CHAPTER III

Synthesis and Characterization of Strontium Hexaferrite Nanoparticles: SrFe$_{12}$O$_{19}$
3.1 Introduction

The strontium hexaferrite (SrFe$_{12}$O$_{19}$) is a hard magnetic material with magnetoplumbite structure [79]. This material has attracted much attention in past few decades due to their scientific and technological applications in the region of microwave to radio frequencies. This is due to high magnetocrystalline anisotropy, high Curie temperature, high electrical resistivity, high dielectric constant as well as high magnetization and coercivity [80-83]. The dielectric and magnetic properties of ferrite materials in the nano regime are significantly different from their bulk counterparts. M-type SrFe$_{12}$O$_{19}$ has a space group P6$_3$/mmc and often expressed as RSR*S*. The S and R block stands for spinal and hexagonal structure. R* and S* are the blocks obtained by 180° rotation of R and S with respect to c-axis having equivalent atomic arrangements [84,85]. The hexagonal hard ferrite contains two 64 ions per unit cell on 11 different sites. The Fe$^{3+}$ ions are distributed over five distinct crystallographic sites, three octahedral sites (12k, 2a, 4f$_2$), one tetrahedral site (4f$_1$) and trigonal bipyramidal site (2b) [86]. These crystallographic sites are coupled by O$^{2-}$ ions to form collinear ferrimagnetic order and superexchange interaction between Fe$^{3+}$-O$^{2-}$-Fe$^{3+}$. The superexchange interaction and magnetocrystalline anisotropy are strongly depends upon the site occupation and different crystallographic site construct different role to dielectric and magnetic properties.

In this chapter, citrate precursor technique for the synthesis of SrFe$_{12}$O$_{19}$ nanoparticles has been used. This method allows the subsequent crystallization to occur at low temperature, leading to formation of nanoparticles due to intimated mixing of staring materials on ionic levels and low cost technique for the mass production. The reaction kinetics for the prepared SrFe$_{12}$O$_{19}$ nanoparticles has been examined through differential thermal analysis using non-isothermal model. The effect of calcination temperature and crystallinity on the structural, morphological, dielectric and magnetic properties has been examined. Various parameters such as activation energy, particle size, dielectric constant, magnetization and coercivity have been calculated.

3.2 Experimental
3.2.1 **Synthesis and characterization: SrFe\textsubscript{12}O\textsubscript{19}**

Synthesis of strontium hexaferrite nanoparticles was accomplished in an aqueous reaction matrix containing ferric nitrate nonahydrate, strontium nitrate, lanthanum nitrate hexahydrate and citric acid monohydrate as discussed in chapter 2. DTA (EXSTAR TG/DTA 6300), XRD, FTIR, SEM and VSM have been used to study the effects of substitution on various properties.

3.3 **Results and discussion**

3.3.1 **Thermal analysis**

The trace of DTA/DTG/TG for a precursor powder at the heating rate of 5 K/min in air atmosphere has been shown in Figure 3.1a

![Graph showing TG/DTG/DTA curves](image)

**Figure 3.1a:** TG/DTG/DTA curves of the precursor of strontium hexaferrite at heating rate of 5 K/min.
**Figure 3.1b:** TG/DTG/DTA curves of the precursor of strontium hexaferrite at heating rate of 10 K/min.

**Figure 3.1c:** TG/DTG/DTA curves of the precursor of strontium hexaferrite at heating rates of 50 K/min.

During the thermal analysis, it has been seen from the TG-curve that the weight loss of a precursor happens in three distinct steps in the temperature range from room
temperature to 1430°C. The steps occurred at 74-184°C, 330-409°C and 640-942°C respectively. The precursor exhibited a rapid weight loss up to 400°C indicating the hydrosopic nature. This weight loss can be attributed to the removal of water residues from macro and meso pores [87]. In temperature range from 400°C to 942°C an additional weight loss (few amount) of a precursor has been observed. This can be credited to the combustion and decomposition of citrate precursor, and to the reaction of intermediates [88,89]. The DTA-curve in Figure 3.1a depicts both exothermic and endothermic effects of a precursor in the temperature range of 25-1430°C. The DTA results are consistent with the results of TG/DTG. The existence of an exothermic peak at the point of maximum weight loss i.e. 336°C (DTG) is related to decomposition of a precursor composed of citrate-nitrate gel. The formation of hexaferrite phase is not the single step reaction as observed in the case of spinal ferrite. Thermal analysis reveals that the formation takes place in steps by means of endothermic reaction [90]. The existence of an endothermic peak at 824°C corresponds to the formation of SrF$_{12}$O$_{19}$ as well as intermediate phase. This has also been confirmed by the XRD analysis of a precursor powder calcinated at 700°C and 800°C in air atmosphere. Above the second endothermic peak no further weight loss will be observed in TG-curve indicating the completion of reaction [91].

