4.1 INTRODUCTION

Multiferroic materials, which exhibit uncommon coexistence of coupled ferroelectric (or antiferroelectricity) and ferromagnetism (or antiferromagnetism), have attracted enormous curiosity because of their possible applications in data storage, spin valves, spintronics, memories, sensors and microelectronic devices [34, 40]. However, single phase multiferroic materials are in scarce, as the existence of ferromagnetism and ferroelectric in the same phase is mutually exclusive (ferroelectricity in ABO$_3$ type perovskite requires d0 type electronic configuration on B-site cation whereas ferromagnetism requires partially filled transition metal orbital). BiFeO$_3$ (BFO) is one of the widely studied materials which exhibit ferroelectric and antiferromagnetic (AFM) properties at room temperature in the same phase. In BFO, ferroelectricity originates from the stereochemically active 6s$^2$ pair of electrons on Bi$^{3+}$ ions while the magnetic order appears due to the partially filled 3d orbitals of Fe$^{3+}$ ions. BFO is extensively studied because of its high ferroelectric Curie temperature ($T_c$ ~1103 K) and G-type antiferromagnetic order below Néel temperature ($T_N$ ~643 K) which makes it favorable to exhibit magnetoelectric coupling at and above room temperature [35, 166]. BFO crystallizes in rhombohedrally distorted perovskite structure assigned to space group R3c.

In addition, BFO exhibits room temperature G-type antiferromagnetic order and this spin structure is further modified by a spin cycloid with periodicity of 62 nm along [110]$_h$ axis, which cancels the net macroscopic magnetization and inhibits linear magnetoelectric effect [167]. Hence, the suppression of spiral spin structure becomes an important route to enhance the magnetic properties and magnetoelectric (ME) effect in BFO [168]. In spite of all favourable potential applications, BFO related technology still faces problems like formation of secondary phases during synthesis, high leakage current, weak ferromagnetism and lower magnetoelectric coupling.

Amongst the various ways of improving the multiferroic properties of BFO, lattice site substitution in BFO with appropriate element/ion is found to be the most effective method [169,
The rare earth ions substitution at Bi-site has been already established to achieve magnetic, electrical and magnetoelectric enhancement in BFO (suppression of the helical order) [169-171]. Meanwhile, the Dy substitution may produce the large lattice distortion (ions with same valence as that of Bi and ionic radius of Dy\(^{3+}\) (0.91 Å) is quite smaller than that of Bi\(^{3+}\) ion (1.17 Å)) and also the ferromagnetic coupling between Dy\(^{3+}\) and Fe\(^{3+}\) ions (Dy\(^{3+}\) ion being magnetically active; \(\mu_{\text{eff}} = 10.6 \, \mu\text{B}\)).

**4.2 EXPERIMENTAL DETAILS**

Bi\(_{1-x}\)Dy\(_x\)FeO\(_3\) nanoparticles with \(x = 0.03, 0.05\) and 0.10 were successfully synthesized by sol-gel method. Stoichiometric amounts of Bi(NO\(_3\))\(_3\).5H\(_2\)O, Fe(NO\(_3\))\(_3\).9H\(_2\)O and Dy(NO\(_3\))\(_2\).xH\(_2\)O were weighed and dissolved in de-ionized water followed by addition of dilute HNO\(_3\) in small amount. After which the tartaric acid (in molar ratio of 1:2 to that of metal nitrates) were added as complexion agent. The resultant solutions were evaporated and dried at 100\(^0\)C and the obtained powders were calcined at 550\(^0\)C and 700\(^0\)C for 2 hrs.

The crystal structure of prepared samples was examined by the X-Ray diffractometer (Philips X’pert) using CuK\(\alpha\) radiation. Simulation of the X-ray diffraction (XRD) data was performed by using Rietveld refinement software (FULLPROF). Raman spectra were recorded on Renishaw Raman spectrometer (514.5 nm, Ar\(^+\) laser). The microstructure properties were examined by transmission electron microscopy (TEM) using Philips CM 10. The dielectric measurements were carried out on silver coated pellets by using an impedance analyzer (PSM 1735) in the temperature range 40-400\(^0\)C at various frequencies with step size of 5\(^0\)C. In order to investigate the magnetic properties, room temperature magnetization hysteresis (M-H) measurements were carried out by using SQUID magnetometer. Fourier transform infrared (FTIR) spectra were obtained on Perkin Elmer Spectrum BX-II at a resolution of 1 cm\(^{-1}\) in order to identify the bond formation in the samples.
4.3 RESULTS AND DISCUSSION

