cu$_x$. 
**Figure 3.31** Frequency dependence of dielectric constants of strontium hexaferrite doped with Zr$_x$Mn$_x$.

**Figure 3.32** Frequency dependence of dielectric constants of strontium hexaferrite doped with Zr$_x$Zn$_x$. 
Figure 3.33 Frequency dependence of dielectric constants of strontium hexaferrite doped with Al\textsubscript{x}Ga\textsubscript{1-x}.

Figure 3.34 Frequency dependence of dielectric loss of strontium hexaferrite doped with Zr\textsubscript{x}Cu\textsubscript{1-x}.
**Figure 3.35** Frequency dependence of dielectric loss of strontium hexaferrite doped with Zr$_x$Mn$_x$.

**Figure 3.36** Frequency dependence of dielectric loss of strontium hexaferrite doped with Zr$_x$Zn$_x$. 
Figure 3.37 Dielectric loss as a function of frequency for strontium hexaferrite doped with Al$_x$Ga$_x$.

The compositional dependence of dielectric constant and dielectric loss at two different frequencies for Zr-Cu, Zr-Mn, Zr-Zn and Al-Ga substituted strontium hexaferrite nanomaterials are shown tables 3.8, 3.9, 3.10 and 3.11, respectively. The dielectric constant decreases from 221 to 121 at frequency of 600 kHz and from 183 to 110 at 1000 kHz for Zr-Cu doped samples up to $x \leq 0.4$ but increases on further substitution. Similarly the dielectric loss also decreases up to the same Zr-Cu content and then increases on further increase in dopant concentration i.e. $x > 0.4$ (table 3.8). Since copper ion replaces the iron ion at the octahedral site, reducing the number of Fe$^{3+}$ ions at that site as well as the hopping between Fe$^{2+}$ and Fe$^{3+}$ resulting in the decrease in the values of both the parameters as discussed in relation to resistivity. Also, it has been reported that substitution of copper creates holes according to following equation [173]

\[
\text{Cu}^{2+} + e^- \rightarrow \text{Cu}^+ \tag{3.2}
\]

The hopping of holes is more difficult as compared to that of the electrons and consequently, the ‘$\varepsilon$’ and ‘tan$\delta$’ decrease.
The electrical resistivity of these samples also increases up to the same concentration level i.e. $x \leq 0.4$. The increase in ‘$\varepsilon$’ and ‘$\tan\delta$’ above $x = 0.4$ may cause migration of Fe$^{3+}$ to the octahedral sites and as a result the number as well as the hopping of electrons increases at the octahedral sites causing increase in the dielectric constant and dielectric loss. The ‘$\varepsilon$’ and ‘$\tan\delta$’ are also decreased in case of Zr-Mn substituted samples up to the concentration level of $x = 0.3$ and increased for $x > 0.3$. The Mn$^{2+}$ replaces the iron from 12k and 2a sites (octahedral sites). The replacement of Fe$^{3+}$ by Mn$^{2+}$ at the octahedral sites will result in the reduction of the number and the hopping of electrons at those sites cause to decrease the dielectric constant and dielectric loss up to specific substitution concentration (table 3.9). The similar results have also been reported for the substitution of cobalt in the M-type hexaferrite due to replacement of iron from octahedral sites by cobalt which results to reduce the dielectric constant as well as the dielectric loss [190]. The electrical resistivity in this case also increases up to this concentration level as discussed earlier (figure 3.25).

