Effect of Co-doping Calcium and Scandium on Strontium Hexaferrite: Structural, Magnetic and Mossbauer Study.

Subash Chandra Bhandari

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Subash Chandra Bhandari
Abstract

M-types hexaferrite such as barium hexaferrite (BaM) and strontium hexaferrite (SrM), have a wide range of applications because of its high saturation magnetization, coercivity and remanance values. The magnetic properties of such materials can be altered for better performance by replacing either magnetic or non-magnetic ions at different lattice sites.

The present study investigates the influence of Ca$^{2+}$-Sc$^{3+}$ doping on the magnetic properties of Sr$_{1-x/12}$Ca$_{x/12}$Fe$_{12-x}$Sc$_x$O$_{19}$ ($x = 0.0$ to $2.0$) hexaferrite (SrM) compounds. The samples were prepared via a facile auto-combustion technique followed by sintering. X-ray powder diffraction patterns show the formation of the pure phase of M-type hexaferrite for all $x$. Lattice parameters, both a and c of the compound increased with the substitution. The magnetic property of these compounds is explained based on Sc$^{3+}$ occupancy in M-type magnetoplumbite structure. Both saturation magnetization and coercivity decreased with $x$. The temperature and field-dependent magnetization study (10-300K) revealed spin reorientation transition and change in magnetic anisotropy energy. The Curie temperature dropped to 580K at the maximum substitution of $x=2$. The room temperature Mossbauer spectral analysis confirmed the preferred occupancy of Sc$^{3+}$ at the 4f2 site and the influence of Ca$^{2+}$ on the isomer shift values of the 2b site. Changes in magnetic properties and hyperfine parameters are discussed in light of the preferred occupancy of Sc$^{3+}$ at the spin-down 4f2 site.
Keywords: Hexaferrites, Auto-combustion, Lattice parameters, Magnetoplumbite, Coercivity, Magnetic anisotropy
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List of Abbreviations

BaM .......................... M-type Barium Hexaferrite

BFO .......................... BaFe_{12}O_{19}

FIM .......................... Ferrimagnetic phase

FTIR .......................... Fourier Transform Infrared spectroscopy

FWHM .......................... Full Width Half Maxima

FORC .......................... First Order Reversal Curve

HF .......................... Hyperfine Field

IS .......................... Isomer Shift

PbM .......................... M-type Lead Hexaferrite

PM .......................... Paramagnetic phase

QS .......................... Quadrupole Shift

RT .......................... Room temperature

SCFSO .......................... Sr_{1-x/12}Ca_{x/12}Fe_{12-x}Sc_{x}O_{19}

SEM .......................... Scanning Electron Microscope
SFO ......................... $\text{SrFe}_{12}\text{O}_{19}$

SrM ......................... M-type Strontium Hexaferrite

SQUID ......................... Superconducting Quantum Interference Device

TEM ......................... Transmission Electron Microscope

TGA ......................... Thermogravimetric Analyzer

XRD ......................... X-ray Diffraction

XMCD ......................... X-ray Magnetic Circular Dichroism spectroscopy
Chapter 1

Introduction

1.1 Magnetic Materials

It is believed that, the magnetic materials were first discovered by ancient Greeks. It was not invented but rather found naturally in the form of mineral called magnetite. These types of materials were first known to be used practically as magnetic compass for navigation purpose. But with the advancement of technology to enhance our daily life, magnets are now everywhere from industrial applications to the cell phones and credit cards in our pockets.

Magnetic behavior of elements depends on electric configuration of atoms. Each electron in an atom has orbital as well as spin momentum and these motions produce electric current and hence magnetic moment along a particular direction on the basis of Lenz law. The magnetic moment of an electron by its orbital or spin motion is called Bohr Magneton and represented by $\mu_B$, which value is equivalent to $9.274\times10^{-24}$ Am$^2$.

Basically, there are six types of magnetic materials which are listed and discussed below.

1. Diamagnetic materials

2. Paramagnetic materials
1.1.1 Diamagnetic Materials

Generally, diamagnetic materials are those in which the electrons in the outermost orbital are in pair state. According to the Pauli’s exclusion principle, those pair electrons must be in opposite spin states and hence they produce magnetic moments in opposite direction with equal magnitudes and canceled out. So, the diamagnetic materials do not have inherent magnetic moments. However, if the magnetic field is applied in these materials, the pair electrons produces unequal magnetic moments in opposite directions and a resultant magnetic moment is realized. But the net magnetic moment observed by such action is always opposes the applied magnetic field. For diamagnetic materials, the permeability ($\mu$); the degree of magnetization of material in response to an applied magnetic field, is less than the permeability of free space ($\mu_0$). i.e, $\mu < \mu_0$. Also, the magnetic susceptibility ($\chi$); a measure of magnetization in an applied magnetic field, of these materials is slightly negative. Some examples of diamagnetic materials are, gold, copper, bismuth, air, water, etc.

1.1.2 Paramagnetic Materials

The paramagnetic materials have an unpair electron in the outermost orbital of the atom due to which they exhibit inherent magnetic moment. Each atom contributes a magnetic moment in random orientation and hence, in a bulk, all the magnetic moments canceled out and no perma-
nent magnetic moment exists. However, if an external magnetic field is applied, these magnetic
moments by each atom tends to align in the direction of external magnetic field and the net
magnetic moment in the material exist. The magnetization value of the material increases lin-
early with the applied magnetic field. In paramagnetic materials permeability is greater than
permeability of free space, i.e, $\mu > \mu_0$, and a small positive susceptibility. The examples of
paramagnetic materials are, magnesium, lithium, molybdenum, etc.

1.1.3 Ferromagnetic Materials

The ferromagnetic materials have more than one unpair electrons in outermost orbitals. They have a group of parallel alignment of magnetic moment within a material called do-
main. There are number of such domains which are randomly orientated and gives rise a zero
magnetization in absence of external magnetic field. The permeability ($\mu$) of ferromagnetic
materials is greater than that of free space and increases on increasing the magnetizing field.
The susceptibility of such materials is very large and positive. The examples of ferromagnetic
materials are, iron, nickel, cobalt, etc. In the presence of varying external magnetic field, the
magnetization of these materials traces a loop as in Figure 1.1, called hysteresis loop.
If the ferromagnetic materials are placed in the varying external magnetic field, the magnetization value first increases rapidly and becomes constant. The maximum value of this magnetization is called saturation magnetization ($M_s$). At this point, the maximum number of magnetic dipoles is aligned along the direction of the applied magnetic field. When the field is applied in the reverse direction, the magnetization value does not follow the original path and there remains some magnetization value even at zero applied field. This value of magnetization is called remanence magnetization ($M_r$). On further increasing the value of the applied magnetic field in reverse direction, the magnetization of the material becomes zero and that value of applied magnetic field is called coercivity ($H_c$). Larger the value of coercivity means, high value of reverse magnetic field is required to demagnetize the materials and hence called hard magnetic materials. Likewise, materials with smaller value of coercivity are called soft magnetic materials.

In ferromagnetic materials, the magnetization values vary on the crystallographic direction. This phenomenon of magnetic materials is called magnetocrystalline anisotropy. The magnetic
anisotropy energy of material affected by its symmetry is called magnetic anisotropy energy ($K_1$), which is an intrinsic value for each material [1]. Materials with high magnetocrystalline anisotropy has usually a high coercivity. Which means they are hard to demagnetize and hence known as hard magnets. So, the magnetic anisotropy is one of the most important characteristics in the application of permanent magnets.

### 1.1.4 Antiferromagnetic Materials

In antiferromagnetic materials magnetic moments are antiparallel to each other but equal in magnitude which leads to the net magnetic moment be zero at absolute zero temperature. In the presence of external magnetic field, these materials behaves like the paramagnetic materials. Unlike in paramagnetic materials, the susceptibility ($\chi$) of these materials increase with temperature upto a certain temperature called Neel temperature ($T_N$), which is generally a low temperature. Above this temperature the thermal agitation overcomes the magnetic dipole interaction of materials and susceptibility varies similar to the paramagnetic materials [2]. The examples of antiferromagnetic materials are, nickel oxide (NiO), manganese sulfide (MnS), iron oxide (FeO), etc.

### 1.1.5 Ferrimagnetic Materials

In ferrimagnetic materials, both parallel and antiparallel magnetic moments with unequal population or magnitude are present. Due to which materials have net magnetization even in the absence of external magnetic field and spontaneous magnetization remains below cure temperature. In the aspect of magnetic domain structure and phenomena of hysteresis, ferrimagnetic material resemble the ferromagnetic material. For these materials, the magnetic permeability is much larger than $\mu_0$ and susceptibility is large and positive like ferromagnetic materials. The
ferrimagnetic materials also have the characteristic of magnetocrystalline anisotropy, which is higher along the principal axis. The examples of ferrimagnetic materials are hexagonal ferrites such as \( \text{SrFe}_{12}\text{O}_{19} \), \( \text{PbFe}_{12}\text{O}_{19} \) and \( \text{BaFe}_{12}\text{O}_{19} \).

### 1.1.6 Superparamagnetic Materials

Superparamagnetic materials are generally ferromagnetic or ferrimagnetic nanoparticles. If the size of nanoparticles is relatively small, the magnetization of particles randomly flips under the influence of temperature. The time to flip the magnetization of nanoparticle is called Neel relaxation time. If the magnetization measurement time is longer than Neel relaxation time, the net magnetization of the particle appears to be zero in the absence of applied magnetic field. This condition is known as superparamagnetic state [3]. Normally, in ferromagnetic and ferrimagnetic material paramagnetism occurs above Curie temperature. But the superparamagnetism occurs below Curie temperature. Also, the magnetic susceptibility of superparamagnetic materials is much larger than that of paramagnetic materials. Generally, the superparamagnetic behavior observed on those materials with particle size between 10 nm to 150 nm depending on the types of material [4].

### 1.2 Ferrites

Ferrites is the common term generally refer to the wide range of different ceramic ferrimagnetic materials. They are electrically nonconductive and and spontaneously magnetized in the presence of external magnetic field. Based on the coercivity; a resistance to being demagnetized, there are two types of ferrites; soft ferrites and hard ferrites. Soft ferrites are those with low coercivity and hence easy to demagnetize. These materials are used in electronic industries to make efficient magnetic cores called ferrite cores for transformers, antennas, high frequency
inductors and microwave components. Likewise, hard ferrites have high coercivity so that they are hard to demagnetize. They are used to make permanent magnet applications such as small motors, loudspeakers and automobiles.

In ferrites, positively charged metal ions (Fe$^{3+}$, Me$^{2+}$) and negatively charged divalent oxygen ions (O$^{2-}$) forms the interlocking network. Where, Me$^{2+}$ is the divalent metal ion like, Mn$^{2+}$, Cu$^{2+}$, Ni$^{2+}$, Co$^{2+}$, Fe$^{2+}$, etc. The arrangement of these ions in the crystal structure plays an important role in magnetic properties of the ferrites. Based on the arrangement of the ions and the structure of the crystal, ferrites are classified into three types viz. spinels, garnets and hexagonal ferrites.

