6.1 INTRODUCTION

Multiferroics is an essential class of multifunctional materials with coupled electric and magnetic order parameters in the same phase. These materials have attracted extensive attention of the researchers worldwide, not only because of their fascinating fundamental science linked with magnetoelectric (ME) effect, but because of their potential applications in advanced multifunctional devices such as spintronics, multiple-state memories, and sensors [35, 166]. Among all the studied single phase multiferroics BiFeO$_3$ (BFO) is a very promising candidate for the device applications which exhibits high ferroelectric ($T_C\sim 1143$ K) and antiferromagnetic ($T_N\sim 643K$) ordering at room temperature (RT). Pure BFO exists in the rhombohedral structure with $R3c$ space group. Currently, bulk BFO could not be suitable for device applications because of some limitations including high conductivity, formation of secondary phases, and presence of oxygen vacancies. Moreover, the presence of incommensurate cycloid spin structure, with a periodicity of 62 nm, results in the cancellation of macroscopic magnetization [166]. In order to improve electrical and magnetic properties of BFO, partial substitution of rare-earth ions has proved an efficient approach. A site substitution with (Ho$^{3+}$, Eu$^{3+}$, Gd$^{3+}$ and Dy$^{3+}$) [221-224] has been carried out by several research groups, however, there are fewer reports about the influence of Sm$^{3+}$ ion substitution on structural, magnetic and optical properties of BFO. In this work, we prepare Bi$_{1-x}$Sm$_x$FeO$_3$ ($x=0.03$, 0.05, and 0.10) nanoparticles by a tartaric acid modified the sol–gel method and report their structures, magnetic and optical properties.

6.2 EXPERIMENTAL DETAILS

The nanoparticles in the powder form of Bi$_{1-x}$Sm$_x$FeO$_3$ (BSFO) ($x=0.03$, 0.05, and 0.10) were synthesized by metal ion ligand complex based precursor solution evaporation method using Bi(NO$_3$)$_3$.5H$_2$O, Fe(NO$_3$)$_3$.9H$_2$O and Sm(NO$_3$)$_3$.6H$_2$O. Homogeneous solution of precursors in the suitable molar ratio was formed and tartaric acid was added into it as a chelating agent. Later on this solution was kept on the hot plate at 70-80°C with vigorous stirring. The obtained powder samples were calcined at optimized temperatures of 550°C for $x = 0.03$, 0.05, and 0.10 for 2 h.
The pellets were sintered at 100°C higher than their calcination temperature. The structural analysis of all the samples was carried out by using the X-ray diffraction technique (XRD, Brucker D8 Advance) in a 2θ range 20 to 80°C. Raman spectra were measured by Renishaw Raman spectrometer (50 mW, 514.5 nm, Ar+ laser). The nanocrystalline nature of the samples was investigated by using transmission electron microscope (TEM) (JEOL, JEM 2100). Magnetic measurements were carried out with vibrating sample magnetometer (VSM, LakeShore7410) at room temperature. ESR spectra with X-band (9.8 GHz) were recorded on Bruker EMX spectrometer and the optical characterization was done by using UV–Visible diffuse reflectance spectra.

6.3 RESULTS AND DISCUSSION

6.3.1 STRUCTURAL STUDIES
6.3.1.1 X-RAY DIFFRACTION STUDIES

Room temperature XRD pattern of Bi$_{1-x}$Sm$_x$FeO$_3$ (x = 0.03, 0.05, and 0.10) samples are displayed in Figure 6.1. All the Patterns shows formation of pure phase BFO and a systematic change in number of peaks with increasing percentage of Sm substitution is also evident from the figure. The double split peaks situated around (104), (110) and (006), (202) starts merging to form broad peak with increasing the Sm concentration. Calculations of lattice parameters shows the continual change of lattice constant because of replacement of the Bi$^{3+}$ ion with the Sm$^{3+}$ ion.