The variation of ‘$\varepsilon$’ and ‘$\tan\delta$’ with the concentration of the dopants i.e. Zr-Zn and Al-Ga in Sr-hexaferrite is shown in tables 3.10 and 3.11, respectively. The dielectric constant increases from 221 to 298 and from 183 to 254 for Zr-Zn substituted samples but it decreases from 221 to 146 and 183 to 129 in case of Al-Ga substituted strontium hexaferrite at frequency of 600 and 1000 kHz, respectively. Similar behavior is observed for the dielectric loss that it also increases with the increase in the concentration of Zr-Zn but decreases as the Al-Ga content increases. The zirconium and zinc both ions substitute the iron ion at 4f$_1$ site which is the tetrahedral sites. When both ions enter into the tetrahedral site some of the iron ions may migrate from tetrahedral to octahedral sites. As a result, the concentration of Fe$^{3+}$ increases at octahedral site which is responsible for the increase in the hopping of electrons between Fe$^{2+}$ and Fe$^{3+}$. As the polarization in hexaferrites is due to the hopping of electrons between ferrous and ferric ions at octahedral sites consequently, the values of ‘$\varepsilon$’ and ‘$\tan\delta$’ increase with the increase in the Zr-Zn content. The decrease in the values of both the ‘$\varepsilon$’ and ‘$\tan\delta$’ with the increase in the concentration of Al-Ga is due to the substitution of ferric ions by Al and Ga at octahedral sites which is responsible for the decrease in polarization in the substituted samples. The electrical resistivity data in all the series reported here is in agreement with the dielectric data i.e. the sample having higher value of resistivity has lower value of dielectric constant and dielectric loss and vice versa.
The bulk strontium hexaferrite is reported to have the dielectric constant value of 959.3 at 1000 kHz but a sample of same composition (SrFe$_{12}$O$_{19}$) synthesized in the present study has the value of dielectric constant 183 which is much lower than that of the bulk material [32,37]. This is due to the smaller crystallite size (30 nm) as compared to the bulk material (1-4 µm). It is well known that the sample having larger grain size will have fewer grain boundaries and vice versa [24]. If the grain size is smaller number of pores is smaller as reported earlier [182] that the porosity is 12% when the grain size is 1-4 µm and the value of porosity is 0.54% when the crystallite size is 30-40 nm in the present study. As mentioned before, ferrites are assumed to be made up of two layers [186]. First layer is conducting layer consists of large number of grains and the second layer consists of grain boundaries which is poor conductor. As mentioned above the sample having low porosity and small grain size has large number of grain boundaries as there are large numbers of grains boundaries in the synthesized sample which are poor conductors. As a result, the dielectric constant is lower than that of the bulk material with exactly the same composition. The same is the case for the dielectric loss since its value is also smaller for the strontium hexaferrite synthesized in the present study as compared to the bulk SrFe$_{12}$O$_{19}$ synthesized by the standard ceramic method [184].

The dielectric constant (ε) and dielectric loss (tanδ) of all the doped and undoped samples decrease with the increase in frequency. Both the parameters can be lowered by doping with Zr-M (M = Ni, Cu and Mn) and Al-Ga up to a certain level but can be enhanced by doping with Zr-Zn. The decrease in both the parameters is due to the replacement of ferric ions by the doped cations. A simultaneous lowering of dielectric constant and dielectric loss accompanied by an increase in the electrical resistivity are suitable trends for applications in the microwave devices.
3.4 Magnetic Properties

The magnetic susceptibility is measured as a function of temperature by primary and secondary coil set up and the temperature at which the ferromagnetic materials are changed into paramagnetic, the Curie temperature ($T_c$) is calculated from the plots between temperature and inverse of susceptibility ($1/\chi$). Temperature dependence of AC magnetic susceptibility is considered a suitable tool for the analysis of various kinds of magnetic materials because this technique is more sensitive to low impurity content than the Mössbauer or XRD methods [191].

Figure 3.38 shows the temperature dependence of magnetic susceptibility of Zr-Ni substituted strontium hexaferrite as a function of temperature. With increase in temperature, the magnetic susceptibility of all the samples increases but suddenly drop to lower values at specific temperatures suggesting that the synthesized samples are in single phase. The XRD data described in section 3.1.2 also reveals that the samples are pure and the magnetic susceptibility is in agreement with the XRD data (figures 3.7-3.11). The Curie temperature determined from the plot between magnetic susceptibility ($1/\chi$) and temperature for SrFe$_{12}$O$_{19}$ is 748 K as shown in table 3.7. This temperature is in agreement with the reported values of 753 K [19] and 750 K [67] for the same composition.