4.3.1 STRUCTURAL STUDIES

4.3.1.1 X-RAY DIFFRACTION STUDIES

Figure 4.1 shows the XRD patterns of Bi$_{1-x}$Dy$_x$FeO$_3$ (x = 0.03, 0.05 and 0.10) nanoparticles. The diffraction planes (012), (104), (110), (006), (202), (024), (116), (122), (018), (300), (208), (220), (131), (036), (128), (134) for x = 0.03 and 0.05 samples are indexed according to rhombohedral structure with space group R3c of BFO. Besides the planes associated with rhombohedral structure, the low intensity impurity peaks corresponding to Bi$_2$Fe$_4$O$_9$ and Bi$_{24}$Fe$_2$O$_{39}$ were also detected due to kinetics of formation [172].

Figure 4.1: (a) X-ray diffraction patterns for Bi$_{1-x}$Dy$_x$FeO$_3$ nanoparticles with x=0.03, 0.05 and 0.10, (b) represents enlarge view
However, these impurity peaks were annihilated with increasing Dy concentration. The existence of separated peaks with \(2\theta\) values around 32° and 39° for \(x=0.03\) and 0.05 samples suggest the distorted rhombohedral structure with \(R3c\) space group. Interestingly with increasing Dy concentration, the peak splitting behavior decreases gradually. The distinct XRD peaks for (104) and (110); (006) and (202) planes are noticed for \(x=0.03\) and 0.05 samples, whereas for \(x=0.10\) sample, the two peaks for (104) and (110); (006) and (202) planes nearly merged into single broad peak, suggesting a compositional driven phase transition from rhombohedral to orthorhombic phase which has also been observed in other rare earth doped BFO [173-175]. This compositional driven phase transition from rhombohedral to orthorhombic phase is attributed to incorporation of Dy\(^{3+}\) ions into the lattice of BFO and the structural distortion resulting from the reduced particle size.

Figure 4.2: Rietveld refined XRD patterns for \(\text{Bi}_{1-x}\text{Dy}_x\text{FeO}_3\) nanoparticles (a) \(x = 0.03\) (b) 0.05 and (c) 0.10. (d) Williamson–Hall plot of all the samples
The crystal structures of the samples were further analyzed by Rietveld refinement (using FULLPROF software) and are shown in Figure 4.2 (a-c). The Bragg peaks were modeled with Thompson–Cox–Hastings pseudo-Voigt function and the background was estimated by linear interpolation between selected background points. Rietveld refinement for \( x = 0.03 \) and 0.05 samples was carried out by considering \( R3c \) space group with ionic position for Bi at 6a, Fe at 6b and oxygen at 18c for \( x = 0.03 \) and 0.05 while \( Pbmn \) space group with ionic position for Bi/Dy at 4c, Fe at 4a and oxygen at 4c and 8d was used for \( x = 0.10 \) sample. Initial simulation was carried out by considering some fixed parameters. After final cycle of refinement, it was noticed that the observed and calculated profiles matches with each other. Based on fitting parameters like smaller values of \( R_p \) and \( R_{wp} \) it was established that structure stays as rhombohedral for \( x = 0.03 \) and 0.05 samples whereas for \( x = 0.10 \) sample it takes orthorhombic structure. The lattice parameters, atomic positions, bond lengths and R factors obtained from Rietveld refinement are listed in Table 4.1.