To aid the further investigation of crystallization process, similar analysis have been carried out under same conditions except the heating rates, 10 and 50 K/min presented in Figure 3.1b and 1c respectively. Similar behavior has been observed for all the measurements with slight shift of DTA peaks to upward direction. It is concluded that for the different heating rates, there are different temperatures for the completion of reaction. The lower the heating rate; lower will be the reaction temperature. The present thermal investigations of a precursor powder at different heating rates will aid in the selection of reaction temperature with proper heating rate for formation of single phase strontium hexaferrite nanoparticles.

There are several models available for calculation of activation energy of crystallization process based on isothermal and non-isothermal processes. In present work we report, the kinetics of crystallization based on non-isothermal kinetic models i.e. Kissinger’s method, Augis and Bennett approximation and Matusita-Sakka theory.
The Kissinger expressed the activation energy of the crystallization process of the prepared sample at crystallization temperature for the particular heating rates following equation using the Arrhenius and rate of crystallization equation:

$$\ln \frac{\beta}{T_C^2} = \frac{E}{RT_C} + \ln \frac{AR}{E}$$  \hspace{1cm} (1)

where $\beta$ is the heating rate (K/min), $T_C$ is the maximum peak temperature of DTA curve.

$E$ is the activation energy for the crystallization process, $R$ is the universal gas constant (8.314 J mole$^{-1}$K$^{-1}$) and $A$ is the pre-exponential factor.

![Figure 3.2a: Kissinger's plot for the crystallization process of SrFe$_{12}$O$_{19}$ precursor powder.](image)

The plots of $\ln(\beta/T_C^2)$ against $\ln(1000/T)$ at different heating rates gives a straight line known as Kissinger’s plot (Figure 3.2a). Thus, the activation energy value has been obtained from slope of the straight line of these plots. The calculated value of activation energy for crystallization process of SrFe$_{12}$O$_{19}$ is, 157 KJ/mol. Activation energy have been verified by employing Augis-Bennett approximation (Figure 3.2b) Matusita-Sakka theory (Figure 3.2c) and non-isothermal kinetic models. The
activation energy values determined from these models are in close resemblance to each other as shown in Table 3.1.

![Graph](image)

**Figure 3.2b:** Augis and Bennett plot for the crystallization process of SrFe$_{12}$O$_{19}$ precursor powder.

![Graph](image)

**Figure 3.2c:** Matusita-Sakka plot for the crystallization process of SrFe$_{12}$O$_{19}$ precursor powder.
Table 3.1: Crystallization temperature ($T_c$) and activation energy for crystallization temperature ($E$) of SrFe$_{12}$O$_{19}$ at different heating rates.

<table>
<thead>
<tr>
<th>Heating rate (K)</th>
<th>5</th>
<th>10</th>
<th>50</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_c$(K)</td>
<td>144</td>
<td>1589</td>
<td>1692</td>
</tr>
<tr>
<td>$E$ (Kissinger) /kJmol$^{-1}$</td>
<td></td>
<td>152</td>
<td></td>
</tr>
<tr>
<td>$E$ (Augis and Bennett) /kJmol$^{-1}$</td>
<td></td>
<td>183</td>
<td></td>
</tr>
<tr>
<td>$E$ (Matusita) /kJmol$^{-1}$</td>
<td></td>
<td>170</td>
<td></td>
</tr>
</tbody>
</table>

3.3.2 Structural analysis

3.3.2.1 X-ray diffraction

Crystallization process has been interpreted by means of X-ray diffraction studies; for this the precursor powder ($A_0$) has been further calcinated for different temperatures 700°C ($A_1$), 800°C ($A_2$) and 1200°C ($A_3$). The X-ray diffraction patterns of precursor and calcinated powders have been presented in Figure 3.3(a-d).