On increasing Sm concentration, the induced lattice distortion suppresses the rhombohedral unit cell by reducing the lattice parameters as well as volume of the unit cell as displayed in Table 6.1.
The XRD patterns confirm pure phase formation for x=0.03–0.10 samples without any impurity phase. At diffraction angle $2\theta=32^\circ$, it is evident that reflections (104) and (110) are clearly separated for x=0.03 and 0.05 samples. However, doublet (104) and (110) merged to a single peak for x=0.10 sample. The peak position shifts towards a higher angle with increasing x from 0.03 to 0.10 which indicates that doping yields the compressive lattice distortion. This distortion leads to the evolution of orthorhombic phase in x=0.10 sample. Rietveld refinement of the samples were carried out by using zero point shift, unit cell, scale factor, shape parameters, background parameters and half width profile parameters (u, v, w). In order to further confirm the structural transformation from rhombohedral phase to orthorhombic phase and to calculate the various structural parameters Rietveld refinement of the samples were carried out. Figure 6.2 shows the Rietveld refined XRD patterns for Bi$_{1-x}$Sm$_x$FeO$_3$ nanoparticles.
Rietveld refinement results predict that rhombohedral structure with space group $R3c$ fitted well in $x=0.03$ and 0.05 samples while rhombohedral and orthorhombic phases with space group ($R3c+Pn21a$) coexist for $x=0.10$ sample. The contribution of orthorhombic phase was found to be 29.69%. Similar type of behavior has also been reported for rare earth doped BFO [221, 224]. The lattice parameters of the samples are $a=b=5.5761$ Å, $c=13.8551$ Å; $a=b=5.5757$ Å, $c=13.8287$ Å; $a=b=5.5563$ Å, $c=13.6965$ Å (rhombohedral phase), $a=5.5620$ Å, $b=7.8024$ Å, $c=5.5171$ Å (orthorhombic phase) for $x = 0.03$, 0.05 and 0.10, respectively. The calculated values of lattice parameters indicate that there is a continual change in lattice constant with substitution of Sm$^{3+}$ ions. Calculated lattice parameters, Atomic positions and R-Factors for the various compositions are shown in Table 6.1.

The consequent substitution of Bi$^{3+}$ ions with smaller ionic radii Sm$^{3+}$ ions at A-site would leads to lattice distortion and it can be measured by calculating tolerance factor ($t$) as
where, $R_A$, $R_B$, and $R_O$ are the ionic radii of the A, B, cations and O anions respectively. The calculated values of tolerance factor are 0.890, 0.888, and 0.886 Å for $x = 0.03$-$0.10$ samples, respectively, which indicates the increased in lattice distortion in BFO with increasing concentration of Sm ions. If the value of $t$ is equal to one, it corresponds to the ideal perovskite structure but if this value is less than one, indicating distorted perovskite structure and corresponds to rotation of the FeO$_6$ octahedra. The value of $t$ less than unity indicates the compression in Fe-O bonds and consequently tension in Bi$^{3+}$/Sm$^{3+}$-O bonds increased. On increasing Sm concentration, the induced lattice distortion suppresses the rhombohedral unit cell by reducing the lattice parameters as well as volume of the unit cell as displayed in Table 6.1.

6.3.1.2 RAMAN SPECTROSCOPY STUDIES

Raman spectroscopy is an important tool used to investigate the structural changes in the samples, since Raman modes are sensitive to atomic displacements therefore changes in Raman
modes with the incorporation of Sm ions in BFO lattice gives valuable information about the ionic substitution and structural transition. Figure 6.3 shows the Raman spectra of Sm doped BFO nanoparticles.

![Figure 6.3: Fitted Raman spectra for Bi\(_{1-x}\)Sm\(_x\)FeO\(_3\) samples at room temperature.](image)

Systematic structural transition in accordance with the XRD results has been visualized in Raman spectra as shown in the Figure 6.2. It has been reported that the Raman active modes of the rhombohedral BFO with space group \(R3c\) can be summarized by irreducible representation: \(\Gamma=4A_1+9E\) [137, 207]. According to group theory there are 13 Raman active modes and 5 Raman inactive modes. By fitted the observed Raman spectra into individual Lorentzian component peak position of the Raman modes can be identified. Frequency of the mode is governed by the equation: \((k/M)^{1/2}\) where, \(k\) is the force constant and \(M\) is the reduced mass. A sharp decrease in
intensity of low frequency modes ($A_{1-2}$ and $A_{1-3}$) for $x=0.10$ suggests the evolution of orthorhombic phase.