### 1.2.1 Spinel Ferrites

The materials with general chemical formula AB$_2$O$_4$ with cubic crystal structure are known as spinel ferrites. Where, A and B metallic cations with tetrahedral and octahedral crystallographic sites respectively. Their structure are composed of Fe(III) as one of the main elements. With the another metallic cation Me(II), the chemical formula of spinel ferrites can be expressed as MeFe$_2$O$_4$. **Figure 1.2** shows the general structure of spinel ferrites. In the unit cell of spinel structure, there are 32 close-packed arrangements of oxygen ions. Between the layer of oxygen ions, the metal ions are accommodates in two interstitial sites; tetrahedral and octahedral. The tetrahedral sites (A) are coordinated by 4 nearest neighbouring oxygen ions and the octahedral sites (B) are coordinated by 6 neighbouring oxygen ions. The unit cell of the spinel ferrites contains eight formula unit MeFe$_2$O$_4$, in which 8 A sites out of 64 are occupied by divalent metal ions and 16 B sites out of 32 are occupied by trivalent metal ions [5]. Depending on the crystallographic sites occupied Fe(III) and Me(II), three types of spinel ferrites structures are known which are normal, inverse and mixed structures. In normal spinel ferrites, Me(II) lies at
tetrahedral sites and Fe(III) lies at octahedral sites; In inverse spinel ferrites, Me(II) lies only at octahedral sites where as Fe(III) equally distributed on both octahedral and tetrahedral sites; and in mixed spinel ferrites, both cations are randomly distributed on octahedral and tetrahedral sites [6]. ZnFe$_2$O$_4$, NiFe$_2$O$_4$ and MnFe$_2$O$_4$ are examples of normal, inverse and mixed spinel ferrites respectively. Because of high electrical resistivity and less eddy current, these types of spinel ferrites are used in microwave devices.

![Crystal structure of spinel ferrites](image)

**Figure 1.2:** Crystal structure of spinel ferrites [7]

### 1.2.2 Garnet Ferrites

Another type of ferrite structure is the garnet, the typical structure of which is shown in figure 1.3. The unit cell structure of garnet ferrite is a cubic structure. Unlike the spinel, the oxygen ions in the garnet are arranged in polyhedral combination rather than closed packed arrangement. Crystallographically, the formula for garnet is $C_3A_2D_3O_{12}$; where A is tetrahedral site (four fold), D is octahedral site (six fold) and C is dodecahedral (eight fold) site. Since Fe(III) is the primary cation in most ferrites, chemical formula for garnet ferrites can be express as $\text{Re}_3\text{Fe}_5\text{O}_{12}$ with Re as a rare-earth element such as yttrium, gadolinium, lanthanum, etc. The rare-earth cations occupy the dodecahedral sites, whereas $\text{Fe}^{3+}$ ions distributed among
the tetrahedral and octahedral sites. The unit cell of the garnet ferrite contains 8 formula unit
\( \text{Re}_3\text{Fe}_5\text{O}_{12} \), in which there are 16 octahedral, 24 tetrahedral and 16 dodecahedral sites. One
unit cell formula of garnet, \( \text{Re}_3\text{Fe}_5\text{O}_{12} \), is distributed as 3ReO3 in dodecahedral, 3Fe2O3 in
tetrahedral and 2Fe2O3 octahedral [8]. The garnet is also mainly used in microwave devices.

Figure 1.3: (a) Crystal structure of garnet ferrites and (b) Crystallographic sites of \( \text{Y}_3\text{Fe}_5\text{O}_{12} \) [9]

1.2.3 Hexagonal Ferrites

The natural magnetic mineral, magnetoplumbite, was first discribed in 1925 and in 1938
the structure was deduced as hexagonal [10]. Since iron is a major metallic component in
this mineral and hexagonal in structure, it is also called hexaferrite. Later in 1950s, Philips
Laboratories published detail reports on main hexaferrite phases [11], and this period is known
as the first synthesis and development of hexaferrites.

The crystal structure of hexaferrites have closely packed oxygen ion layers, in which divalent and trivalent metallic cations are located in the interstitial sites, the heavy ions such as, Ba, Sr, Pb are present substitutionally in the oxygen layers. There are three basic blocks base on which hexaferrite structure can be described, namely, S block, R block and T block. The S block, also known as spinel block, consist of double spinel and has the unit formula of $\text{Me}_2\text{Fe}_4\text{O}_8$. In this structure, three metal atoms are present in each layer of four oxygen atoms at four octahedral sites and two tetrahedral sites. The R block has the unit formula of $\text{DFe}_6\text{O}_{11}$ and consist of three layers of oxygen atoms with D atom at the center layer of one of the oxygen atom position, which creates asymmetry in cation sites and developed five octahedral sites and one trigonal bipyramidal sites. Where D denotes Sr, Ba or Pb and Me denotes divalent metallic cation. The T block has the unit formula of $\text{D}_2\text{Fe}_8\text{O}_{14}$ and composed of three layers of oxygen atom with D atom at the position of one of the oxygen atoms in the center two layers [12, 13]. The crystal structures of S, R and T blocks are shown in Figure 1.4.
Based on the stacking sequence of these basic blocks and chemical formula, hexaferrites are classified into six different types as M, Y, W, Z, X and U types, which are listed in Table 1.1 along with their chemical formula and stacking sequence. The symbol $S^*$, $R^*$ and $T^*$ represents the rotation of S, R and T blocks by 180° about c-axis; D denotes Sr, Ba or Pb and; Me denotes divalent metallic cation.

**Figure 1.4:** Crystal structure of (a) two layers of S block, (b) R block and (c) T block [14]
Table 1.1: Types of hexaferrites with their chemical formula and stacking sequence [13, 14]

<table>
<thead>
<tr>
<th>S.N.</th>
<th>Hexaferrites</th>
<th>Combination</th>
<th>Unit cell</th>
<th>Molecular formula</th>
<th>Stacking sequence</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>M-Type</td>
<td>M</td>
<td>2M</td>
<td>DFe$<em>{12}$O$</em>{19}$</td>
<td>RSR<em>S</em></td>
</tr>
<tr>
<td>2</td>
<td>Y-Type</td>
<td>Y</td>
<td>3Y</td>
<td>D$<em>2$Me$<em>2$Fe$</em>{12}$O$</em>{22}$</td>
<td>TSTSTS</td>
</tr>
<tr>
<td>3</td>
<td>W-Type</td>
<td>M+S</td>
<td>2W</td>
<td>DMe$<em>2$Fe$</em>{16}$O$_{27}$</td>
<td>RSSR<em>S</em>S*</td>
</tr>
<tr>
<td>4</td>
<td>Z-Type</td>
<td>M+Y</td>
<td>2Z</td>
<td>D$<em>3$Me$<em>2$Fe$</em>{24}$O$</em>{31}$</td>
<td>RSTSR<em>S</em>T<em>S</em></td>
</tr>
<tr>
<td>5</td>
<td>X-Type</td>
<td>2M+S</td>
<td>3X</td>
<td>D$<em>2$Me$<em>2$Fe$</em>{28}$O$</em>{46}$</td>
<td>RSR’S’S’</td>
</tr>
<tr>
<td>6</td>
<td>U-Type</td>
<td>2M+Y</td>
<td>U</td>
<td>D$<em>4$Me$<em>2$Fe$</em>{36}$O$</em>{60}$</td>
<td>RSR’S’T’S’</td>
</tr>
</tbody>
</table>

1.3 M-Type Hexaferrite

The first known M-type hexaferrite is barium hexaferrite, BaFe$_{12}$O$_{19}$, which was confirmed to have hexagonal and magnetoplumbite structure after characterized magnetically by Philips in 1950s [11]. It is a hard magnet with high coercivity, large electrical resistivity and high magnetocrystalline anisotropy along c-axis. Later, the barium ion was replaced by strontium or lead ion and modified M-type of hexaferrites were developed. The physical properties of barium hexaferrite (BaM), strontium hexaferrite (SrM) and lead hexaferrite (PbM) are listed in Table 1.2 [10].

Table 1.2: Structural properties of M-type hexaferrites

<table>
<thead>
<tr>
<th>Hexaferrites</th>
<th>Density (g/cm$^3$)</th>
<th>Molecular mass (g)</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>$T_c$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaM</td>
<td>5.295</td>
<td>1112</td>
<td>5.8876</td>
<td>23.1885</td>
<td>725</td>
</tr>
<tr>
<td>SrM</td>
<td>5.101</td>
<td>1062</td>
<td>5.8844</td>
<td>23.0623</td>
<td>732</td>
</tr>
<tr>
<td>PbM</td>
<td>5.708</td>
<td>1181</td>
<td>5.8941</td>
<td>23.0984</td>
<td>718</td>
</tr>
</tbody>
</table>

1.3.1 Crystal structure of M-type hexaferrite

The molecular unit of M-type hexaferrite is composed of the stacking sequence of S and R blocks in the form of RSR*S* and the unit formula can be expressed as MeFe$_{12}$O$_{19}$. Where * represents the rotation of block by 180° and Me is the divalent ion such as Sr, Ba or Pb. The
crystal structure of M-type hexaferrite is shown in Figure 1.5 and the lattice parameters are listed in the Table 1.2.

Figure 1.5: Crystal structure of M-type hexaferrite, SrM [15]

The M-type hexaferrites have 64 ions per unit cell with 11 different symmetry sites. For instance, in SrM, there are 2 strontium ions, 24 iron ions and 38 oxygen ions. There are five distinct interstitial sites with three octahedral sites (2a, 12k and 4f2), one tetrahedral site (4f1) and one bipyramidal site (2b). The 24 iron ions are distributed among these lattice sites in which 2a, 2b and 12k are parallel sites whereas 4f1 and 4f2 are antiparallel sites, which are coupled by superexchange interaction through oxygen ions [16, 17, 18]. The number of Fe$^{3+}$ ions in different interstitial sites for a unit formula MeFe$_{12}$O$_{19}$ are listed in Table 1.3. In the crystal 2Fe$^{3+}$ ions are in 2a site, 2Fe$^{3+}$ ions are in 2b and 12Fe$^{3+}$ ions are in 12k sites and hence altogether 16Fe$^{3+}$ ions are in parallel spin states. Similarly, 4Fe$^{3+}$ ions are in 4f1 and 4Fe$^{3+}$ ions are in 4f2 with altogether 8Fe$^{3+}$ ions are in antiparallel spin states. These 8 antiparallel spin states cancels out with the 8 parallel spin states and hence net magnetization is given by the remaining 8 parallel spin states in unit cell of two formula unit [19]. So, in
the single formula unit of SrM, 4Fe$^{3+}$ ions from the parallel spin states contributes for the net magnetization. There are 5 unpair electrons of Fe$^{3+}$ ion in the 3d orbital, which gives magnetic moment of 5$\mu_B$ by a single Fe$^{3+}$ ion and hence 4Fe$^{3+}$ ions provide the magnetic moment of 20$\mu_B$ [20, 21]. Where $\mu_B$ is the Bohr magneton. So, in the single crystal or in the two formula unit of M-type hexaferrite, the net magnetic moment is 40 $\mu_B$.

**Table 1.3:** Number of Fe$^{3+}$ ions in different interstitial sites of M-type hexaferrites along with their spin direction [21]

<table>
<thead>
<tr>
<th>Geometry</th>
<th>Site</th>
<th>No. of Fe$^{3+}$ ions</th>
<th>Spin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Octahedral</td>
<td>12k</td>
<td>6</td>
<td>Up</td>
</tr>
<tr>
<td>Octahedral</td>
<td>2a</td>
<td>1</td>
<td>Up</td>
</tr>
<tr>
<td>Octahedral</td>
<td>4f2</td>
<td>2</td>
<td>Down</td>
</tr>
<tr>
<td>Tetrahedral</td>
<td>4f1</td>
<td>2</td>
<td>Down</td>
</tr>
<tr>
<td>Bipyramidal</td>
<td>2b</td>
<td>1</td>
<td>Up</td>
</tr>
</tbody>
</table>

The M-type hexaferrites are well-known ferrimagnets with high magnetocrystalline anisotropy along c-axis. The main origin of this uniaxial anisotropy is due to the 2b lattice site in which there is a large assymetry because of Fe$^{3+}$ surrounded by five oxygen ions [22].