The calculated value of ‘$T_c$’ decreases from 748 K to 549 K with the increase in the Zr-Ni concentration in the strontium hexaferrite as shown in table 3.7. This decrease in Curie temperature can be explained on the basis of the occupation of lattice sites by the doped cations. Since Zr$^{4+}$ is a nonmagnetic ion replacing the magnetic ion (Fe$^{3+}$) at 4f$_1$ site, the interactions between 12k-4f$_1$ and 2a-4f$_1$ are expected to decrease. As a result, the Curie temperature decreases. The decrease in Curie temperature was also observed by Jancarik et al [191] for the dopant of Sn-Ni substituted samples of M-type hexaferrite.

The effect of temperature on the magnetic susceptibility of strontium hexaferrite nanomaterials doped with Zr-Cu, Zr-Mn, Zr-Zn and Al-Ga is shown in figures 3.39-3.42. The absence of any hump before the Curie temperature of all the series studied here indicates that the samples are in single phase. The XRD patterns (figures 3.7-3.11), as discussed in section 3.1.2, have also shown that there is no extra peak in these samples. The values of Curie temperature determined from magnetic susceptibility data for the samples doped with Zr-Cu (table 3.8), Zr-Mn (table 3.9),
Zr-Zn (table 3.10) and Al-Ga (table 3.11) decreases with the doping of different cations at iron site in all the series of samples. Due to substitution of both nonmagnetic zirconium and zinc ions at 4f site in Zr-Zn doped series weakening the interactions of different site with 4f causes the Curie temperature to decrease. The Cu$^{2+}$ along with Zr$^{4+}$ has a smaller magnetic moment than Fe$^{3+}$ which also weakens the interaction. Although, Mn$^{2+}$ has a similar value of magnetic moment as that of the Fe$^{3+}$ yet the combined doping of Zr-Mn is responsible for the weakening of interactions. In case of Al-Ga series, both Al$^{3+}$ and Ga$^{3+}$ occupy the 12k (octahedral site) and both are nonmagnetic therefore it is expected that their substitution will lead to a decrease in the Curie temperature.

![Figure 3.38](image.png)

**Figure 3.38** Plots of magnetic susceptibility ($1/\chi$) of strontium hexaferrite doped with Zr$_x$Ni$_x$ as a function of temperature.

A few studies have been reported on the effect of temperature on the magnetic susceptibility for the M-type hexaferrites. The temperature dependence of magnetic susceptibility data for M-type hexaferrite doped with Ti$^{4+}$-Zn$^{2+}$, Ti$^{4+}$-Co$^{2+}$, Ti$^{4+}$-Mn$^{2+}$, Ru$^{4+}$-Zn$^{2+}$ and Ru$^{4+}$-Ni$^{2+}$ and Ru$^{4+}$-Sn$^{2+}$ showed that the ‘$T_c$’ decreases due to the replacement of iron by nonmagnetic (Ti$^{4+}$ and Ru$^{4+}$) ions [25, 192-194]. In the present studies, it is logical to believe that the iron must have been replaced by the nonmagnetic (Zr$^{4+}$, Al$^{3+}$ and Ga$^{3+}$) ions to be responsible for observed ‘$T_c$’ decrease.
Figure 3.39 Plots of magnetic susceptibility ($1/\chi$) of strontium hexaferrite doped with $\text{Zr}_x\text{Cu}_x$ as a function of temperature.

Figure 3.40 Plots of magnetic susceptibility ($1/\chi$) of strontium hexaferrite doped with $\text{Zr}_x\text{Mn}_x$ as a function of temperature.
Figure 3.41 Plots of magnetic susceptibility ($1/\chi$) of strontium hexaferrite doped with $Zr_xZn_x$ as a function of temperature.

Figure 3.42 Plots of magnetic susceptibility ($1/\chi$) of strontium hexaferrite doped with $Al_xGa_x$ as a function of temperature.
The other magnetic properties such as saturation magnetization \((M_s)\), remanence \((M_r)\) and coercivity \((H_c)\) are determined from the hysteresis loop (some representative hysteresis loops are shown in figure 3.43) of each sample and the effect of annealing temperature on these properties is also investigated.