![X-ray diffraction patterns](image)

**Figure 3.3**: X-ray diffraction patterns of SrFe$_{12}$O$_{19}$ (a) precursor powder and sample calcinated at (b) 700°C, (c) 800°C, (d) 1200°C.
The diffraction pattern of a precursor (Figure 3.3a) shows broad peaks, indicating the presence of nanocrystalline phase. This can be attributed to the existence of organic compounds in precursor powder [95]. As the calcination temperature of precursor powder increases, the diffraction peaks become narrower and intense, representing enhancement of crystallite size and crystallinity respectively. The diffraction patterns of \( A_1 \) and \( A_2 \) samples shows the formation of ferrite phase along with the presence of secondary phases such as \( \alpha \) (\( \gamma \))-Fe\(_2\)O\(_3\) and SrFe\(_2\)O\(_4\) [96-98]. The existence of secondary phases indicates the incomplete reaction between Fe\(^{3+}\) and Sr\(^{2+}\) under these synthesis conditions. The presence of \( \alpha \)-Fe\(_2\)O\(_3\) phase, indicates the system need longer and high calcination temperature for the completion of reaction. This is because, the crystal structure of \( \alpha \)-Fe\(_2\)O\(_3\) is orthorhombic hexahedron and difficult to convert into ferrite phase as compared to \( \gamma \)-Fe\(_2\)O\(_3\) [99]. The sample \( A_3 \) (Figure 3.3d) represents the sharp, intense and narrower diffraction peaks, and disappearance of secondary phase indicating the formation of single phase M-type hexaferrite with high crystallinity. All the apparent peaks (110), (114), (107), (203), (205), (206), (208), and (303) in diffraction pattern have been similar to standard (JCPDS: 80-1198) diffraction pattern of hexagonal ferrite. The diffraction peak broadening technique has been employed for most intense (114) peak to calculate the crystallite size. The crystallite size for SrFe\(_{12}\)O\(_{19}\) nanoparticles has been calculated using (eq. 8) Scherrer's formula [100,101]. The calculated crystallite size has been shown in Table 3.2 and it can be seen that the crystallite size increases with the increasing calcination temperature in the direction parallel to c-axis (114).

Table 3.2: Variation of crystallite size with different calcination temperatures.

<table>
<thead>
<tr>
<th></th>
<th>Standard 20° (°)</th>
<th>Obscured 20° (°)</th>
<th>Miller indices (MI)</th>
<th>D (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>700°C</td>
<td>34.19</td>
<td>34.08</td>
<td>(114)</td>
<td>26.80</td>
</tr>
<tr>
<td>800°C</td>
<td>34.19</td>
<td>34.13</td>
<td>(114)</td>
<td>30.77</td>
</tr>
<tr>
<td>1200°C</td>
<td>34.19</td>
<td>34.32</td>
<td>(114)</td>
<td>69.28</td>
</tr>
</tbody>
</table>
The sample A3 stands for maximum crystallite size but still smaller than the single domain crystal particle size ~270 nm as reported earlier [102,103]. The crystallinity and crystal growth of nanoparticles are closely related to calcination. The growth of crystallite size with increasing calcination temperature can be accredited to the fusion of nanoparticles with each other by melting their surfaces. The fusion of nanoparticles well below their melting point is owing to weak binding of surface atoms result in sharp decrease of surface melting point [104,105].

3.3.2.2 Mid-Infrared spectral region analysis

The Mid-IR spectra of a precursor and calcinated powder are shown in Figure 3.4(a-d).

![Figure 3.4: Mid-IR spectra of SrFe12O19 (a) precursor powder and sample calcinated at (b) 700°C, (c) 800°C, (d) 1200°C.](image)