### 1.3.2 Magnetic Properties of M-Type Hexaferrite

#### 1.3.2.1 Magnetic Moment

The magnetic moment of the material depends on the electronic configuration and the substitution of ions in the different crystallographic sites. In M-type hexaferrries, the magnetic moment is mainly due to the substitution of Fe$^{3+}$ ions in 5 different interstitial sites, 2a, 2b, 12k, 4f1 and 4f2. The 2a, 2b and 12k sites are parallel spin sites along the direction of crystallographic c-axis while, 4f1 and 4f2 sites are aniparallel spin sites. So, the resultant magnetization (M) at a temperature (T) of M-type hexaferrites in a single formula unit can be approximated
by the following formula.

\[ M(T) = 6\sigma_{12k}(T) + \sigma_{2a}(T) - 2\sigma_{4f1}(T) - 2\sigma_{4f2}(T) + \sigma_{2b}(T) \]  

(1.1)

Where, \( \sigma_i \) represents the magnetic moment of \( i \)Fe\(^{3+} \) ion. The net magnetization of M-type hexaferrite at 0K is 20 \( \mu_B \), assuming the magnetic moment of 5 \( \mu_B \) by each Fe\(^{3+} \) [10, 21].

1.3.2.2 Coercivity

The potential application of the hexaferrites depends on the coercivity, one of the most important characteristics of the material. It is an extrinsic property which depends on the particles shape and size. The coercivity classifies the material into hard or soft magnets and describes the stability of remanent magnetization.

1.3.2.3 Magnetocrystalline Anisotropy

The magnetocrystalline anisotropy is known as the energy of the magnetic materials associated with the orientation of magnetization with respect to the crystal axis. It is an intrinsic property of the ferromagnetic materials which do not depend on the particles shape and size, and strongly affects the shape of hysteresis loop along with the coercivity and remanence values. For the single crystal, the magnetocrystalline anisotropy can be defined as the energy required to orient the magnetic moment from the easy magnetization axis to hard magnetization axis. The M-type hexaferrites have easy magnetization along c-axis and hence they are known to have uniaxial magnetocrystalline anisotropy along c-axis. The energy per unit volume of mag-
netocrystalline anisotropy for these materials can be express as,

\[ E_k = k_1 \sin^2 \theta + k_2 \sin^4 \theta + ... \] (1.2)

Where \( \theta \), \( k_1 \) and \( k_2 \) are the angle between c-axis and magnetization direction, first order, and second order magnetocrystalline anisotropy constant respectively [10].

1.3.2.4 Curie Temperature

In the magnetic materials like ferromagnetic and ferrimagnetic, generally, the magnetization of the material is decreased with the increase in temperature. Above the certain temperature the magnetization of these materials decreases sharply, and the material shows paramagnetic behavior. This temperature is called curie temperature \( (T_c) \). Above the curie temperature, the magnetic dipoles are randomly oriented due to the thermal agitation and the susceptibility of the magnetic material decreases sharply. The curie temperature for M-type hexaferrites are shown in Table 1.2.

The other intrinsic magnetic properties such as, anisotropy field strength and domain wall energy are known as secondary properties as they are derived from other primary properties. The anisotropy field \( (H_a) \) of the material is the maximum value of the coercivity for that material and the domain wall energy is the energy difference between magnetic moments of the materials before and after the formation of domain wall.
1.3.3 Application of Ferrites

Hard magnetic ferrites are used in the permanent magnetic applications, microwave applications, dielectric media, recording media, electromagnetic wave absorbers, dielectric media, telecommunication, a memory circuit, stealth aircraft, etc [23]. Hard ferrites can also be used as a drug delivery agent in the hyperthermia treatment of cancer [24]. Because of high corrosion resistivity and high cohesive force these ferrites are the strong candidates of powerful permanent magnet materials [25].

Soft magnetic ferrites can be easily magnetized and demagnetized easily without loss of energy, so they are used in transformer cores. Soft ferrites with high resistivity prevent devices from overheating due to eddy current. So, they are used in the radio frequency transformer and inductor coil. Soft ferrites are made up of rusted iron and hence these ferrites are low in cost and have high corrosion resistance [26]. These ferrites also have important application in electromagnetic wave absorber, microwave devices, and sensors. Nickel and zinc ferrites are examples of soft magnetic materials that are applicable in transformers, microwave devices, sensor application, telecommunication, and electromagnetic wave absorbers [27].
Chapter 2

Literature Review

2.1 M-type Strontium Hexaferrite

After the development of M-types barium hexaferriets (BFO) in 1950s by Philips company [28], many improvements are achieved with the replacement of barium ion by strontium ions or lead ions. The material is also improvised by the various synthesis techniques like, conventional ceramic [29], hydrothermal[30, 31], microwave hydrothermal [32], low temperature solid state reaction [33] and sol-gel auto combustion [34, 35]. In the last two decades, a large amount of research has been conducted on M-type hexaferrites to improve magnetic and microwave properties. Our research is mainly focus on the M-type strontium hexaferrite(SrM), which have gathered more interest in recent years because of some different properties than barium hexaferrite (BaM) and lead hexaferrite (PbM). Along with the pure hexaferrites, researchers have doped various elements to enhance the properties of these hexaferrites. Some of the research work that has been done in the field of M-type strontium hexaferrite to improve the magnetic and microwave properties are summarized below.
2.1.1 Pure Strontium Hexaferrite

X. Obradors et al., in 1988 [36], studied the room temperature structure of SrM refined by X-ray single crystal data. Obradors et al reported the same hexagonal structure of SrM as in BrM. They also mention the fast diffusion of bipyramidal Fe ion within a quasiharmonic double-well potential as in the BrM. However, some structural difference in R block was observed between BrM and SrM, which may lead to difference in dynamic, magnetic and crystallochemical behaviors.

A. Ataie et al., in 1995 [37], hydrothermally synthesized the fine particle of SrM with narrow size distribution from the aqueous mixture of strontium and iron nitrate. The samples were prepared under different synthesis condition and studied the magnetic properties. The increase in saturation magnetization upto a plateau was observed, while the coercivity decreased with the increase in synthesis temperature. The decrease in coercivity was also noticed by increasing synthesis time from 2h to 5h with no significant change in saturation magnetization. The SrM powder with high saturation magnetization of 67.26 emu/g was successfully synthesized.

A. Ataie et al., in 2001 [38], synthesized the uniform size and ultra-fine SrM particles ranging from 0.1 \( \mu \)m to 0.2 \( \mu \)m by modified co-precipitation method from aqueous mixture of strontium nitrate and iron nitrate. The SrM particles were confirmed as single domain particles with significantly higher coercivity of 5.55 KOe. The effect of calcination temperature on magnetic properties, shape and size of the particles were investigated and observed that the rapid increment in coercivity with increase in calcination temperature from 650 °C to 750 °C and optimum value at 850 °C. The increase in saturation magnetization was also observed beyond the calcination temperature of 650 °C.

L. A. Garcia-Cerda et al., in 2003 [39], synthesized SrM powder via sol-gel method and
studied the effect of calcination temperature on the phase composition and magnetic properties. They confirmed the formation of single phase strontium hexaferrite at the temperature of 800 °C by X-ray diffraction and the saturation magnetization value of 56.97 emu/g with the coercivity value of 4783 Oe for the sample calcined at 900 °C.

J. Wang et al., in 2004 [40], successfully synthesized the SrM nanoparticles in the hydrothermal cell under the conditions of applied magnetic field of 0.35 T and zero magnetic field. In both cases, formation of SrM nanoparticles was confirmed by X-ray diffraction. However, flake-like structure in zero magnetic field and nanowires of average length 2.5 µm with average diameter of 100 nm under applied magnetic field were confirmed by transmission electron microscope. Also, the higher saturation magnetization was observed for the particle synthesized under applied magnetic field with compare to zero magnetic field. It was concluded that the improvement of magnetic properties was mainly due to the applied magnetic field which helps to order the magnetic lattice providing fewer barrier for domain wall motion.

M. M. Hessien et al., in 2007 [41], synthesized the nanocrystalline SrM powder via co-precipitation-calcination route from the aqueous mixture of strontium carbonate and ferric chloride. The magnetic properties, crystalline size, morphology and formation were studied under the effect of annealing temperature, PH and Fe³⁺/Sr²⁺ mole ratio. It was observed that at annealing temperature of 900 °C for 2h and PH 10, SrM achieve single phase on decreasing the Fe³⁺/Sr²⁺ mole ratio from 12 to 9.23. The maximum saturation magnetization of 84.15 emu/g was achieved at mole ratio of 9.23 and 1000 °C annealing temperature. The wide range of coercivity from 2937 Oe to 5607 Oe was also observed under different synthesis conditions and hence concluded that the magnetic properties and microstructure of SrM strongly depend on synthesis condition.

E. Kiani et al., in 2013 [33], successfully synthesized the ultra fine SrM nanoparticles by
low temperature solid state method without ball milling process. The formation of single phase SrM at low temperature of 750 °C compared to the other ceramic techniques was confirmed by XRD analysis. Also, the particles with size of 30 nm - 100 nm were obtained with this method. It was observed that the particle size depends on Na⁺/Sr²⁺ mole ratio and the synthesis temperature. It was concluded that the particles synthesized with this method are suitable for various applications such as microwave devices and high density magnetic recording media.

J. Zhao et al., in 2019 [42], synthesize the SrM particles by salt assisted spry drying method to control the grain growth and agglomeration of particles. The effect of precursor solution on magnetic properties, crystalline growth and morphology was investigated. The particles size of nano to submicron scale and non-agglomerated in NaCl salt matrix of SrM partciles were observed. The coercivity and saturation magnetization of 6042 Oe and 47.3 emu/g respectively for SrM particles prepared from sol solution annealed at 750 °C, and the coercivity of 5927 Oe with saturation magnetization of 57.6 emu/g were observed for SrM prepared via no treatment precursor solution and moletn salt assisted annealing at 850 °C. It was concluded that the result attributes the influence of salt matrix calcination and precursor polymerization on magnetic properties, morphology and crystal growth.

2.1.2 Doping on Fe-site of Strontium Hexaferrite

Q. Fang et al., in 2005 [43], synthesized SrFe₁₂₋ₓCrₓO₁₉ (x = 0-1) nanoparticles via chemical sol-gel route and structural and magnetic properties were studied. The coercivity of the of the material continuously decreased while the saturation magnetization value slightly increased upto x = 0.4 and then decreased. Also, there was a single phase of hexagonal structured upto x = 0.4, but the secondary phase of α - Fe₂O₃ appeared after x = 0.6. The magnetic measurement reveals the decrease in Hopkinson peak and increase in peak width as the concentration
of chromium iron in the structure increases.

H. Luo et al., in 2012 [44], synthesized the highly aluminum doped \( \text{SrFe}_{12-x}\text{Al}_x\text{O}_{19} \) \((x = 0-12)\) via autocombustion method which was annealed for 12 h in air at 1100 °C. The prepared samples were identified as a high purity hexaferrite phase by x-ray diffraction analysis and observed the decrease in lattice parameters due to the replacement bigger ion \( \text{Fe}^{3+} \) by smaller ion \( \text{Al}^{3+} \). The saturation magnetization was continuously decreased with the increase in aluminum content whereas the coercivity increased to the maximum value of 18,100 Oe at \( x = 4 \) which was nearly 321% increase compared to the pure \( \text{SrFe}_{12}\text{O}_{19} \) (SFO).

J. N. Dahal et al., in 2014 [45], prepared polycrystalline \( \text{SrFe}_{12-x-y}\text{Al}_x\text{Co}_y\text{O}_{19} \) \((x = 1.0-4.0 \text{ and } y = 0.0-2.0)\) samples by autocombustion method and studied the structural and magnetic characteristics. The single phase Al-Co substituted SFO was obtained at \( y < 1 \) and secondary phase of \( \text{CoFe}_2\text{O}_4 \) was segregated for higher \( \text{Co}^{2+} \) substitution. The coercivity was reduced and the saturation magnetization was enhanced with the increase in cobalt content in \( \text{SrFe}_{12-x-y}\text{Al}_x\text{Co}_y\text{O}_{19} \). Rapid decline in anisotropy field was observed due to the preferential site occupancy of \( \text{Co}^{2+} \) and \( \text{Al}^{3+} \) ions. The cure temperature was reduced with the \( \text{Co}^{2+} \) content due to decrease in strength and superexchange interaction between \( \text{Fe}^{3+} \) sites. It was concluded that the magnetic properties of this compound could be controlled by adequate ratio of \( \text{Al}^{3+} \) and \( \text{Co}^{2+} \) ions and the compound could offer rich choice for hard and soft magnetic material.