Figure 3.44 shows the variation of all the above mentioned magnetic properties with annealing temperature for the pure strontium hexaferrite nanoparticles. The saturation magnetization \((M_s)\), remanence \((M_r)\) and coercivity \((H_c)\) increase with the annealing temperature and maximum value for each property is obtained at an annealing temperature of 1293 K. Above this temperature, the saturation magnetization, remanence and coercivity tend to decrease. This behavior can be explained on the basis that the particle size increases with the temperature [195]. It is also well known that particle size has a significant effect on the magnetic properties of materials. The particles smaller than the critical single domain size are mainly in single domain. On the other hand, the particle size becomes bigger than the critical value most of the particles exist in multi-domain. As the annealing temperature is increased the particle size increases towards the critical single domain size and consequently the coercivity \((H_c)\), remanence \((M_r)\) and saturation magnetization \((M_s)\) increase eventually reaching maximum values at single domain size. As the annealing temperature increases above the critical temperature size of more and more of the particles increase. However, as the particles become larger than the single domain size at higher annealing temperature, the values of \(H_c\), \(M_r\) and \(M_s\) decrease. Similar results have also been reported by other authors i.e. the magnetic properties increase with increase in temperature and after a specific temperature these properties starts to decrease [69, 71]. In the earlier reports maximum values of saturation magnetization and coercivity for strontium hexaferrite systems were obtained at 1373 K but in the present study the maximum values are obtained at 1293 K (80 K less).
Figure 3.43 Hysteresis loops for different samples (a) = SrZr$_{0.8}$Ni$_{0.8}$Fe$_{10.6}$O$_{19}$ at different annealing temperature (b) = Zr-Mn, (c) = Zr-Zn and (d) = Al-Ga doped Sr-hexaferrite nanomaterials.

Figure 3.44 Effect of annealing temperature on the saturation magnetization (Ms), remanence (Mr) and coercivity (Hc) of strontium hexaferrite.
Figure 3.45 shows the effect of annealing temperature on the saturation magnetization ($M_s$), remanence ($M_r$) and coercivity ($H_c$) of SrZr$_{0.8}$Ni$_{0.8}$Fe$_{10.4}$O$_{19}$. Maximum values of the saturation magnetization and remanence were obtained at an annealing temperature of 1393 K. It means that Zr-Ni doped samples require higher temperature to arrange the particle in a single domain as compared to undoped strontium hexaferrite because the undoped sample has the maximum saturation magnetization annealed at the annealing temperature of 1293 K. The coercivity ($H_c$) of the samples decreases with the annealing temperature. The decrease in coercivity with temperature is due to an increase in the particle size.

![Graph showing the effect of annealing temperature on $M_s$, $M_r$, and $H_c$.](image)

**Figure 3.45** Effect of annealing temperature on the saturation magnetization ($M_s$), remanence ($M_r$) and coercivity ($H_c$) of strontium hexaferrite doped with Zr$_{0.4}$Ni$_{0.4}$.

The behavior of coercivity ($H_c$), remanence ($M_r$) and saturation magnetization ($M_s$) as a function of Zr-Ni content is shown in figure 3.46 annealed at 1393 K. The saturation magnetization increases from 72 to 98 kA m$^{-1}$ and this can be explained on the basis of the occupation of the substituted ions. The Zr$^{4+}$ replaces Fe$^{3+}$ at 2b sites when it is in small concentration ($x \approx 0.1$) but for higher content of substitution ($x > 0.1$) it replaces Fe$^{3+}$ at 4f$_1$ (tetrahedral). Whereas Ni$^{2+}$ replaces iron ions at 4f$_2$ (octahedral) so long as its content is low ($x \approx 0.1$) and at 12k (octahedral) for larger
substitution \((x > 0.1)\). It can be seen from table 1.2 and figure 3.47 that 4f₁ has electron spins in downward direction while 12k in upward. The Zr\(^{4+}\) is a nonmagnetic while Ni\(^{2+}\) has the magnetic moment of \(2\mu\text{B}\) which is smaller than that of the Fe\(^{3+}\) (5\(\mu\text{B}\)). When Zr\(^{4+}\) replaces the Fe\(^{3+}\) from the site having spin in downward direction the total number of unpaired electrons in the upward direction increases. As a result, the total magnetic moment increases which is responsible for the increase in the total saturation magnetization. It is observed that the saturation magnetization increases up to a dopant content of \(x = 0.6\). The decrease in \(M_s\) above \(x = 0.6\) may be due to the higher content of nonmagnetic ion which may weaken the exchange interactions between iron and oxygen ions.