**Table 4.1:** Rietveld Refined structural parameters for Bi\(_{1-x}\)Dy\(_x\)FeO\(_3\) samples

<table>
<thead>
<tr>
<th>Compositions</th>
<th>Lattice Parameters</th>
<th>Atoms</th>
<th>Positions</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
<th>Bond Length (Å)</th>
<th>R-Factors (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( x = 0.03 )</td>
<td>( a = 5.570 ) (Å) ( c = 13.802 ) (Å) ( V = 370.82 ) (Å(^3))</td>
<td>Bi/Dy</td>
<td>6a</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>Bi-O Fe-O</td>
<td>( R_p = 4.42 ) ( R_{wp} = 6.09 )</td>
</tr>
<tr>
<td>( x = 0.05 )</td>
<td>( a = 5.565 ) (Å) ( c = 13.772 ) (Å) ( V = 369.35 ) (Å(^3))</td>
<td>Bi/Dy</td>
<td>6a</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>Bi-O Fe-O</td>
<td>( R_p = 6.21 ) ( R_{wp} = 8.76 )</td>
</tr>
<tr>
<td>( x = 0.10 )</td>
<td>( a = 5.543 ) (Å) ( b = 5.595 ) (Å) ( c = 7.843 ) (Å) ( V = 243.28 ) (Å(^3))</td>
<td>Bi/Dy</td>
<td>6a</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>Bi-O Fe-O</td>
<td>( R_p = 5.78 ) ( R_{wp} = 8.25 )</td>
</tr>
</tbody>
</table>

The crystallite size and lattice strain of Bi\(_{1-x}\)Dy\(_x\)FeO\(_3\) nanoparticles were calculated from the broadening of the XRD peaks by using Williamson–Hall approach [176] given by following equation:
\[ \beta_{hkl} \cos \theta = \left[ \frac{k \lambda}{D} \right] + 4 \varepsilon \sin \theta \]  

Where \( k \) is the shape factor, \( \lambda \) is the X-ray wavelength, \( \theta \) is the Bragg’s angle, D is the crystallite size, \( \varepsilon \) is the strain, and \( \beta_{hkl} \) is the full width at half maxima. By plotting the graph between \( 4 \sin \theta \) on x-axis and \( \beta_{hkl} \cos \theta \) on y-axis (Figure 4.2 (d)), slope of the line tells the micro strain and the intersection with the vertical axis gives the crystallite size \( D \). The calculated crystallite sizes are 28.1, 25.2 and 23.5 nm for \( x=0.03, 0.05 \) and 0.10 samples respectively.

Goldschmidt has defined the tolerance factor \( t \) in order to evaluate the degree of matching between A-site ions and B-site ions. The value of \( t \) can be calculated by using following relation:

\[ t = \left( (1-x)r_{Bi^{3+}} + x r_{Dy^{3+}} + r_{O^{2-}} \right) \sqrt{2 \left( r_{Fe^{3+}} + r_{O^{2-}} \right)} \]  

Where \( r_{Bi^{3+}}, r_{Dy^{3+}}, r_{Fe^{3+}} \) and \( r_{O^{2-}} \) are the ionic radii of \( Bi^{3+}, Dy^{3+}, Fe^{3+} \) and \( O^{2-} \) ions respectively. In case of ideal perovskite crystal, the value of tolerance factor equals to one and the oxygen octahedron tilting angle is zero. In present case, the values of “\( t \)” are found to be 0.888, 0.886 and 0.881 for \( x=0.03, 0.05 \) and 0.10 samples, respectively. Deviation of “\( t \)” from 1 increases with increasing distortion in the perovskite structure. As the ionic radius of \( Dy^{3+} \) is smaller than that of \( Bi^{3+} \), the substitution of \( Dy^{3+} \) ion in place of \( Bi^{3+} \) ion would result in decrease in the tolerance factor and increase in the angle of octahedron tilting. Due to this the Fe-O bond would be compressed and the Bi/Dy-O bond would be stretched and when the distortion is beyond the limit of the rhombohedral structure, the structure transformation to the orthorhombic phase takes place. The variation of lattice parameters as a function of Dy concentration \( x \) in BFO lattice is shown in Figure 4.3. The lattice parameters were found to decrease with increasing value of \( x \). The larger ionic radius of \( Bi^{3+} \) (1.17 Å) than of \( Dy^{3+} \) (0.91 Å) is attributed for decrease in lattice parameters.
4.3.1.2 RAMAN SPECTROSCOPY STUDIES