W. M. S. Silva et al. in 2015 [46], synthesized \( \text{SrFe}_{12-x}\text{Mn}_x\text{O}_{19} \) \((x = 0-1)\) by proteic sol-gel process and the formation of nanocrystalline strontium hexaferrite phase was observed by thermogravimetric and differential thermal analysis, after annealed at 1000 °C. The single phase M-type hexaferrite was demonstrated by XRD analysis and no significant change in lattice parameters were observed whereas the crystalline size was about 46.4nm - 52.6 nm. FTIR
absorption band in the frequency range around 435 cm\(^{-1}\) to 535 cm\(^{-1}\) and 595 cm\(^{-1}\) also strengthen the formation of hexaferrite structure. The room temperature Mossbauer analysis revealed the preferably occupation of manganese ion at 12k, 4f1,4f1 and 2a sites. The saturation magnetization, remanance and coercivity of the materials were also decrease with the increasing content of manganese.

E. Roohani et al., in 2016 [19], successfully prepared the nanocrystalline SrFe\(_{12-x}\)Co\(_x\)O\(_{19}\) (\(x = 0-1\)) by sol-gel auto combustion technique and studied the crystalline structure, morphology and magnetic properties of the samples. FTIR spectra confirms the three vibrational modes indicating metal oxygen stretching bands in hexagonal structure after calcination treatment. For \(x \leq 0.5\), single phase structure of SrFe\(_{12-x}\)Co\(_x\)O\(_{19}\) was observed whereas for \(x > 0.5\) cubic CoFe2O4 phase appeared on the XRD spectra. The particle size was larger for higher cobalt content and they are in the range of 87 nm to 110 nm. The coercivity of the material was continuously decreased with the cobalt concentration whereas, maximum value of saturation magnetization was observed for \(x = 0.5\).

V. Y. Ivanov et al., in 2017 [47], studied the anisotropic magnetic and magnetoelectric properties of single crystal SrSc\(_x\)Fe\(_{12-x}\)O\(_{19}\) (\(x = 1.4-1.7\)) in the temperature range 2K-800K and magnetic field upto 50 KOe. In all the compositions, spontaneous transition of collinear ferrimagnetic single axis phase to conical structure was detected in which the transition temperature increased and the curie temperature decreased with the increasing Sc content. The magnetic field induced the electric polarization in conical magnetic structure which was more than 40 \(\mu\)C/m\(^2\) at \(T = 4\)K. In this work, the possibilities of controlling the conical structure and the dependence of polarization on the orientation and value of magnetic field are investigated.

T. Xie et al., in 2018 [48], synthesized SrFe\(_{12-x}\)Sm\(_x\)Co\(_x\)O\(_{19}\) (\(x = 0.1-0.5\)) via one step chemical co-precipitation method and studied the structural and magnetic properties of the
samples. The crystalline size was in the range of 29.7 nm to 32.9 nm and the lattice constant a and c are close to 5.88 Å and 23.05 Å respectively. It was observed that for \( x = 0.2 \) and 0.4, \( \text{Fe}^{3+} \) ions were substituted by \( \text{Sm}^{3+} \) and \( \text{Co}^{2+} \) at 12k or 2a sites whereas for \( x = 0.1, 0.3 \) and 0.5 \( \text{Fe}^{3+} \) ions at 12k and 2a were substituted by \( \text{Sm}^{3+} \) ions and \( \text{Fe}^{3+} \) ions at 4f2 site were replaced by \( \text{Co}^{2+} \) ions.

M. Zhang et al., in 2019 [49], successfully synthesized the Co and Ti doped SFO at the Fe-site by sol-gel method. The Rietveld refinement confirms the single phased hexagonal crystal of all prepared samples and FE-SEM revealed the increase in particle size with the increase in doping content. The coercivity of the material decreased largely from 1697 Oe to 20 Oe while slightly decrease in saturation magnetization on increasing the doping content from \( x = 0.5 \) to 1.5. It was also noted that with the substitution of Co-Ti, the magnetocrystalline anisotropy of the material gradually turn from uniaxial to planer with the transition point nearly at \( x = 1.5 \), which is beneficial to formation of conical structure to induce electric polarization.

### 2.1.3 Doping on Sr-site of Strontium Hexaferrite

L. Lechevallier et al., in 2003 [18], prepared the \( \text{Sr}_{1-x}\text{Sm}_x\text{Fe}_{12}\text{O}_{19} \) with \( x = 0, 0.125 \) and 0.25, by conventional ceramic process involving calcination, milling and scintering. The presence of secondary phases \( \text{SmFeO}_3 \) and \( \alpha - \text{Fe}_2\text{O}_3 \) along with the main M-type hexagonal phase were revealed by the XRD analysis. The number of secondary phases were also proportional to the \( x \) content. The Mossbauer and XRD analysis revealed the evolution of hyperfine parameter with the presence of Sm ion in M-type Phase. The increase in coercivity and decrease in remanance of the calcined material were observed with increasing \( x \) content, which were attributed to the microstructural changes with the presence of secondary phases and the introduction of Sm in M-type phase.
M. Küpferling et al., in 2006 [50], prepared the La substituted SFO with different La concentrations, $x$, and observed the structural and magnetic properties. For the full La substitution, LaFe$_{12}$O$_{19}$, the hexagonal crystal structure with space group $P6_3/mmc$ of SFO change into the orthorhombic structure with space group $Cmcm$ below 100K. At low temperature, magnetocrystalline anisotropy of LaFe$_{12}$O$_{19}$ was largely increased and formation of Fe$^{2+}$ orbital momentum occurs together with lattice distortion. From the mossbauer analysis, localization of Fe$^{2+}$ around 2a site was observed showing the orbital momentum in hyperfine field. However, no phase transition and Fe$^{2+}$ formation was observed for $x < 1$.

M. J. Iqbal et al., in 2010 [51], synthesized the Sr$_{1-x}$Ca$_x$Fe$_{12}$O$_{19}$ ($x = 0-0.6$) nanoparticles by chemical co-precipitation method on which the presence of nitrate ions was disappeared after annealing at 950 °C and the crystalline size were observed between 17nm to 29 nm. For the sample with calcium content $x \leq 0.2$, a single hexagonal magnetoplumbite phase was observed where as a non-magnetic phase of $\alpha$-Fe$_2$O$_3$ was present for $x > 0.2$. The DC electrical resistivity was also increased with increasing the calcium content up to $x = 0.2$.

Z. Ullah et al., in 2012 [52], synthesized the Sr$_{1-x}$Pb$_x$Fe$_{12}$O$_{19}$ ($x = 0-0.2$) nanoparticles via sol-gel auto-ignition technique and studied the structural, electrical and magnetic properties of the samples. Stable single hexaferrite phase was confirmed by X-ray analysis after annealed the samples at 800 °C for 2h. Doping Pb on SFO slightly increased the lattice parameters and crystalline size as Pb$^{2+}$ ion is slightly larger than Sr$^{2+}$. Along with the porosity of the ferrite particles, dielectric constant and dielectric tangent loss were also decreased with increasing concentration of Pb$^{2+}$ ion which favor the use of material in high frequency applications. As the concentration of Pb$^{2+}$ ion increased, the saturation magnetization and remanance decreased whereas the coercivity of the material increased.

T. Singh et al., in 2014 [53], prepared the rare-earth substituted ferrite Sr$_{1-x}$Re$_x$Fe$_{12}$O$_{19}$
(x = 0-0.3), where Re = La, Gd and Dy, by ceramic technique and observed the magnetic properties of samples. The increase in coercivity and decrease in saturation magnetization as well as remanance were observed with increasing concentration of Re substitution.

B. H. Bhat et al., in 2016 [54], successfully synthesized the Sr$_{1-x}$Nd$_x$Fe$_{12}$O$_{19}$ (x = 0-0.2) nanoparticles by citrate precursor method and TEM result revealed the average particle size of 80 nm. The magnetic behaviour of the Nd doped hexaferrite was analyzed by using first order reversal curves (FORCs) and suggest that the substituted system is formed of interacting nanoparticles. Also, no significant variation in saturation magnetization was observed while the coercivity was increased with increasing the Nd$^{3+}$ concentration.

G. P. Nethala et al., in 2018 [55], prepared the Sr$_{1-x}$Ce$_x$Fe$_{12}$O$_{19}$ (x = 0-0.25) nanoparticles by sol-gel technique and studied the structural and magnetic properties of prepared samples. The single phase M-type hexagonal magnetoplumbite structure was confirmed by XRD and FTIR analysis. The coarseness with porosity in the sample as seen in the SEM images were decreased with increasing Ce$^{3+}$ concentration. The magnetic properties of SFO were found weakened on dopong the Ce$^{3+}$. The mossbauer analysis revealed the existance of iron ion in Fe$^{3+}$ state and all five sextets are attributed to Fe$^{3+}$ ions.

### 2.1.4 Co-doping on Sr and Fe-Site of Strontium Hexaferrite

L. Lechevallier et al., in 2008 [56], synthesized Sr$_{1-x}$Re$_x$Fe$_{12}$O$_{19}$ and Sr$_{1-x}$Re$_x$Fe$_{12-2x}$Co$_x$O$_{19}$ (x = 0-0.4 and Re = Pr, Nd) M-type hexaferrite powders by conventional ceramic method. X-ray and Mossbauer analysis revealed the dependence of rare earth ions solubility in the M-type phase on presence of Co and nature of rare earth elements. It was observed that the presence of Co increased the solubility of rare-earth ion and, the solubility of Pr was also higher than that of Nd. The modification in the surrounding site of Sr$^{2+}$ by the presence of Co$^{2+}$ ion appeared
the easier introduction of light rare earth ions with oblate electronic distribution in the M-type structure.

X. Liu et al., in 2009 [57], prepared Sr$_{1-x}$La$_x$Fe$_{12-x}$Co$_x$O$_{19}$, La-Co substituted M-type strontium ferrite, by ceramic process and studied the structural and magnetic properties of the materials. The magnetic disaccommodation, which cannot be obviously found in pure strontium hexaferrite, were present in the measurement range of 80K to 500K and represented by means of isochronal curves. The observed three peaks in Sr$_{1-x}$La$_x$Fe$_{12-x}$Co$_x$O$_{19}$ in the curves were explained in terms of site occupancy of Co$^{2+}$ ion and presence of Fe$^{2+}$ ion, within the hexagonal crystal.

S. Kanagesan et al., in 2012 [58], synthesized a series of Ni-Co substituted barium strontium hexaferrite materials, Ba$_{0.5}$Sr$_{0.5}$Fe$_{12-2x}$Ni$_x$Co$_x$O$_{19}$ ($x = 0-0.8$), by sol-gel method and single hexagonal magnetoplumbite phase was confirmed by X-ray analysis. The lattice parameters $a$ and $c$ were increased, whereas the magnetic parameters such as saturation magnetization and coercivity decreased, with the increase in substitution content $x$ and varied over a wide range.

Y. G. Yang et al., in 2014 [59], prepared Sr$_{1-x}$La$_x$Fe$_{12-x}$Cu$_x$O$_{19}$ ($x = 0-0.35$), M-type hexaferrite magnetic powders by ceramic method and single magnetoplumbite structure was confirmed by x-ray diffraction analysis. With the increase in doping concentration $x$, the remanance and the maximum energy product increased upto $x = 0.2$ and then decreased, whereas the intrinsic coercivity and magnetic induction coercivity decreased continuously with increasing $x$ content.