FTIR-spectrum of a precursor in Figure 3.4(a) shows that the characteristic bands have appeared in the range of 3200-3270 cm\(^{-1}\) and 1638 cm\(^{-1}\). These bands are
assigned to be hydroxyl and carboxyl group of citric acid respectively [106,107]. The absorption peak at 1059 cm\(^{-1}\) corresponds to C-O stretching vibration of C-O-H band. Frequency bands near 1460.37 cm\(^{-1}\), 1383.59 cm\(^{-1}\) and 858.82 cm\(^{-1}\) are attributed to nitrate ions [108]. After the calcination of precursor at 700°C, peak appears at 1465.72 cm\(^{-1}\) in Figure 3.4(b) and is ascribed to absorption of strontium carbonate bands [109,110]. The observed absorption bands in the range 400-800 cm\(^{-1}\) are due to iron oxide [98,111-113]. The absorption band at 2916.52 cm\(^{-1}\) arise from Fermi resonance between stretching vibration of O-H band and combination of frequency of stretching vibration of C-O and bending vibration of C-O-H band [89]. The metal-oxygen stretching bands are prominent and other bands start decreasing but still persist (Figure 3.4c) after heating the precursor powder at 800°C. Characteristic bands of CO\(_2^+\) group and NO\(_3^-\) ions have been diminished after heating the sample to 1200°C which shows the completion of redox reaction in which citrate ions act as reductant and nitrate ions as oxidant [106,107]. A new set of completely resolved bands have been appeared (Figure 3.4d) at wavenumber of 435.05, 551.04 and 594.26 cm\(^{-1}\) and identified as stretching vibration of metal-oxygen bond indicating the formation of hexaferrite [98,108,114].

### 3.3.3 Morphology of strontium ferrite nanoparticles

The SEM micrographs of sample calcinated at different temperatures have been depicted in Figure 3.5(a-c). The average grain size of strontium hexaferrite estimated from SEM micrograph to be \(\sim 100\) nm. SEM micrograph for precursor has been presented in Figure 3.5(a). It can be seen from the micrograph that the particles are embedded in a sheet like structure due to the presence of impurities or incomplete reaction in sample as confirmed from X-ray diffraction analysis. Small size particles are formed due to fragmentation of sheet like structure with the increase of calcination temperature may be the calcination is responsible for this. It is known that the microstructure of nanoparticles can be influenced and improved by heat treatment [115]. The sample calcinated at 700°C becomes plate or needle like shape (Figure 3.5b). This can be attributed to increase in crystallinity of particles, but morphology of particles still not flawless. It has also been observed from the micrograph that the
particles exhibit porous and agglomerated microstructure. The ignition of sample causes evolution of large amount of gases during combustion or decomposition process and magnetic nature of particles has been responsible for high porosity and agglomeration respectively [116,117].

Figure 3.5: SEM micrographs of SrFe$_{12}$O$_{19}$ (a) precursor powder and sample calcinated at (b) 700°C, (c) 1200°C.

The calcination temperature mends the crystallinity of ferrite phase and can be describe in terms of Ostwald ripening [118]. Ostwald ripening is a process in which large number of nanoparticles are formed initially, but later only few of them remain which grow in size at the cost of smaller ones. The ultrafine and homogeneous
particles have been formed with immaculate and well resolved hexagonal structure for the sample calcinated at 1200°C (Figure 3.5c).

3.3.4 Magnetic analysis

The magnetic properties of a precursor and calcinated powder have been measured from hysteresis loops and can be seen in Figure 3.6.

![Hysteresis loops](image)

**Figure 3.6:** Hysteresis loops of SrFe$_{12}$O$_{19}$ (a) precursor powder and sample calcinated at (b) 700°C, (c) 800°C, (d) 1200°C.

The magnetic properties of ferrite system are influenced by chemical composition, calcination temperature, impurities, and morphology as well as preparation technique [119]. The measured values are listed in Table 3.3. It is observed from Figure 3.6(d) that the magnetic properties perk up as the calcination temperature increases and the optimum values for prepared SrFe$_{12}$O$_{19}$ have been obtained for the sample calcinated at 1200°C. The continuous improvement in magnetic parameters can be indorsing to
the progressive reaction between un-reacted constituents of iron oxide and non-ferromagnetic monoferrite to form 100% single phase hexaferrite, as discussed above the crystallinity increases with calcination. The low $H_C$ and $M$ value of a precursor powder corresponds to the presence of $\gamma$-Fe$_2$O$_3$ and non-magnetic phase of strontium oxide respectively [98]. The improvement in crystallinity, phase homogeneity and increase in magnetic domain size of particles result in the alignment of magnetic spins along the direction of applied field [104], and as a consequence the magnetization and coercivity value increases [120,121]. The obtained optimum results for sample calcinated at 1200°C are consistent with the thermal analysis indicating the formation of pure ferrite phase. The variation of coercivity (reverse magnetic field to demagnetize the nanoparticles) with crystallite size has been shown in Figure 3.7.