Raman spectroscopy was employed to study the possible structural changes in Bi$_{1-x}$Dy$_x$FeO$_3$ samples. Group theory ($\Gamma_{\text{Raman}} = 4A_1+9E$) predicts 13 Raman active modes for Rhombohedral $R3c$ structure [137]. All the 13 ($4A_1+9E$) Raman active modes were observed for $x=0.03$ and 0.05 samples which are in accordance with the group theory prediction for $R3c$ rhombohedral structure. Figure 4.4 shows the fitted Raman spectra for Bi$_{1-x}$Dy$_x$FeO$_3$ samples with 10 Raman active modes in the range 100–700 cm$^{-1}$. In the present study, Raman mode assignment is in correspondence with study reported by Yang et al. [138]. For $x=0.03$ sample, three strong peaks at 138, 168 and 217 cm$^{-1}$ and a weak peak at 443 cm$^{-1}$ were observed which are assigned to $A_1$-1, $A_1$-2, $A_1$-3 and $A_1$-4 modes, respectively. With increasing Dy content, broadening and shifting of the peaks occur due to relaxation of lattice periodicity which may be incorporated due to substitution of Dy ions into BiFeO$_3$ lattice. Ferroelectric ordering in BFO is
governed by stereochemically active Bi	extsuperscript{3+} ions with lone pair 6s	extsuperscript{2} electrons which take part mainly in low frequency range.

![Room temperature Raman spectra of Bi	extsubscript{1-x}Dy	extsubscript{x}FeO	extsubscript{3} nanoparticles.]

The A	extsubscript{1}-1, A	extsubscript{1}-2, A	extsubscript{1}-3, E-1 and E-2 modes are associated with Bi-O covalent bond whereas higher frequency E modes (>400 cm	extsuperscript{-1}) are assigned to Fe-O bonds [137]. Frequencies of Raman modes depend upon ionic masses and force constant. Mass of Dy	extsuperscript{3+} (162.5) ion is lower as compared to Bi	extsuperscript{3+} (208.98) ion and hence with the substitution of Dy ions average mass on A-site reduces due to which A	extsubscript{1}-1, A	extsubscript{1}-2, A	extsubscript{1}-3 modes shift towards higher frequency side. The
shifting, broadening and merging of the Raman modes with increasing Dy content is attributed to the increased lattice distortion which arises due to the competition between rhombohedral and orthorhombic structure. The reported Raman data on BFO by Yang et al. [138] and observed Raman data for Bi$_{1-x}$Dy$_x$FeO$_3$ nanoparticles are shown in Table 4.2.

<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>138</td>
<td>139</td>
<td>142</td>
</tr>
<tr>
<td>A$_1$-2</td>
<td>171</td>
<td>168</td>
<td>169</td>
<td>172</td>
</tr>
<tr>
<td>A$_1$-3</td>
<td>217</td>
<td>217</td>
<td>218</td>
<td>229</td>
</tr>
<tr>
<td>A$_1$-4</td>
<td>430</td>
<td>443</td>
<td>444</td>
<td>--</td>
</tr>
<tr>
<td>E</td>
<td>260</td>
<td>--</td>
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<td>E</td>
<td>274</td>
<td>271</td>
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</tr>
<tr>
<td>E</td>
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<td>E</td>
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<td>472</td>
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<td>E</td>
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<td>527</td>
</tr>
<tr>
<td>E</td>
<td>611</td>
<td>600</td>
<td>605</td>
<td>607</td>
</tr>
</tbody>
</table>

Table 4.2: Observed and reported Raman modes of Bi$_{1-x}$Dy$_x$FeO$_3$ ceramic at room temperature with wave-number range 100-700 cm$^{-1}$

For detailed analysis of the effect of Dy substitution on BFO lattice, second phonon Raman spectra of Dy doped BFO samples have also been recorded. Figure 4.5 (a) shows the room temperature Raman spectra in the wavenumber range 100-1400 cm$^{-1}$ and Figure 4.5 (b-d) represents deconvoluted two phonon Raman spectra for E-7, E-8 and E-9 normal Raman modes in the wave number range 900-1400 cm$^{-1}$. These broad bands can be labelled as 2E-7, 2E-8 and 2E-9 i.e. two phonon Raman modes as they appear at double energy values of E-7, E-8 and E-9 in
normal Raman spectra of BFO [134]. The presence of two phonon modes may be associated with the strong spin lattice coupling in the present samples arising from the interaction between the adjacent magnetic sublattices. The two phonon modes can be fitted into three Gaussian bands at around 977, 1100 and 1258 cm\(^{-1}\) for \(x=0.03\) sample, at 982, 1102 and 1259 cm\(^{-1}\) for \(x=0.05\) sample and at 984, 1104 and 1260 cm\(^{-1}\) for \(x=0.10\) sample. It has been reported that the \(A_1\) modes and low frequency E modes (< 400 cm\(^{-1}\)) are attributed to Bi-O1 bonds [149].