Z. Wu et al., in 2018 [60], synthesized the Sm-Cu co-doped Sr$_{1-x}$Sm$_x$Fe$_{12-x}$Cu$_x$O$_{19}$ ($x = 0-0.2$) samples by co-precipitation method and pure M-type hexaferrite nanoparticles were confirmed by XRD and FTIR analysis. The shape of the particles were hexagonal sharp crystal and the particles size increased with the increasing doping concentration. The coercity of the
material was also reached to maximum of 6862 Oe for doping concentration $x = 0.15$.

A. Hilczer et al., in 2018 [61], synthesized single phase nanocrystal of Sr$_{0.95}$Ba$_{0.05}$Fe$_{12-2x}$Al$_x$O$_{19}$ ($x = 0.36-1.08$) particle by hydrothermal process and studied the structural and magnetic properties. The magnetic properties of the materials were observed in the temperature range of 10K-300K and observed that the doped Al$^{3+}$ ion substitute the ferric ion in 4f2, 2a and 12k Wycoff sites and the change in magnetization occurred. Also, the electric dipoles were induced in the trigonal bipyramidal regions with the substitution of Al$^{3+}$ ion in 12k and 4f2 sites which resulted the apparent dielectric and electric response. The coexistence of non-collinear and uniaxial magnetic moments was revealed on zero field cooling/heating in the field of 100 Oe.

H. Kaur et al., in 2018 [25], prepared M-type Ba$_{0.5}$Sr$_{0.5}$Fe$_{12-2x}$Ga$_x$Co$_x$O$_{19}$ ($x = 0-1$), by double sintering ceramic method and studied the microwave and magnetic properties of the material. Some traces of $\alpha$-Fe$_2$O$_3$ was observed as a minor phase in the substituted composition for $x > 0.2$. The enhancement of microwave absorption and band width in the frequency range 8.2 GHz to 12.4 GHz were observed along with decreased thickness and improved impedance matching. For the composition of $x = 0.2$, the optimum reflection loss of -29.74 dB was observed at 8.28 GHz with thickness of 2mm. The maximum coercivity was also found with the composition of $x = 0.2$.

Z. Wu et al., in 2019 [62], prepared the Yb-Co co-doped Sr$_{1-x}$Yb$_x$Fe$_{12-2x}$Co$_x$O$_{19}$ ($x = 0-0.2$) samples by co-precipitation method and observed the single phase M-type hexaferrite structure up to $x=0.1$, whereas the multiphase of $\alpha$-Fe$_2$O$_3$ and CoFe$_2$O$_4$ appeared for doping concentration $x > 0.1$. The saturation magnetization, remanance and the coercivity reached maximum at $x = 0.1$ with respective values, 60.89 emu/g, 31.96 emu/g and 6846 Oe.
2.2 Rational of This Project

The majority of the works done in hexaferrites are to improve the magnetic properties via doping atoms at one of the five sites viz. 2a, 2b, 12k, 4f1 and 4f2. Usually, the resistivity of hexaferrites is reported to improve by grain refinement or by doping non-magnetic atoms such as Al, Ga, and Ca at the cost of magnetization. For example, the substitution of $\text{Al}^{3+}$ in place of $\text{Fe}^{3+}$ in $\text{SrFe}_{12}\text{O}_{19}$ has shown to bring an unprecedented increase in coercivity up to 18 kOe, while further improvement in coercivity was reported by co-doping Ca-Al [63]. However, magnetization in both these cases was severely compromised. On the other hand, co-doping La-Zn has brought a little improvement in magnetization, but the coercivity been compromised [64]. Also, several attempts have been made with co-doping Ce-Mn [65], Nd-Sc [61], Mn-Y [66], Pr-Zn [67], La-Cu [68], Gd-Cu [69], and Ce-Zn [70]. But all of these efforts have led to severe deterioration in magnetization either due to charge compensation effect, lattice distortion affecting super-exchange interaction, reduced magnetocrystalline anisotropy, or even formation of secondary phases. Many of these studies are limited to low doping levels. Thus, in spite of some desired improvement, the cost-effectiveness for large scale synthesis is marginal or, in some cases not feasible.

The study delineates strategy for co-doping $\text{Ca}^{2+}$-$\text{Sc}^{3+}$ in $\text{SrFe}_{12}\text{O}_{19}$, with $\text{Ca}^{2+}$ substitution for $\text{Sr}^{2+}$ and $\text{Sc}^{3+}$ substitution for $\text{Fe}^{3+}$. The study follows an earlier study $\text{Ca}^{2+}$-$\text{Al}^{3+}$ co-doped hexaferrite showed marked coercivity increase with a rapid drop in magnetization value. The authors argued that the presence of $\text{Ca}^{2+}$ ion in the vicinity of 2b and the occupancy of $\text{Al}^{3+}$ at the 12k and 2b site could bring an unprecedented increase in the coercivity [63]. In view of this, the present effort is to understand if the magnetization value of the doped compound could be maintained to a high value even at a high level of doping with the substitution of non-maganetic similar atom such as $\text{Sc}^{4+}$ in the hexaferrite.
The study elucidates the synthesis of $\text{Sr}_{1-x/12}\text{Ca}_{x/12}\text{Fe}_{12-x}\text{Sc}_x\text{O}_{19}$ (SCFSO) via autocombution method followed by high-temperature annealing. A detailed structural and temperature and field-dependent magnetic and Mossbauer study was carried out to understand the structure-property relation of the compound. The study shows that upon co-doping Ca-Sc, the material rapidly becomes soft-magnet. With $\text{Fe}^{3+}$ being replaced at 4f2 site, a rapid reduction in $M_r$ and $H_c$ value was observed, while saturation magnetization showed a moderate reduction.

**Objective of Research**

The purpose of this work is to study the structural and magnetic properties of prepared SCFSO material in detail for which the following tasks are to be done.

1. Synthesis of high purity single phase of SCFSO nanoparticles.
2. Study the structural variation in lattice parameters of the prepared samples.
3. Study the magnetic properties of the prepared samples and extract magnetic parameters.
4. Thermal study to determine the curie temperature of the materials.
5. Mossbauer study to determine the site occupancy of dopants in the crystal structure and influence on hyperfine parameters.
Chapter 3

Experimental Details

3.1 Sample preparation

Various synthesis techniques have been developed and followed to prepare hexaferrite materials. However, the work would be more productive if the prepared material acquires high purity in less effort of time and cost, for which the preparation technique plays an important role. Apart from this, the synthesis route also depends on the precursor chemicals. After the literature review, it can be notice that some preparation techniques have limitations. For instance, in ceramic method [18, 22] and co-precipitation method [51, 62], there are high chances of getting secondary phases. In some techniques, even the quality of the material has been compromised. Hence, by weighing the merits and demerits of various techniques, sol-gel auto-combustion technique was purposed to synthesize the $\text{Sr}_{1-x/12}\text{Ca}_{x/12}\text{Fe}_{12-x/2}\text{Sc}_x\text{O}_{19}$ (SCFSO) particles in this work. The auto-combustion technique is easy, safe and required less amount of time to prepare the hexaferrite materials. The samples prepared from this technique are homogeneous powder with high purity and low particle size distribution [71].

In the sol-gel auto-combustion technique, also known as modified sol-gel technique, the so-
olution of metal nitrates and citric acid are prepared in the stoichiometric ratio, and the PH value of the solution is maintained at 6.5 - 7 by adding the base dropwise. The brown solution thus obtained is then heated on the hot plate at around 100 °C to 150 °C until the solution becomes gel-like structure. The temperature is then raised up to 220 °C - 250 °C to proceed the reaction [72, 73]. The auto-combustion route is an exothermic reaction, in which the metal nitrate acts as an oxidizing agent and the citric acid acts as a reducing agent as a result the decomposition of citric polymer occur. The large amount of heat is developed in the reaction and the foamy powder is obtained followed by self combustion of the compound. Thus, prepared foamy structure is then crushed into the mortar and annealed at high temperature to obtain the ferrite material.

Analytical grade chemical reagents (purity 99.99%, Sigma-Aldrich, St. Louis, MO, USA) strontium nitrate ((Sr(NO$_3$)$_2$)$_2$), iron (III) nitrate nonahydrate ((Fe(NO$_3$)$_3$.9H$_2$O), calcium nitrate tetrahydrate (Ca NO$_3$)$_3$.6H$_2$O), scandium (III) nitrate hydrate ((ScNO$_3$)$_3$.9H$_2$O) and citric acid were used for the synthesis of Sr$_{1-x/12}$Ca$_{x/12}$Fe$_{12-x}$Sc$_x$O$_{19}$ ($x = 0.0, 0.25, 0.5, 0.75, 1.0, 1.25, 1.5, and 2.0$) compound. The stoichiometric composition of nitrate salt used for the synthesis is listed in Table 3.1. For the synthesis process, the sol-gel auto-combustion technique was followed. In this process, the stoichiometric ratio of these chemicals was dissolved in water and sonicate. Once the solution became clear, ammonium hydroxide was added dropwise and maintained the pH at 6.5. The solution was then heated on a hot plate at 150 °C until it became a highly viscous gel, and after that, the temperature was increased to 250 °C. The gel then started to burn and formed a voluminous material. The powder thus obtained was crushed in the mortar and annealed at 1100 °C for 12 hours in box furnace in air.
Table 3.1: Stoichiometric amount of chemicals used for the synthesis of SCFSO compound

<table>
<thead>
<tr>
<th>x</th>
<th>(SrNO₃)₂</th>
<th>(Ca NO₃)₃·6H₂O</th>
<th>(FeNO₃)₃·9H₂O</th>
<th>(ScNO₃)₃·9H₂O</th>
<th>Citric acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>0.199367</td>
<td>0</td>
<td>4.567045</td>
<td>0</td>
<td>2.573498</td>
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<tr>
<td>0.25</td>
<td>0.195898</td>
<td>0.004651</td>
<td>4.48759</td>
<td>0.054587</td>
<td>2.582528</td>
</tr>
<tr>
<td>0.5</td>
<td>0.192406</td>
<td>0.009335</td>
<td>4.407575</td>
<td>0.109559</td>
<td>2.591622</td>
</tr>
<tr>
<td>0.75</td>
<td>0.188888</td>
<td>0.014052</td>
<td>4.326994</td>
<td>0.16492</td>
<td>2.60078</td>
</tr>
<tr>
<td>1.00</td>
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<td>0.018802</td>
<td>4.245843</td>
<td>0.220673</td>
<td>2.610003</td>
</tr>
<tr>
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<td>0.023586</td>
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<td>2.619292</td>
</tr>
<tr>
<td>1.50</td>
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<td>0.028404</td>
<td>4.08180</td>
<td>0.333374</td>
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<tr>
<td>2.00</td>
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<td>0.038145</td>
<td>3.915396</td>
<td>0.447696</td>
<td>2.647558</td>
</tr>
</tbody>
</table>

3.2 Sample Characterization

The phase structure of as-prepared \( \text{Sr}_{1-x/12} \text{Ca}_{x/12} \text{Fe}_{12-x} \text{Sc}_x \text{O}_{19} \) was analyzed using x-ray diffraction analysis (XRD). XRD was carried out in the \( 2\theta \) range of 20 to 70 degrees with Cu-Kα (\( \lambda = 1.540600 \text{ Å} \)) radiation with a step size of 0.024 and acquisition time 0.2 s. To confirm the formation of M-type hexaferrite metal-oxygen bond Fourier transmission infrared (FTIR) spectra were collected in the range of 400-2000 \( cm^{-1} \) via Thermo Nicolet iS10 FTIR spectrometer. DC magnetizations of all prepared products were measured using a superconducting quantum interference device (PPMS DynaCool, Quantum Design, San Diego, CA, USA) as a function of field and temperature. A thermogravimetric analyzer (TGA, Instrument Specialist, USA), equipped with a permanent magnet, was used to determine the Curie temperature of the samples. The room temperature \(^{57}\text{Fe} \) Mossbauer experiments were performed using a conventional constant-acceleration type spectrometer (SEE Co. Minneapolis, MN USA) with a \(^{57}\text{Co} \) in Rh source. The velocity scale was calibrated with a standard \( \alpha \)-Fe foil. The hyperfine parameters were extracted from Mossbauer spectra using WMoss software (SEE Co. Minneapolis, MN USA).
Chapter 4