The changes in the low frequency modes ($A_{1-1}$, $A_{1-2}$, $A_{1-3}$ and $E-2$) are related to the change in the occupation level of Bi atoms of perovskite unit, whereas the high frequency modes (>400 cm$^{-1}$) are caused by internal vibration of Fe atoms in the FeO$_6$ octahedral unit [178]. Broadening and shifting of Raman modes to higher frequencies can be attributed to the change in Bi-O covalent bond with Sm$^{3+}$ doping. The changes of the Raman modes serve independent evidence supporting the obtained polar–nonpolar phase transition from the rhombohedral structure to the orthorhombic phases at $x=0.10$. The observed Raman modes in the samples was found in good agreement with the reported data as shown in Table 6.2.

**Table 6.2:** Deconvoluted Raman modes of Bi$_{1-x}$Sm$_x$FeO$_3$ nanoparticles with $x = 0.03$, 0.05 and 0.10.

<table>
<thead>
<tr>
<th>Raman modes (cm$^{-1}$)</th>
<th>Yang et al. [138] (cm$^{-1}$)</th>
<th>$x = 0.03$ (cm$^{-1}$)</th>
<th>$x = 0.05$ (cm$^{-1}$)</th>
<th>$x = 0.10$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{1-1}$</td>
<td>139</td>
<td>137</td>
<td>138</td>
<td>139</td>
</tr>
<tr>
<td>$A_{1-2}$</td>
<td>171</td>
<td>172</td>
<td>175</td>
<td>176</td>
</tr>
<tr>
<td>$A_{1-3}$</td>
<td>217</td>
<td>222</td>
<td>225</td>
<td>--</td>
</tr>
<tr>
<td>$A_{1-4}$</td>
<td>260</td>
<td>259</td>
<td>273</td>
<td>--</td>
</tr>
<tr>
<td>$E$</td>
<td>274</td>
<td>280</td>
<td>--</td>
<td>277</td>
</tr>
<tr>
<td>$E$</td>
<td>306</td>
<td>--</td>
<td>319</td>
<td>313</td>
</tr>
<tr>
<td>$E$</td>
<td>344</td>
<td>--</td>
<td>355</td>
<td>--</td>
</tr>
<tr>
<td>$E$</td>
<td>368</td>
<td>372</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>$E$</td>
<td>430</td>
<td>425</td>
<td>--</td>
<td>440</td>
</tr>
<tr>
<td>$E$</td>
<td>468</td>
<td>473</td>
<td>472</td>
<td>--</td>
</tr>
<tr>
<td>$E$</td>
<td>520</td>
<td>529</td>
<td>530</td>
<td>523</td>
</tr>
<tr>
<td>$E$</td>
<td>611</td>
<td>611</td>
<td>612</td>
<td>613</td>
</tr>
</tbody>
</table>
6.3.1.3 MORPHOLOGICAL STUDIES

Figure 6.4 (a) and (b) represent TEM images for Bi$_{1-x}$Sm$_x$FeO$_3$ (x=0.03 and 0.10) nanoparticles respectively. It is evident from these images that the particles are aggregated and possessed irregular shapes. The particle size varies in the range 30-50 nm and 20-40 nm for x=0.03 and 0.10 samples respectively. The reduction in particle size of the compositions was clearly noticeable in the micrographs with increasing Sm$^{3+}$ concentration which may be attributed to the smaller ionic radius of Sm$^{3+}$ ions (1.079 Å) compared to Bi$^{3+}$ ions (1.17 Å).