![Figure 4.5](image.png)

**Figure 4.5:** (a) Room temperature Raman spectra for Bi\(_{1-x}\)Dy\(_x\)FeO\(_3\) nanoparticles in the wavenumber range 100-1400 cm\(^{-1}\) and (b)-(d) shows fitted two phonon Raman modes in the range 900-1400 cm\(^{-1}\) for \(x=0.03\), 0.05 and 0.10 samples respectively.
However, higher frequency E modes are attributed to Fe-O1 and Fe-O2 bonds, where O1 and O2 are axial and equatorial ions respectively [137]. The 2E-8 and 2E-9 overtones have been assigned to Fe-O1 and Fe-O2 bonding, respectively, by Ramirez et al. and related it with the octahedral rotation critical to weak ferromagnetism [134]. The oxygen rotation influences the antiferromagnetism in BFO through superexchange interaction, which depends on bond angles. The structural distortion in AFM structure should be reflected in the evolution of Raman spectra and therefore, different evolutions of two phonon overtones may be attributed to spin-phonon coupling. It is clear from Figure 4.5 (b-d) that the intensity of 2E-9 overtone reduces continuously with increasing Dy$^{3+}$ ions concentration. This reduction in intensity of 2E-9 overtone indicates the spin-two phonon coupling in the samples, which arises due to distortion in the structure. This spin-two phonon coupling indicates that magnetic properties of x=0.03-0.10 samples might improve with increasing Dy$^{3+}$ concentration.

4.3.1.3 MORPHOLOGICAL STUDIES

![Figure 4.6](image_url)

**Figure 4.6:** Transmission electron micrographs for Bi$_{1-x}$Dy$_x$FeO$_3$ nanoparticles with (a) $x=0.03$, (b) $x=0.05$ and (c) $x=0.10$ samples. (d) Selected area electron diffraction pattern for $x=0.03$ sample.
To study the morphology and influence of Dy substitution on particle size, transmission electron microscopy (TEM) studies were carried out. Figure 4.6 (a-c) shows the TEM images of \( \text{Bi}_{1-x}\text{Dy}_x\text{FeO}_3 \) samples in which the average particle size is noticed to decrease with increasing \( \text{Dy}^{3+} \) concentration in BFO lattice. The reduction in particle size may be attributed to the addition of \( \text{Dy}^{3+} \) ions in BFO lattice, which inhibits the grain growth [177]. The particle size varies in the range 30-50 nm for \( x = 0.03 \) and 0.05 samples whereas the particles with size ranging from 20-40 nm are observed for \( x = 0.10 \) sample. The selected area electron diffraction (SAED) pattern for \( x = 0.03 \) sample is shown in Figure 4.6 (d). SAED image shows a nice dot pattern which clearly exhibits the highly crystalline nature of the nanoparticles. The observed SAED pattern is analysed to calculate lattice spacing. The calculated lattice spacing of 3.95, 2.80, 2.26 and 1.99 Å corresponds to (012), (110), (202) and (024) lattice planes of rhombohedral structure of BFO, respectively.