Result and Discussion

4.1 X-ray Diffraction Analysis

Figure 4.1(a) shows XRD patterns of Ca\(^{2+}\)-Sc\(^{3+}\) doped strontium hexaferrites, SCFSO, with different doping content. XRD patterns of the samples with x up to 2.0 show pure SFO phase \((\text{SrFe}_{12}\text{O}_{19})\) with space group \(\text{P6}_{3}/\text{mmc}\). In the absence of any impurity peak, it is concluded that Ca\(^{2+}\) and Sc\(^{3+}\) ions, within the reported concentration range, substituted Fe\(^{3+}\) ions completely within the \(\text{SrFe}_{12}\text{O}_{19}\) lattice. The Figure 4.1(b) shows the close-up view of the XRD pattern in the range of \(33^\circ\) to \(35^\circ\). The gradual shift of the peaks towards the lower angle is indicative of unit cell lattice expansion with doping. XRD data was profile fitted using TOPAZ (Bruker, USA) to extract lattice parameters, \(a\) and \(c\). The lattice parameters are listed in Table 4.1. As can be seen from Figure 4.2, both \(a\) and \(c\) increase linearly, leading to volume expansion with the increase in Ca\(^{2+}\)-Sc\(^{3+}\) content in the compound. The increase in \(a\) and \(c\) is mainly due to the replacement of Sr\(^{2+}\) (0.118 nm) with a slightly smaller Ca\(^{2+}\) (0.10 nm) and replacement of Fe\(^{3+}\) (0.645 Å) with a bigger Sc\(^{3+}\) (0.745 Å) ions. The expansion along the \(c\)-axis leads to an increase in the distance between stacking layers along the \(c\)-axis. According
to Wagner [74], an examination of c/a parameter ratio may be used to quantify the structure type, as the M-type (magnetoplumbite) structure can be assumed if the ratio is observed to be in the range 3.917 and 3.963. As per Table 4.1, the c/a ratios of as-prepared samples are in the range of 3.92 to 3.94, assuring the as-prepared samples have maintained the M-type structure.

Figure 4.1: XRD pattern of SCFSO compound with different doping content in (a) 20°-70° range and (b) closeup view in 33°-35° range
The crystallite size (D) of the prepared ferrite powder samples was determined by Scherrer’s formula [75],

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

(4.1)

where \( k \) denotes the Scherrer constant (\( k = 0.9 \)), \( \lambda \) is the wavelength of x-ray source (\( \lambda = 1.54 \text{ Å} \)), \( \beta \) is the full-width-half-maximum of a diffraction peak and \( \theta \) is the diffracted angle of the powder samples.

The mean crystallite size and microstrain were also deduced from the Halder-Wagner-Langford’s (HWL) plot technique [76] applied to the XRD data. The HWL equation relates the FWHM of peaks, \( \beta \), with the mean crystallize size, “T,” and the micro deformation of a

**Figure 4.2:** Plot for Lattice parameters with different doping content of SCFSO compound.
grain, \( \varepsilon \), as follows:

\[
\left( \frac{\beta^*}{d^*} \right)^2 = \frac{1}{T} \left( \frac{\beta^*}{d^*} \right)^2 + \frac{\varepsilon}{2}
\]

(4.2)

Where \( \beta^* \) is given by \( \beta^* = \frac{\beta}{\lambda} \cos \theta \), where \( \lambda \) is the x-rays wavelength, and \( d^* \) is given as \( \frac{2}{\lambda} \sin \theta \). The slope of the plot of \( \left( \frac{\beta^*}{d^*} \right)^2 \) vs. \( \left( \frac{\beta^*}{d^*} \right)^2 \), shown in Figure 4.3, defines the crystallite size, and the constant term determines the strain value. The crystallite size (D) and microstrain value obtained from plotting equation 4.2 of the powder samples are listed in Table 4.1. From the data, the crystallite size of pure SrFe\(_{12}\)O\(_{19}\) is 62 nm, while upon Ca\(^{2+}\)-Sc\(^{3+}\) doping, the crystallite size of SrM increases up to 70 nm for \( x = 2.0 \).

![Figure 4.3: HWL plot of different SCFSO compound](image)

Figure 4.3: HWL plot of different SCFSO compound
Table 4.1: Lattice parameters, crystalline size and micro-strain of SCFSO compound for different doping content

<table>
<thead>
<tr>
<th>x</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>c/a</th>
<th>V_{cell} (Å³)</th>
<th>Crystalline size, D(nm)</th>
<th>Strain ε</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>5.8769</td>
<td>23.0423</td>
<td>3.9208</td>
<td>689</td>
<td>62.61</td>
<td>61.73</td>
</tr>
<tr>
<td>0.25</td>
<td>5.8835</td>
<td>23.0941</td>
<td>3.9252</td>
<td>692</td>
<td>63.44</td>
<td>64.10</td>
</tr>
<tr>
<td>0.50</td>
<td>5.8892</td>
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<td>64.53</td>
<td>64.94</td>
</tr>
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<td>65.93</td>
<td>66.67</td>
</tr>
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<td>5.9014</td>
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<td>700</td>
<td>66.58</td>
<td>68.03</td>
</tr>
<tr>
<td>1.25</td>
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<td>23.2672</td>
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<td>703</td>
<td>67.56</td>
<td>69.44</td>
</tr>
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<td>1.50</td>
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<td>3.9417</td>
<td>706</td>
<td>68.52</td>
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<tr>
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<td>3.9458</td>
<td>715</td>
<td>69.62</td>
<td>71.94</td>
</tr>
</tbody>
</table>

4.2 FTIR Study

FTIR spectra obtained between 400-2000 cm\(^{-1}\) of the SCFSO compound is shown in Figure 4.4, and the observed band positions are listed in Table 4.2. The spectra show three distinct bands below 600 cm\(^{-1}\). The bands at around 421-412 cm\(^{-1}\) and 588-584 cm\(^{-1}\) are assigned to the Fe-O bending vibration and Fe–O stretching vibrations, respectively [77, 78]. The observed band at 542-524 cm\(^{-1}\) was assigned to the Sr–O bending vibration [79]. The formation of these bonds with corresponding frequency modes confirms the presence of metal-oxygen (M-O) stretching bands in hexaferrite structure [46]. All absorption bands broadened along with a shift to lower wavenumber with the increase in the Ca\(^{2+}\)-Sc\(^{3+}\) content in the compound. This shift in the band position to lower wavenumber is due to increased frequency of vibrations upon substitution of lighter Ca and Sc atom for heavier Sr and Fe atoms [80].
Figure 4.4: FTIR spectra of SCFSO compound for different doping content.

Table 4.2: FTIR peak position in wavenumber of SCFSO compound for different doping content.

<table>
<thead>
<tr>
<th>$x$ content</th>
<th>0.00</th>
<th>0.25</th>
<th>0.50</th>
<th>0.75</th>
<th>1.00</th>
<th>1.25</th>
<th>1.50</th>
<th>2.00</th>
</tr>
</thead>
<tbody>
<tr>
<td>FTIR peak positions, wavenumber (cm$^{-1}$)</td>
<td>421</td>
<td>424</td>
<td>419</td>
<td>417</td>
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<td>524</td>
<td></td>
</tr>
<tr>
<td>588</td>
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<td>581</td>
<td>584</td>
<td>584</td>
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<td></td>
</tr>
</tbody>
</table>

4.3 Thermal Analysis

Thermal studies were performed up to 823 K using modified thermogravimetric analyzer equipped with a permanent magnet. The Curie temperature ($T_c$), temperature at Hopkinson peak ($T_p$) and blocking temperature ($T_B$), obtained from thermogravimetric curves, Figure 4.5, are listed in Table 4.3.

As the temperature increases on the thermogravimetric curve, after a certain temperature, the susceptibility of the magnetic material increases sharply as a result of the sharp increase in mag-
netization occur. This temperature is known as blocking temperature, \( T_B \). Below \( T_B \), the superparamagnetic relaxation of material is negligible, and the magnetization vector always directed near easy axis along the direction of magnetization [81].

After the sharp increase in susceptibility at \( T_B \), the susceptibility of the material becomes maximum just below the curie temperature, \( T_c \), and a peak in the thermogravimetric curve appears. This phenomenon is known as Hopkinson effect [82]. Beyond the temperature corresponding to Hopkinson peak, the susceptibility of the material decreases sharply upto the curie temperature. There is a drastic fall in magnetocrystalline anisotropy of the material beyond the Hopkinson peak and a superparamagnetic relaxation take place. The sharp peak is associated with the transition of ferrimagnetic state to superparamagnetic state, as a result rapid decrease in magnetization occur [81].

![Figure 4.5: Thermo-magnetic plot of SCFSO measured using modified thermogravimetric analyzer](image)

**Figure 4.5:** Thermo-magnetic plot of SCFSO measured using modified thermogravimetric analyzer
Table 4.3: Thermal parameters of SCFSO compound for different doping content

<table>
<thead>
<tr>
<th>x content</th>
<th>0.00</th>
<th>0.25</th>
<th>0.50</th>
<th>0.75</th>
<th>1.00</th>
<th>1.25</th>
<th>1.50</th>
<th>2.00</th>
</tr>
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<td>$T_B$</td>
<td>763</td>
<td>735</td>
<td>709</td>
<td>681</td>
<td>646</td>
<td>617</td>
<td>586</td>
<td>562</td>
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<tr>
<td>$T_p$</td>
<td>769</td>
<td>741</td>
<td>713</td>
<td>688</td>
<td>652</td>
<td>626</td>
<td>592</td>
<td>568</td>
</tr>
<tr>
<td>$T_c$</td>
<td>772</td>
<td>746</td>
<td>716</td>
<td>693</td>
<td>655</td>
<td>634</td>
<td>601</td>
<td>580</td>
</tr>
</tbody>
</table>

4.4 Magnetic Properties

For magnetic characterization, the M–H hysteresis loops of the SCFSO samples were measured in the temperature range from 10 K to 300 K with an applied magnetic field of up to ±60 kOe. Detailed magnetic measurements were performed on $\text{Sr}_{1-x/12}\text{Ca}_{x/12}\text{Fe}_{12-x}\text{Sc}_x\text{O}_{19}$ ($x = 0.0, 0.5, 1.0, 1.5, \text{and} \ 2.0$). Figure 4.7 shows magnetization vs. field curves obtained in the temperature range of 10-300 K. The saturation magnetization, extracted from M vs. H curves, Figure 4.7, is plotted as a function of temperature in Figure 4.8. It is evident that the saturation magnetization, $M_s$, value increases with the decrease in temperature. A maximum is observed in the low-temperature region for $x = 1.5$ and 2.0 samples. Similarly, the temperature-dependent spontaneous magnetization curves obtained at a fixed field of 20 kOe show a maximum for $x = 1.5$ and 2.0. These maxima can be attributed to the temperature $T^*$ of transition from a collinear ferrimagnetic structure to a conical one [83]. Temperature $T^*$ decreases from $T \approx 91$ K at $x = 2.0$ to $T \approx 82$ K at $x = 1.5$ with $T^*$ disappearing for samples $x < 1.5$. At low temperatures, the freezing of the magnetic moments under a magnetic field could lead to a transverse conical structure. An increase in the temperature may release the magnetic moments back to the longitudinal conical structure, as shown in Figure 4.9. Using elementary approximation, the cone opening angle can be approximated as $\cos \Theta = M(\text{cone})/M(\text{ferri})$, where $M(\text{cone})$ and $M(\text{ferri})$ are the extrapolated value at 5K in the plot of Figure 4.9. The estimated value of $\cos \Theta = 29.68$ and 37.80 for $x = 1.5$ and 2.0 samples, respectively. For high doping content, the change in
spin arrangement from collinear to conical is the result of the temperature dependence of the exchange energy, most likely being induced by the increased lattice distortion and increased random substitution at Fe$^{3+}$ ion sites. Evidence of similar transition temperatures reflecting spin reconfigurations has been observed for Sc doped BaFe$_{10.2}$Sc$_{1.8}$O$_{19}$ and SrFe$_{10.2}$Sc$_{1.8}$O$_{19}$ [84], SrSc$_{x}$Fe$_{12-x}$O$_{19}$ [47], BFSO [85] and BaTi$_{x}$Co$_{2}$Fe$_{12-2x}$O$_{19}$ [86, 87] compounds. An Ab-initio study on magnetic anisotropy change in SrTi$_{x}$Co$_{2}$Fe$_{12-2x}$O$_{19}$, authors suggest that the substitution at the 4f2 site leads to the reduction of uniaxial magnetic anisotropy which could facilitate the formation of conical magnetic structure [88]. As evident from the Mossbauer analysis in this study, the preferred substitution of Sc$^{3+}$, in fact, is occurring at the 4f2 site, which could be the reason for the observed reduction in the uniaxial magnetic anisotropy leading to the formation of the conical magnetic structure. Figure 4.10 depicts the T-x phase diagram of Sr$_{1-x/12}$Ca$_{x/12}$Fe$_{12-x}$Sc$_{x}$O$_{19}$ compound showing the transition of conical, ferrimagnetic (FIM) and paramagnetic (PM) phases. Where, the transition temperature T$^*$ is calculated from the magnetization curve at 20 Koe (Figure 4.9) and curie temperature is calculated from thermomagnetic plot (figure 4.5).