The remanence \((M_r)\) of Sr-hexaferrite doped with Zr\(_x\)Ni\(_x\) \((x = 0.0-0.8)\) is not changed significantly. It is clear from the figure 3.46 that the coercivity is decreased continuously from 137 to 34.1 kA m\(^{-1}\) by increasing concentration of the dopant ions. It has been reported that the 12k and 2a sites have a negative influence on the magnetocrystalline anisotropy \([174]\). As Ni replaces the iron from 12k site the consequent decrease in magnetocrystalline anisotropy constant which is responsible for the decrease in coercivity of the doped samples.

![Figure 3.46](image_url)  

**Figure 3.46** Effect of Zr-Ni doping on the saturation magnetization, remanence and coercivity of strontium hexaferrite.
The magnetic moment (\(n_B\)) is also calculated for each sample using equation 2.17. The calculated values of the magnetic moments for the Zr-Ni substituted strontium hexaferrites are given in table 3.7. The values of the magnetic moment increase from 11.18 \(\mu_B\) to 14.00 \(\mu_B\) for \(x \leq 0.6\) while for \(x \geq 0.6\) its value decreases. The increase in magnetic moment is due to an increase in the number of unpaired electrons having the spin in upward direction due to substitution of Zr\(^{4+}\) at the site having spin in downward direction. The behavior of magnetic moment is similar to that of the saturation magnetization because both these are directly related to each other according to equation 2.17. The saturation magnetization and magnetic moment data (table 3.7) is in good agreement with each other.

\[12K\]
\[4f_1\]
\[4f_2\]
\[2a\]
\[2b\]

\textbf{Figure 3.47} Spin orientations for Fe\(^{3+}\) at each site and the net magnetic moment in SrFe\(_{12}\)O\(_{19}\).

The variations of the saturation magnetization (\(M_s\)), remanence (\(M_r\)) and coercivity (\(H_c\)) as a function of dopant impurity i.e. Zr-Cu, Zr-Mn and Zr-Zn, content are shown in figures 3.48, 3.49 and 3.50, respectively. All the samples of the above mentioned series are annealed at an optimized temperature of 1393 K because the maximum values of \(M_s\), \(M_r\) and \(H_c\) are obtained at this annealing temperature for these series. The saturation magnetization in each series increases with the increase in concentration of dopants i.e. Zr-M (M = Cu, Mn and Zn) for \(x \leq 0.4\) (figures 3.48-3.50). Above this concentration, ‘\(M_s\)’ tends to decrease while the coercivity decreases
regularly with the increase in Zr-M contents. The saturation magnetization ($M_s$) increases from 71 kA m$^{-1}$ to 84 kA m$^{-1}$ on doping with Zr-Cu content of $x \leq 0.4$. It is well known that Cu$^{2+}$ ions occupy the $4f_2$ (octahedral site) which has spin in downward direction [196]. As has already been discussed in section 3.2, that Zr$^{4+}$ also occupies the site of spin down (4f$_1$). Both these site contribute negatively to the total saturation magnetization. If both the substituted ions replace the Fe$^{3+}$ ions from a site with downward spin the total number of spin in the upward direction increases and as a result the total magnitude of the saturation magnetization increased (figure 3.47). The replacement of Fe$^{3+}$ ions by Mn$^{2+}$ ions mainly do not effect the saturation magnetization because both (Fe$^{3+}$ and Mn$^{2+}$) ions have five unpaired electrons in their outermost shell and both have the magnetic moment of 5µB. The improvement in the saturation magnetization from 71 to 87 kA m$^{-1}$ due to doping with Zr-Mn ($x = 0.0$-0.4) is due to the replacement of Fe$^{3+}$ ion by Zr$^{4+}$ ion at the 4f$_1$ site which has downward spin. The saturation magnetization increases from 71 to 91 kA m$^{-1}$ with doping of Zr-Zn content ($x = 0.0$ - 0.4) which is due to the replacement of Fe$^{3+}$ from the site having downward spin (4f$_1$) by Zn$^{2+}$ and Zr$^{4+}$ ions.