6.3.2 MAGNETIC STUDIES
6.3.2.1 VSM STUDIES

The room temperature magnetic hysteresis loops (M-H curves) for Bi$_{1-x}$Sm$_x$FeO$_3$ samples are shown in Figure 6.5. The M-H curves clearly indicate weak ferromagnetism in the samples. The magnetization increases with Sm content and reaches a maximum value from 0.87 emu/g for x = 0.03 sample to 1.87 emu/g for x=0.10 sample. The coercive field (H$_C$) decreases from 261.680 to 24.016 Oe with increasing x from 0.03 to 0.10. The enhancement in the magnetization may have several reasons, primarily, the alteration of the spiral spin structure caused by the distortion in the crystal structure by Sm$^{3+}$ ions doping.
The particles of size less than 62 nm also suppress the cycloidal spin structure which results in a weak ferromagnetism. Further, Sm$^{3+}$ ions substitution can bring Sm$^{3+}$-Fe$^{3+}$ super exchange (SE) interaction which in turn increases the magnetization. In addition to SE interaction, Dzialoshinski-Moriya (DM) type antisymmetric exchange interaction between Fe$^{3+}$-Fe$^{3+}$ ions plays an important role here due to which the Fe$^{3+}$ spins also get canted [169]. In these nanoparticles, in addition to interionic SE and DM interactions, the non-exact compensated/ canted surface spins due to increased surface to volume ratio also contributes to the weak ferromagnetism [178]. The magnified view of the M-H loops is displayed in Figure 6.6. Furthermore, careful analysis of M-H loops shows that there is a shift in the hysteresis loop.
towards negative axis (inset of Figure 6.6), indicating exchange coupling between the antiferromagnetic core and ferromagnetic surface [169]. This establishes that the exchange interaction may contributes to some extent to the observed ferromagnetic behavior of x=0.10 sample.

![Figure 6.6: Magnified view of magnetization versus magnetic field (M-H) curves for Bi$_{1-x}$Sm$_x$FeO$_3$ samples](image)

6.3.2.2 ESR STUDIES

To further understand the magnetic behavior, room temperature ESR measurement was carried out at frequency 9.8 GHz as displayed in Figure 6.7. For all the samples only one absorption peak was observed which is associated with resonance absorption in cycloid spin structure and denoted as P$_{cyc}$ [210]. The g-values of the samples were calculated by using the formula: $h\nu = g\mu_B H_r$, where $h$ is Planck’s constant, $\nu$ is operating frequency, $\mu_B$ is Bohr Magneton and $H_r$ is resonance field. The calculated g values are 2.430, 2.437 and 2.484 for x=0.03, 0.05 and 0.10, respectively, which clearly indicates the ferromagnetic coupling between
Sm$^{3+}$-Fe$^{3+}$ and increase in degree of spin canting (deviation from g=2). Degree of spin canting is directly related to g values through the vector coefficient D by the relation: $D = (\Delta g/g)J_{\text{super}}$, where $\Delta g$ is the deviation of g values from 2 and $J_{\text{super}}$ is the super exchange interaction coefficient. By assuming $J_{\text{super}}$ constant for all the samples, higher value of D was obtained for x=0.10 sample. Line width ($\Delta H$) decreases from 2819.362 to 2807.376 Oe on increasing Sm$^{3+}$ concentration. The super exchange interaction between magnetic moments of Sm$^{3+}$ and Fe$^{3+}$ may be responsible for narrowing of the line width [198]. The increase in the magnetization may be attributed to the increase in degree of spin canting as suggested by the narrowing of the line width.

**Figure 6.7:** Room temperature ESR spectra for Bi$_{1-x}$Sm$_x$FeO$_3$ samples
Table 6.3: ESR parameters for Bi$_{1-x}$Sm$_x$FeO$_3$ nanoparticles

<table>
<thead>
<tr>
<th>Compositions</th>
<th>g</th>
<th>Δg/g</th>
<th>ΔH (Oe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>x = 0.03</td>
<td>2.43</td>
<td>0.22</td>
<td>2819.3</td>
</tr>
<tr>
<td>x = 0.05</td>
<td>2.46</td>
<td>0.23</td>
<td>2812.4</td>
</tr>
<tr>
<td>x = 0.10</td>
<td>2.48</td>
<td>0.24</td>
<td>2807.3</td>
</tr>
</tbody>
</table>