![Graph showing variation of coercivity (Hc) and magnetization ratio (Mr/M) with crystallite size (D)](image)

**Figure 3.7:** The coercivity and squareness ratio of SrFe$_{12}$O$_{19}$ as a function of crystallite size.

According to Stoner-Wohlfarth single domain theory the coercivity for single domain nanoparticles is approximated by eq. (16) [122]. $H_C$ is directly proportional to energy barrier according to the eq. (15) [120]. The $E_A$ is also proportional to $V$ under the same magnetization direction and thus, the coercivity of nanoparticles is closely related to crystallite size. The increment in coercivity of hexaferrite nanoparticles with
an increase of crystallite size can be explained on basis of Herzer theory [123]. According to Herzer theory, the coercivity of nanoparticles is proportional to $D^5$ when the crystallite size is within the range of single domain size and inversely proportional to $D$ for multi-domain sized particle. Also, Figure 3.7 depicts the relationship between squareness ratio with crystallite size. The $Mr/M$ ratio is generally known as squareness ratio (SQR), where $Mr$ is remanence. The SQR is very important factor in the field of recording media of high density and permanent magnets. Generally, high SQR values have been preferred in such applications. It has been clear from Table 3.3 that SQR increases with increase in temperature (or D) and maximum for highest temperature. However, the samples calcinated at lower temperature shows lower SQR values and it may be attributed to the presence of intermediate phases. The SQR ratio is found to be $\sim 0.51$-$0.56$ for all three cases which is the expected value for randomly packed single domain hard magnetic materials. It is comparable remanence value for the same given by the Stoner–Wohlfarth model.

Table 3.3: Values of magnetization, coercivity and squareness ratio for SrFe$_{12}$O$_{19}$ sample.

<table>
<thead>
<tr>
<th>SrFe$<em>{12}$O$</em>{19}$</th>
<th>$M$ (emu/g)</th>
<th>$H_C$ (Oe)</th>
<th>$Mr/M$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precursor Powder</td>
<td>25.46</td>
<td>232.8</td>
<td>0.27</td>
</tr>
<tr>
<td>700°C</td>
<td>30.17</td>
<td>4272.34</td>
<td>0.52</td>
</tr>
<tr>
<td>800°C</td>
<td>41.98</td>
<td>6235.75</td>
<td>0.51</td>
</tr>
<tr>
<td>1200°C</td>
<td>57.76</td>
<td>6828.54</td>
<td>0.56</td>
</tr>
</tbody>
</table>

3.4 Conclusions

Hexagonal shaped nanoparticles (69 nm) of SrF$_{12}$O$_{19}$ have been successfully synthesized when the precursor is calcinated at 1200°C for 4h, using citrate precursor technique. The morphology and crystallite size are strongly influenced by the calcination temperature. The DTA technique reveals that the highly crystalline nanoparticles are formed by the endothermic reaction. The reaction kinetics for the crystallization process of SrF$_{12}$O$_{19}$ yielded overall activation energy of 157 kJ/mole using Kissinger’s non-isothermal model. The crystallization involves the weight loss
of a precursor in three distinct steps. The intense weight loss in the temperature range 30-400°C indicates the hydrosopic nature. The formation of ferrite phase was followed by reaction between intermediates rather than single step formation. The average crystallite size of SrF₄O₁₀ nanoparticles measured from SEM is larger than the crystallite size calculated from X-ray peak broadening technique. This is attributed that the SEM gives the size of secondary particles rather than size of primary particles. The magnetic parameters are closely related to the crystallinity of particles. It is found that the sample calcinated at 1200°C have higher \( M \) and \( H_C \) value while comparing with sample calcinated at 700°C. This improvement in hysteresis is considered to be the progressive reaction of intermediates with the calcination temperature. The prepared strontium hexaferrite nanoparticles with preeminent hexagonal crystal structure and size are used as a dielectric or magnetic filler to minimize the electromagnetic interference. The high coercivity and single domain sized nanoparticles can be aid to obtained desired signal to noise ratio (SNR) which can be used for high density perpendicular recording media.