The abrupt fall in the saturation magnetization ($M_s$) (figures 3.47-3.49) of strontium hexaferrites on doping with Zr-M $x < 0.4$ is firstly, due to the presence of large amount of a nonmagnetic ion (Zr$^{4+}$) in each series and Zn$^{2+}$ in Zr-Zn substituted series and Cu$^{2+}$ ions which are also less magnetic than iron. All these ions probably decrease the superexchange interactions between 4f$_1$-12k, 4f$_2$-12k and 4f$_1$-2a which may cause a decrease in the saturation magnetization. Secondly, this abrupt fall in the saturation magnetization is believed to be caused by the loss of magnetic collinearity leading to the “spin canting” as it is also observed in the electrical resistivity data. The remanence almost remain constant in case of Zr-Cu substituted samples while in Zr-Mn and Zr-Zn its value increases from 56-61 and 56-59 kA m$^{-1}$, respectively.

The coercivity ($H_c$) decreases with the increase in Zr-M content in the entire concentration range of the doped cations. The observed decrease in coercivity (figures 3.48-3.50) is because of the reduction in magnetocrystalline anisotropy. It is known that in M-type hexaferrites the 12k, 4f$_2$ (octahedral) and 2b (trigonal bipyramidal) site are the major contributor to the magnetocrystalline anisotropy [197-198]. As mentioned above that Cu$^{2+}$ occupy the 4f$_2$ and Mn$^{2+}$ occupy the 12k site while the Zr$^{4+}$ is also has preference to 2b site and as a result it cause negative impact on the magnetocrystalline anisotropy consequently the coercivity decreased.
**Figure 3.48** Effect of Zr-Cu substitution on the saturation magnetization (\(M_s\)), remanence (\(M_r\)) and coercivity (\(H_c\)).

**Figure 3.49** Effect of Zr-Mn substitution on the saturation magnetization (\(M_s\)), remanence (\(M_r\)) and coercivity (\(H_c\)) of \(\text{SrZr}_x\text{Mn}_x\text{Fe}_{12-2x}\text{O}_{19}\).
Figure 3.50 Effect of Zr-Zn substitution on the saturation magnetization ($M_s$), remanence ($M_r$) and coercivity ($H_c$) of SrFe$_{12}$O$_{19}$.

The variations of saturation magnetization ($M_s$), remanence ($M_r$) and coercivity ($H_c$) with the substitution of different Al-Ga content ($x = 0.0-0.8$) of Sr-hexaferrite samples is shown in figure 3.51. It is clear that the values of saturation magnetization, remanence and coercivity decrease with increasing the substitution level of Al-Ga. The decrease in saturation magnetization and remanence is clear from the magnetic structure of M-type hexaferrite. As discussed earlier in section 3.2 that both the substituents preferred to enter in the 12k (octahedral) site which has spin in upward direction (table 1.2 and figure 3.47). The replacement of Fe$^{3+}$ by the nonmagnetic ions from the site of upward spin reduce the number of electrons with upward spin and result in decreasing the net magnetic moment as well as the saturation magnetization and remanence. The decrease in coercivity for the Al-Ga doped samples is due to the replacement of iron ions from 12k site to results in a reduction in the magnetocrystalline anisotropy. This consequently decreases the coercivity for the samples of this series. Similar variations of the saturation magnetization and coercivity have also been reported for Al and Cr doped barium hexaferrite samples [27, 199-200].
Figure 3.51 Effect of Al-Ga substitution on the Saturation magnetization ($M_s$), remanence ($M_r$) and coercivity ($H_c$) of Sr-hexaferrite.