6.3.3 OPTICAL STUDIES

6.3.3.1 UV-VIS DIFFUSE ABSORPTION STUDIES

UV-Vis absorption spectra of Bi$_{1-x}$Sm$_x$FeO$_3$ samples derived from the diffuse reflectance spectroscopy is shown in Figure 6.8. Two bands centered at 1.37 and 1.88 eV correspond to on-site d-d crystal field transitions of Fe$^{3+}$ ions [214]. The band around ~2.5 eV on the tail of a strong 3.0 eV band is assigned to dipole-allowed p-d charge transfer (C-T) transitions in FeO$_6$ octahedra [110]. The familiar 3.0 and 4.5 eV electronic excitations are assigned as minority channel dipole-allowed charge transfer (C-T) features [160]. The energy band gap of the nanoparticles were calculated by using classical Tauc's approach i.e. plotting $(\alpha h\nu)^2$ versus E (h\nu) and $\alpha h\nu = A(h\nu-E_g)^n$ where $h\nu$ is the photon energy, A is the parameter that related to the effective masses associated with the valence and conduction bands constant, $E_g$ is energy band gap, $\alpha$ is absorption coefficient. The value of n is depends upon the nature of electronic transition responsible for absorption and it can have any value $\frac{1}{2}$, 3/2, 2 or 3. For direct band gap value of n taken is $\frac{1}{2}$. The band gap of the nanoparticles were found to be 2.35, 2.30, and 2.26 eV for x=0.03, 0.05, and 0.10 samples respectively.

The red shift in energy band gap of doped samples may be attributed to increased internal chemical pressure and rearrangement of molecular orbital and distortion induced in the FeO$_6$ octahedra.
6.3.4 ELECTRIC STUDIES

6.3.4.1 DIELECTRIC STUDIES

To study the effect of Sm substitution on the dielectric BFO samples, frequency-dependent dielectric measurements were carried out at room temperature. The room temperature frequency dependent dielectric constant and dielectric loss for $\text{Bi}_{1-x}\text{Sm}_x\text{FeO}_3$ samples are illustrated in Figure 6.9.
It has been predicted from these graphs that the values of $\varepsilon_r$ and $\tan \delta$ decreases regularly with increasing frequency. This decrease in dielectric loss with increasing doping concentration conforms the suppression in oxygen vacancies as well as Bi$^{3+}$ ions volatilization, which in turn leads to decrease in leakage current. Low frequency dispersion behavior in both dielectric constant and dielectric loss indicate presence of dc conductivity in the samples. It was found that dielectric constant and dielectric loss reduces with increasing frequency which is attributed to the dipole relaxation, as at high frequency Fe$^{2+}$-Fe$^{3+}$ dipole are not able to follow the field reversal. Large value of dielectric constant at low frequency attributed to the interfacial polarization and grain boundary effects.

### 6.4 CONCLUSIONS

Rietveld refined X-ray diffraction patterns suggest rhombohedral crystal symmetry for $x=0.03$ and 0.05 samples and coexistence of rhombohedral and orthorhombic phases for $x=0.10$ sample. The change in the phonon frequencies and line width in Raman spectra also confirm the lattice distortion and structural transformation in the samples. The magnetization of the nanoparticles increases due to the uncompensated surface spins and super ferromagnetic interaction between Sm$^{3+}$-Fe$^{3+}$ ions. Magnetization increases up to 1.766 emu/g for $x = 0.10$.
sample and shift in the hysteresis loop toward negative axis indicating exchange coupling between the antiferromagnetic core and ferromagnetic surface for $x = 0.10$. The variation in peak position of electron spin resonance spectra indicates weak ferromagnetic coupling and destruction in spin cycloid with inducing doping ions. Dielectric loss decreases with increasing doping concentration indicates the reduction in oxygen vacancies in the samples. UV-Visible spectra show two d-d crystal field transitions of Fe$^{3+}$ ions along with charge transfer transitions in FeO$_6$ octahedra. The red shift in energy band gap of doped samples may be attributed to increased internal chemical pressure.