Furthermore, M$_s$ value decreases from 76 emu/g for x = 0.0 to 58 emu/g for x=2.0, a net reduction of 23% at room temperature. The rate of decrease in M$_s$ value is only -9 emu/g per x substitution. However, this rate of decrease is much slower than that observed, for example, in the case of Ca-Al doped system,Sr$_{1-x/12}$Ca$_{x/12}$Fe$_{12-x}$Al$_{x}$O$_{19}$ [63], where the M$_s$ value reached 38 emu/g at x=2 with a rate of decrease of -14.1 emu/g per x substitution. The decrease in saturation magnetization with substitution could occur from (1) the magnetic dilution effect arising from the decrease in the molar magnetic moment caused by replacing Fe$^{3+}$ (4.36 µB) with a non-magnetic Sc$^{3+}$ ion, (2) the lattice distortion, which could weaken Fe$^{3+}$-$O^{2-}$-Fe$^{3+}$ superexchange interactions, and (3) decrease in the number of superexchange pairs upon substitution.
for Fe$^{3+}$. For the M-type hexaferrite, the Fe$^{3+}$ ions are located at five distinct crystallographic sites, including the 12k↑, 2a↑, and 2b↑ sites and the 4f1↓ and 4f2↓ sites. These sites have distinct site symmetry of which, 2b has bi-pyramidal, 12k, 2a, and 4f2 has octahedral, and 4f1 has tetrahedral site symmetry. According to Pauling’s rule, the atomic size difference most likely decides the preference of Sc$^{3+}$ ion for a particular site. For instance, the Fe$^{3+}$ ion has different ionic radii for octahedral, bi-pyramidal, and tetrahedral sites: 0.65 Å, 0.51Å and 0.49Å, respectively [89]. While Sc$^{3+}$ ionic radii in octahedral sites is 0.745Å[46]. Thus, comparing the ionic radius ratio at octahedral site for Sc$^{3+}$ (cation) to O$^{2−}$ (R(Sc$^{3+}$/O$^{2−}$ ∼ 0.745Å/1.4 Å= 0.532) [46], as per the Pauling’s rule, Sc$^{3+}$ will prefer the octahedral sites, either 12k, 2a or 4f2. A rather modest decrease in Ms value with x content indicates that the substitution of Sc$^{3+}$ is most likely favored at octahedral sites with the spin-down configuration. This fact is later corroborated via Mossbauer spectral analysis. On the other hand, in Ca-Al doped Sr$_{1−x/12}$Ca$_{x/12}$Fe$_{12−x}$Al$_{x}$O$_{19}$, the preferred substitution site for Al$^{3+}$ is reported to be at the 12k and 2a sites [90]. This could be the reason for the rapid deterioration of Ms value in Ca$^{2+}$-Al$^{3+}$ substituted compound as the substitution ion removes Fe$^{3+}$ from the majority spin-up sites.
Figure 4.7: Hysteresis loops of Sr$_{1-x/12}$Ca$_{x/12}$Fe$_{12-x-z}$Sc$_{z}$O$_{19}$ compound in the temperature range 10K-300K for (a) $x = 0.0$, (b) $x = 0.5$, (c) $x = 1.0$ (d) $x = 1.5$, and (e) $x = 2.0$
**Figure 4.8**: Temperature dependent saturation magnetization, $M_s$ of SCFSO compound for different doping content.

**Figure 4.9**: Temperature dependent magnetization of SCFSO compound for different doping content at the applied field of 20 Koe
Figure 4.10: T-x phase diagram of \(\text{Sr}_{1-x/12}\text{Ca}_{x/12}\text{Fe}_{12-x}\text{Sc}_x\text{O}_{19}\) compound, which reflects the transition of paramagnetic (PM) phase to ferrimagnetic (FIM) and conical phase for the applied field of 20 KOe

The average coercive fields \((H_c)\) and remanent magnetization \((M_r)\) extracted from the hysteresis loops were quantified as \(H_c = (H_{c1} - H_{c2})/2\), where \(H_{c1}\) and \(H_{c2}\) are the left and right coercive fields and \(M_r = |M_{r1} - M_{r2}|/2\) where \(M_{r1}\) and \(M_{r2}\) are the magnetizations with positive and negative points of intersection with \(H = 0\), respectively. The calculated values of \(H_c\) as a function of temperature are plotted in Figure 4.11 and are listed in Table 4.4. The room temperature coercivity decreases from 5458 for \(x = 0.0\) to 370 for \(x = 2.0\) sample. The coercivity field, \((H_c)\) value refers to the field intensity value required to reduce the magnetization of a sample to zero after the sample has been magnetized. Being an extrinsic property, the value of \(H_c\) depends on the variations in the stoichiometry, crystallinity, and anisotropy. In addition, the magnetic anisotropy depends on the magnetocrystalline, shape, and the induced magnetic, and stress anisotropies. The observed decrease in coercivity with \(\text{Ca}^{2+}-\text{Sc}^{3+}\) substitution is as-
cribed mainly to the decrease in the crystalline anisotropy field. This decrease in the anisotropy field arises from the slow change of the magnetization axis from the c-axis to the basal plane [11, 91, 92]. It is reported earlier that the crystalline anisotropy field contribution of 2b and 4f2 sublattice sites weighs more than any other sites in hexaferrite [93, 94]. Since the Sc substitution SCFSO compound mainly occurs at the 4f2 site, as corroborated via Mossbauer study, the observed reduction in $H_c$ with $x$ is due to the reduced contribution to crystalline anisotropy field at the 4f2 site.

Figure 4.11: Temperature dependent coercivity of SCFSO compound for different doping content
A noticeable feature observed in Figure 4.11 is the temperature dependency of coercivity. In the temperature region above and below $T= 100K$, the coercivity increases for all samples. As it is evident for this material from Table 4.4, for example, coercivity at room temperature for $x = 1.5$ samples is $H_C (300 K) = 360$ Oe. However, it decreases as the temperature is reduced, reaching a minimum of around $100 K$, $H_C (100K) = 321$ Oe. Finally, $H_C$ increases again at lower temperatures reaching a maximum value of $749$ Oe at $10K$. This kind of temperature-dependent coercivity behavior is more or less reflected in all samples. It is possible that due to the incommensurate spin arrangement and the stronger anisotropy, $H_C$ attains higher value than the room temperature values. While lower $H_C$ values were observed at $10K$ for samples, $x = 0.0$, 0.5, and 1.0 than at the room temperature, again due to the incommensurate spin arrangement and due to weaker anisotropy. The lowering of coercivity $H_C$ at around $100K$ is accompanied by a reduction in $M_r/M_s$ ratio, Figure 4.13, for $x =1.5$ and 2.0 samples. Interestingly similar
temperature behavior has been reported in the case of $\varepsilon$-Fe$_2$O$_3$, where based on XMCD and Mossbauer study, authors conclude that at the temperature range where the transition from the commensurate to incommensurate magnetic state begins, a reduction in Fe orbital magnetic moment, $m_{\text{orb}}$, occurs due to the lattice distortion, that weakens spin-orbit interactions which leads to a decrease in the anisotropy constant and the reduction of $H_C$ [95, 96]. It is a known fact that transition metal oxides present weak spin-orbit coupling due to the so-called orbital quenching [97]. The decrease in the orbital magnetic moment was attributed to the reduction in electron transfer between Fe and O ions. After moving through the transition temperature, the magnetic orbital moment could recover leading to an increase in the coercivity at the low temperature. Furthermore, overall low coercivity and $M_r/M_s$ ratio displayed by samples, $x = 1.5$ and $2.0$, could be attributed to the weakening of spin-orbit coupling due to quenching of Fe orbital moments due to large lattice distortion ensuing from substantial substitution.

![Figure 4.13: Temperature dependent $M_r/M_s$ of SCFSO compound for different doping content](image)
The “Law of approach” was applied to first quadrant M vs. H curve to determine magnetocrystalline anisotropy K1. The magnetization near the saturation \( M_s \) can be written as \([98]\),

\[
M = M_s \left( 1 - \frac{A}{H} - \frac{B}{H^2} \right) + \kappa_{eff} H
\]

Where \( M \) is the magnetization, \( H \) is the applied magnetic field, and \( M_s \) is the saturation magnetization. The term \( \kappa H \) represents the field-induced increase in the spontaneous magnetization of the domains. This term is very small at a temperature well below the Curie temperature and may be neglected. The term “A” is generally interpreted as due to microstrain and ignored in the high field region, and “B” as due to crystal anisotropy (anisotropy parameter) for hexaferrite, with hexagonal crystal, is defined as \( B = H_a^2 / 15 \), where \( H_a \) is crystalline anisotropy field \([99]\). The effective magnetic anisotropy constant \( K_1 \) is obtained from \( K_1 = (H_a . M_s) / 2 \). Where \( M_s \) in emu/g was obtained by assuming the average density of 5.3g/cm\(^3\) for SrFe\(_{12}\)O\(_{19}\). Table 4.4 lists the value of \( K_1 \) as a function of substitution and temperature, while the temperature dependence variation of \( K_1 \) is plotted in figure 4.14. Corroborating the coercivity behavior, the magnetic anisotropy K1 was observed to decrease for \( x = 0.0, 0.5 \) and 1.0 below \( x < 100K \) while increases significantly for \( x = 1.5 \) and 2.0 samples. As discussed above, the change in magnetocrystalline anisotropy occurring due to variation in Fe orbital moment could be responsible for the observed temperature dependence of \( K_1 \).
**Figure 4.14:** The plot of magnetocrystalline anisotropy of SCFSO compound for different doping content

**Table 4.4:** Temperature variation of magnetic parameters of SCFSO compound for different doping content

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<th>M_s (emu/g)</th>
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4.5 Mossbauer Study

To determine the preferred occupancy of Sc$^{3+}$ ions, Mossbauer spectra were obtained at room temperature. The fitted spectra are shown in Figure 4.15. The spectra were the least square fitted using the model suggested by Evans et al. for MFe$_{12}$O$_{19}$ (M=Sr, Ba) hexaferrite [100]. The crystal symmetry involving Fe-O bond lengths and Fe-O-Fe bond angles between the magnetic ions in the hexaferrite lattice lead to superexchange interactions, which splits the magnetic structure of M-type hexaferrite into spin-up and spin-down with five inequivalent sublattices viz. 12k, 4f2, 4f1, 2a and 2b. Mossbauer spectra were fitted with five distinct
sextets assigned to the octahedral (12k, 4f2, and 2a) sites, the tetrahedral (4f1) site, and the
tetragonal bipyramidal (2b) iron sites. **Table 4.5** shows the coordination number of the nearest
neighboring sites for iron and strontium in SFO and the corresponding mean distances from
each other.