The magnetic recording media requires the saturation magnetization and remanence values as high as possible and the coercivity values of about 600 Oe or 47.8 kA m$^{-1}$ [27]. In the present study, the saturation magnetization of Sr-hexaferrite is increased 71-98, 71-84, 71-87 and 71-91 kA m$^{-1}$ doping with Zr-Ni, Zr-Cu, Zr-Mn and Zr-Zn while it value decreases on doping with Al-Ga from 71 to 30 kA m$^{-1}$. The value of remanence, however, remains almost constant by doping with Zr-Ni and Zr-Cu. The remanence value increases from 56 to 61 KA m$^{-1}$ and 56 to 59 kA m$^{-1}$ for Zr-Mn and Zr-Zn substituted samples but its value decreases for the Al-Ga substituted strontium hexaferrite. The coercivity is found to decrease for all the series studied here. The Zr-M (M = Ni, Cu, Mn and Zn) substituted samples may be useful for the applications in the high density recording media because these samples have the coercivity in the desired range as stated above and has an enhanced value of the saturation magnetization. It has been reported that by the substitution of Ti-Co, Ti-Mn, Ti-Zn, Ir-Zn and Sn-Co at the iron site in the M-type hexaferrite, the coercivity of the samples can be reduced but unfortunately at the same time the saturation magnetization is decreased [57, 198, 201-204]. The Zr-M substituted Sr-hexaferrite material is an examples of those substances in which the coercivity is reduced and at the same time the saturation magnetization is enhanced making it useful for the
magnetic recording media [66, 99, 205-206]. The coercivity of the Al-Ga substituted series is also decreased but unfortunately the saturation magnetization and remanence are decreased.

The magnetic moment of the samples is calculated from the saturation magnetization data using equation 2.17 and its values are given in tables 3.8, 3.9, 3.10 and 3.11 for the Zr-Cu, Zr-Mn, Zr-Zn and Al-Ga substituted strontium hexaferrites, respectively. It is clear from the above mentioned tables that the magnetic moment increases for Sr-hexaferrite doped with Zr-Cu, Zr-Mn and Zr-Zn up to concentration level of $x \approx 0.4$ while it decreases continuously for the Al-Ga substituted samples in the whole substitution range. This is due to the fact that the saturation magnetization of the Zr-M (where $M = $ Cu, Mn and Zn) substituted samples increases up to the same concentration level of $x \approx 0.4$. However, the saturation magnetization decreases for the Al-Ga substituted series and as a result the magnetic moment decreases for Al-Ga series.

The Curie temperature ($T_c$) of Sr-hexaferrite is lowered on doping it with different cations i.e. Zr-Ni, Zr-Cu, Zr-Mn, Zr-Zn and Al-Ga. The saturation magnetization and remanence of Sr-hexaferrites are enhanced on doping with Zr-M ($M = $ Ni, Cu, Mn and Zn) up to a certain concentration level but both these parameters are decreased by doping with Al-Ga. The coercivity of Sr-hexaferrite can be controlled by doping it with Zr-M and Al-Ga contents. The increase in ‘$M_s$’ and decrease in ‘$H_c$’ reveals that the doped materials are suitable for applications in recording media.
Conclusions

- The chemical co-precipitation method (which is a simple and economic route) has been adopted for the synthesis of Zr-Ni, Zr-Cu, Zr-Mn, Zr-Zn and Al-Ga doped strontium hexaferrite nanomaterials. XRD and AC magnetic susceptibility confirmed that all the synthesized samples are single phase materials.

- The crystallite sizes calculated from the Sherrer’s formula are in the ranges of 30-47, 26-37, 30-40, 30-47 and 30-62 nm for the Zr-Ni, Zr-Cu, Zr-Mn, Zr-Zn and Al-Ga doped strontium hexaferrites. These crystallite sizes are small enough for obtaining the suitable signals-to-noise ratio in the high density recording media.

- The electrical resistivity of undoped Sr-hexaferrite increases from a value of $2.04 \times 10^8$ ohm cm to $35.5 \times 10^8$, $3.71 \times 10^8$, $15.80 \times 10^8$ and $25.96 \times 10^8$ ohm cm on doping with Zr-Ni, Zr-Cu, Zr-Mn and Al-Ga, respectively, but by doping it with Zr-Zn its value decreases to a value of $0.43 \times 10^8$ ohm cm. The increase in electrical resistivity suggests that the former sets of series of samples are more suitable for applications in the microwave devices as compared to Zr-Zn substituted samples.

- The activation energy calculated from the temperature dependence of electrical resistivity data shows almost the same behavior as observed for the electrical resistivity at room temperature. On contrary, the drift mobility shows the reverse behavior to that of the room temperature electrical resistivity and the activation energy.

- The dielectric constant and dielectric loss decrease with the increase in frequency in all the samples of the five series investigated here. The dielectric constant of undoped Sr-hexaferrite decreases from a value of 221 to the value of 118, 121, 153 and 146 for the Zr-Ni, Zr-Cu, Zr-Mn and Al-Ga doped samples, respectively, but increases for the Zr-Zn doped series to 298 at a frequency of 600 kHz. The dielectric loss shows a behavior similar to that observed in the values of the dielectric constant. The DC electrical resistivity data is in good agreement with the dielectric data.

- The Curie temperature of all the series decreases with doping of different metal cations.
The saturation magnetization of Sr-hexaferrite (71 kA m\(^{-1}\)) is enhanced to 98, 84, 87 and 91 kA m\(^{-1}\) on doping with Zr-Ni, Zr-Cu, Zr-Mn and Zr-Zn but in contrast it decreases to 30 kA m\(^{-1}\) by doping with the Al-Ga. The remanence however remains almost constant for Zr-Ni and Zr-Cu substituted series while it increases for the Zr-Mn and Zr-Zn substituted series and decreases for the Al-Ga substituted samples.

The coercivity (H\(_c\)) of undoped sample (137 kA m\(^{-1}\)) decreases to 34, 49, 94, 36 and 15 kA m\(^{-1}\) by doping with Zr-Ni, Zr-Cu, Zr-Mn, Zr-Zn and Al-Ga, respectively.

The synthesized samples in the present work are some of the few examples in which the saturation magnetization is enhanced but at the same time the coercivity decreases. As the magnetic recording media requires the saturation magnetization as high as possible and the coercivity to about the value of 47 kA m\(^{-1}\). In the present study, the saturation magnetization is increased and the coercivity is reduced by doping strontium hexaferrite with Zr-Ni, Zr-Cu, Zr-Mn and Zr-Zn to the range which is required by the magnetic recording media. It is concluded that Zr-Ni, Zr-Cu, Zr-Mn and Zr-Zn doped strontium hexaferrite materials are suitable for applications in the high density recording media.

Although, the coercivity is decreased by doping with Al-Ga but unfortunately the saturation magnetization and remanence are also decreased. Hence these samples are not useful for the recording media but in these samples the electrical resistivity is increased in the whole range of substitution which makes them suitable for applications in microwave devices.
Suggestions for further research

In the present work, the occupation by different cations at different lattice sites of the hexagonal structure has been discussed on the basis of the variation of electrical resistivity and the saturation magnetization due to doping with different metal ions. The Mossbauer spectrometer can be used to determine the exact position of the doped ions and the ratio of, for instance, Fe$^{2+}$ and Fe$^{3+}$ ions in a sample.

The Curie temperature of the samples could not be enhanced by addition of the present set of dopants but it is possible that the Curie temperature may be increased by doping with other cations having greater number of unpaired electrons than that of ferric ion. Eu$^{3+}$ and Gd$^{3+}$ have 6 and 7 unpaired electrons, respectively, which are greater than the Fe$^{3+}$ (5) and their substitution may increase the interactions between the different sites and result in increase of the Curie temperature.

The synthesized materials in the present study can also be used as a microwave absorber. The microwave absorber materials are very useful for the applications in wireless communication, radar, local area network, secret system, satellites communication, precise guidance system and remote sensing techniques. The microwave absorption studies can be carried out at high frequencies (up to 20 GHz) using vector network analyzer.

The dielectric properties are studied in the frequency range of 100 Hz to 1 MHz. These properties can be investigated at different temperature and at higher frequencies to see the relaxation phenomenon.

The thermoelectric power measurement can be carried out to know exactly the mobility of the charge carriers.
References


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