**Table 4.5:** Number of nearest Fe$^{3+}$ and Sr$^{2+}$ neighbors and corresponding mean distances (in
nm) for each Fe$^{3+}$ site in the crystal structure of the m-type phase in SFO [56]

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For the doped compounds, 12k site was split between 12k1 and 12k2 sites. The 12k site
is surrounded by a maximum of four 12k sites at a distance of 0.290 nm and two 4f2 sites
at a distance of 0.349 nm. With the increase in substitution at 4f2 site, as discussed below,
the 12k site observes two different environments, each with magnetic and non-magnetic atom
distribution. Because of this, the 12k site sextet was split with two, with 12K1 representing
a magnetic environment and 12K2 representing a nonmagnetic environment around the 12k
site. Thus, the Mossbauer spectra for the doped compound were fitted with six sextets and
one doublet. A paramagnetic contribution is accounted by using a doublet to justify for the
extra absorption at the center of the spectrum. This contribution, whose relative intensity is
between 2%-7%, is attributed to Fe atoms in Sr$_{1-x/12}$Ca$_{x/12}$Fe$_{12-x}$Sc$_x$O$_{19}$ as paramagnetic im-
purities. All hyperfine parameters of 12k2 sites are close to 12k1 sextet values, expect its
hyperfine field value is observed to be around 340 kOe. The site occupancy of 12k, 4f1, 4f2, 2a and 2b sites were observed to be in the ratio of 50:17:17:8:8 for pure SrFe$_2$O$_{19}$ sample. Due to the increased diamagnetic cation distribution, the line broadening of absorption lines was observed with reduced goodness of fit at higher x content. The hyperfine parameters viz. hyperfine field (HF, kOe), isomer shift (IS, mm/s), quadrupole shift (QS, mm/s) were obtained by fitting Mossbauer data under the assumption that the recoil-free fractions for each site do not change too much with the doping. The observed relative magnitude of hyperfine parameter order was $HF(12k) < HF(2b) < HF(4f1) < HF(2a) < HF(4f2)$ and isomer shift parameter was $\delta(4f1) < \delta(2a) < \delta(12k) < \delta(4f2) < \delta(2b)$. The extracted hyperfine parameters are listed in Table 4.6 and are plotted as a function of x content in Figure 4.16(a).

Considering Figure 4.16(d), the relative area plot, it is evident that the area of the 4f2, a site with down spin, is reduced with increasing x content. This trend in the observed for the area of 4f2 site shows that Sc$^{3+}$ preferably occupies 4f2 site. On the other hand, close observation for the 12k site shows a decreasing trend in area for 12k1 site and an increasing trend for 12k2 site with x. However, the combined area of 12k1 and 12k2 site remains close to 50% of the total area. Following earlier reports [22, 101, 102], the observed splitting of the 12k component is induced by the substitution of Fe$^{3+}$ ions by Sc$^{3+}$ ions at the 4f2 site.

Now replacement of Fe$^{3+}$ from the 4f2 site with Sc$^{3+}$ ions should result in a net decrease in the number of down-spin Fe$^{3+}$, which indicates an overall increase in the net magnetic moment of the compound. However, referring to Figure 4.8, the RT saturation magnetization, $M_s$, appears to decrease slowly with the increase in the x content. The reduction in $M_s$, despite an increase in the number of up-spins with 4f2 substitution, could be ascribed to the magnetic dilution effect upon substitution for Fe$^{3+}$ with non-magnetic ion and reduction in the strength and number of Fe$^{3+}$-$O^{2-}$-Fe$^{3+}$ exchange interactions. The decrease in the exchange interaction
strength could also arise from the lattice distortion upon substitution $\text{Ca}^{2+}$-$\text{Sc}^{3+}$ ions in the lattice. This fact is also evident from the hyperfine field plot, Figure 4.16(a). Only a 5\% reduction in the hyperfine field for 12k site while an 8\% reduction in 4f2 hyperfine field value was observed at a maximum substitution of $x = 1.5$. Overall, weight average hyperfine field value shows only a 7\% reduction at $x = 1.5$ substitution. The effect on the hyperfine value of 12k site due to substitution at 4f2 sites is weak because the 12k site is located at a greater distance from the 4f2 site ($12k-4f2 \sim 0.349 \text{ nm}$) as compared to 12k ($12k-12k \sim 0.290$).

The isomer shift plot as a function of $x$ is shown in Figure 4.16(b). The isomer shift values in the range from 0.26-0.43 corresponded to the characteristic charge states of $\text{Fe}^{3+}$. The s-electron charge density usually influences isomer shift value at the $\text{Fe}^{3+}$ nucleus. The change in s-electron density at $\text{Fe}^{3+}$ site can occur due to changes in electron environment (density) or lattice distortion or both. It is evident from Figure 4.16(b) that the isomer shift value for all sites almost remain unaffected or slightly increased except for the site 2b. The isomer shift value for the site 2b increases rapidly with the $\text{Ca}^{2+}$-$\text{Sc}^{3+}$ substitution. The observed increase in isomer shift value of the 2b site may arise from the increase in $\text{Ca}^{2+}$ substitution at the $\text{Sr}^{2+}$ site. The closest sites of $\text{Sr}^{2+}$ sites are 12k, 4f2, and 2b. The 2b sites are located in the same plane as $\text{Sr}^{2+}$ ions (at a distance of 0.340 nm), while the 4f2 and 12k sites are located in the adjacent planes at nearly the same distance from $\text{Sr}^{2+}$ viz. $\text{Sr}^{2+-12k} \sim 0.365 \text{ nm}$ and $\text{Sr}^{2+-4f2} \sim 0.366 \text{ nm}$ [36, 21]. $\text{Ca}^{2+}$ with overall fewer electrons (Ar[4s$^2$]) as compared to $\text{Sr}$ (Kr[5s$^2$]) has a positive effect on the isomer shift, that is increased substitution of $\text{Ca}^{2+}$ reduces the net s-electron charge density at the 2b site, which in turn increases the isomer shift value at the 2b site. The overall weighted average isomer shift increases with the $\text{Ca}^{2+}$-$\text{Sc}^{3+}$ content due to a decrease in electron density with the volume expansion of the unit cell. Furthermore, the increase in isomer shift value with $\text{Ca}^{2+}$-$\text{Sc}^{3+}$ substitution also reflects the increased ionicity.
of the ions, which could be related to the decease of \(m_{\text{orb}}\) in light of the study by Sadoc et al. [95]. The fading of \(m_{\text{orb}}\) could lead to the increased spin non-collinearity and weakening of spin-orbit and hence magnetocrystalline anisotropy.

Similarly, the quadrupole shift values for all sites remain largely invariant with the substitution, Figure 4.16(c), except for the site 2b. The high quadrupolar shift of the 2b site is related to the asymmetric character of its trigonal bipyramidal site symmetry [103]. The change in 2b site quadrupole site value reflects the change in electric field gradient due to the variation in its electronic environment, mainly due to \(\text{Ca}^{2+}\) substitution at the \(\text{Sr}^{2+}\) ions, and concomitant lattice distortion with 4f2 substitution along the c-axis of the lattice (Figure 4.16(c)). To sum up, \(\text{Ca}^{2+}\)-\(\text{Sc}^{3+}\) substitution reflects an important change in hyperfine parameters of 4f2 and 2b sites, because they have three Sr nearest neighbors, and less important change at the 12k, because it has only one \(\text{Sr}^{2+}\) nearest neighbor [63]. A noticeable fact to observe is a continuous and significant increase of the quadrupolar shift of the 2b site. This is due to the continuous increase of the c lattice constant with \(x\), which decreases the symmetry of the oxygen bipyramid of the 2b site [104].
Table 4.6: RT Hyperfine parameters extracted from fitting Mossbauer spectra from Figure 4.15

<table>
<thead>
<tr>
<th>x</th>
<th>12k (↑)</th>
<th>12k1</th>
<th>4f1 (↓)</th>
<th>4f2 (↓)</th>
<th>2a (↑)</th>
<th>2b (↑)</th>
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<td>0.274</td>
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Figure 4.15: Mossbauer spectra of SCFSO compound for different doping content obtained at room temperature.
Figure 4.16: Mossbauer analysis of SCFSO compound for different doping content; (a) hyperfine field, (b) isomer shift, (c) quadrupole shift and (d) relative area.
Chapter 5

Conclusion

The M-type Ca\(^{2+}\)-Sc\(^{3+}\) doped hexaferrites Sr\(_{1-x/12}\)Ca\(_{x/12}\)Fe\(_{12-x}\)Sc\(_x\)O\(_{19}\) were successfully synthesized employing auto-combustion method. The important results obtained from this study are summarized below.

1. The co-doping Ca\(^{2+}\)-Sc\(^{3+}\) results the increase of lattice parameters and hence the volume expansion of the unit cell.

2. The crystalline size of the compound increased, whilst the micro-strain of the material decreased with the substitution of Sr\(^{2+}\)-Fe\(^{3+}\) ions by Ca\(^{2+}\)-Sc\(^{3+}\) ions.

3. The shift in wavenumber of Fe-O bending vibration as well as stretching vibration and Sr-O stretching vibration in FTIR spectra further confirms the well substitution of doped ions within the M-type hexagonal structure.

4. The decrease in curie temperature, \(T_C\), and saturation magnetization at room temperature on the co-doping is attributed to the weakening of superexchange interaction and magnetic dilution.

5. The spontaneous magnetization as well as the saturation magnetization increased with
the decrease in temperature. The maximum value of magnetization at low temperature for higher doping content can be attributed to the transition temperature, \( T^* \), from collinear ferrimagnetic phase to the conical phase.

6. The magnetocrystalline anisotropy of the compound is affected by weakening of the orbital magnetic moment with the replacement of Fe\(^{3+}\) ion at 4f2 site, and influence of Ca\(^{2+}\) ion in 2b site. As a result, large decrease in coercivity, from 5458Oe to 370Oe, at room temperature is observed with the co-doping of Ca\(^{2+}\)-Sc\(^{3+}\) ions.

7. In the observation of temperature dependent coercivity curve, the minima at low temperature is due to the quenching of orbital magnetic moment at transition temperature from collinear ferrimagnetic phase to conical phase. The coercivity increased on further decreasing the temperature with the recovery of orbital magnetic moment.

8. The reduction of relative area plot for 4f2 site and, splitting of 12k sites into magnetic and non-magnetic sites in mossbauer study is also an evidence of Sc\(^{3+}\) and Ca\(^{2+}\) ion substitution in respective sites.

9. The rapid increase of isomer shift and high quadrupole shift for the 2b site with Ca\(^{2+}\)-Sc\(^{3+}\) substitution may rise form the increase of Ca\(^{2+}\) content on Sr\(^{2+}\) site.

In conclusion, the strontium hexaferrite is converted into soft magnetic material retaining its high saturation magnetization with the substitution of Sr\(^{2+}\)-Fe\(^{3+}\) ions by Ca\(^{2+}\)-Sc\(^{3+}\) ions. The material became more soft magnet for higher concentration (less than 400 Oe for x=2) without much reduction in saturation magnetization.
Future Work

Although a detail study on structural, magnetic and mossbauer characteristics of the SCFSO has been done in this work, further study can be done in future as listed below.

1. Dielectric, microwave and magnetic hyperthermia properties of SCFSO.

2. Effect of silica and reduces graphene oxide (rGO) coating on hexaferrite materials.

3. Polymer synthesis to tune the morphology of the hexaferrite material.

4. Effect of co-doping Sc and Al on strontium hexaferrite.
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