4.3.2 MAGNETIC STUDIES
4.3.2.1 VSM AND SQUID STUDIES

It is well known that bulk BFO does not exhibit any macroscopic magnetization due to its spiral spin structure of 62 nm. Therefore, synthesis of pure and doped BFO nanoparticles is one of the strategies to release latent magnetization locked in the spiral spin structure. In this study we have prepared Dy doped BFO nanoparticles to enhance magnetic properties. Moreover, to study the effect of particle size (which depends upon sintering temperature) on magnetic properties of BFO, the samples were sintered at 550°C (nanoparticles) and at 700°C (bulk). The magnetic properties of Dy doped BFO samples sintered at two different temperatures have been studied by VSM and SQUID magnetometer respectively. Figure 4.7 (a) shows room temperature magnetization-magnetic field hysteresis (M-H) loops for \( \text{Bi}_{1-x}\text{Dy}_x\text{FeO}_3 \) samples sintered at 550°C. At sintering temperature 550°C, all the samples illustrate a typical ferromagnetic (superparamagnetic) ordering as shown in Figure 4.7 (a). The expanded view of the M-H loops is shown in Figure 4.7 (b). The ferromagnetic (superparamagnetic) like behaviour with large magnetization in antiferromagnetic nanoparticles has been attributed to the incomplete spin compensation between the two sublattices [178]. The long range antiferromagnetic ordering is
frequently interrupted at the particle surface in case of antiferromagnetic nanoparticles and hence the incomplete spin compensation between two sublattices in antiferromagnetically ordered materials gives rise to enhanced magnetization. This ferromagnetic (superparamagnetic) behaviour is further enhanced with increasing x from 0.03 to 0.10 indicating the effect of Dy$^{3+}$ ions substitution on magnetization of BFO nanoparticles. The values of saturation magnetization ($M_S$) for x= 0.03, 0.05 and 0.10 sample are measured as 2.9, 3.3 and 5.5 emu/g, respectively.

![Figure 4.7](image)

**Figure 4.7:** (a) Room temperature magnetization-magnetic field hysteresis (M-H) loops for Bi$_{1-x}$Dy$_x$FeO$_3$ samples sintered at 550°C and (b) The expanded view of the M-H loops.

**Figure 4.8** shows the magnetization-magnetic field hysteresis loops for Dy doped samples sintered at 700°C. The hysteresis loops clearly indicate the effect of increasing sintering temperature (i.e. particle size) on the magnetic properties of the samples. **Figure 4.8** shows that as the temperature increases from 550°C to 700°C, the loops do not saturate up to 6 Tesla of applied magnetic field, however, an enhancement in magnetization has been observed with increasing Dy concentration from x=0.03 to 0.10. Non-zero remnant magnetization ($M_r$) and coercive field ($H_c$) have been observed for all the samples. The values of maximum
magnetization ($M_H$) and remnant magnetization ($M_r$) are found to be 0.57 and 0.0117 emu/g, 0.78 and 0.0177 emu/g, 1.32 and 0.1315 emu/g, respectively, for $x=0.03$, 0.05 and 0.10 samples.

Figure 4.8: Room temperature magnetization-magnetic field hysteresis (M-H) loops for Bi$_{1-x}$Dy$_x$FeO$_3$ samples sintered at 700°C

The coercive field ($H_c$) values are 679.930, 1166.855 and 987.664 Oe for $x = 0.03$, 0.05 and 0.10 samples, respectively. The observed magnetic parameters for samples sintered at 550°C to 700°C are listed in Table 4.3. The double hysteresis loop observed for $x=0.10$ sample is similar to the behaviour reported in Ho doped BFO [179] which indicates that additional factors contribute to the magnetization. The enhancement in the net magnetization with Dy$^{3+}$ ions substitution is attributed to the combined result of several factors. First, the substitution of smaller Dy$^{3+}$ ions for larger Bi$^{3+}$ ions results in large lattice distortion which destroyed spin
cycloid of BFO and induced structural transformation from rhombohedral to orthorhombic phase, which results in release of latent magnetization.

The spin-two phonon coupling as evident from Raman spectra (Figure 4.5 (b-d)) also predicted the enhancement in magnetization. Therefore, this structural distortion induced enhancement in magnetization is consistent with Raman studies confirming the spin-two phonon coupling in the samples. Second, Dy$^{3+}$ is magnetically active ion with large magnetic moment ($\mu_{\text{eff}} = 10.6 \mu_B$) and with the substitution of Dy$^{3+}$ ions, Bi-O-Dy chains formed and these Bi-O-Dy co-ordinations become magnetic sublattices [180]. In addition, Dy$^{3+}$ ion possesses unpaired electrons and because of the effect of these unpaired electrons additional magnetic interaction is likely to occur which is responsible for enhanced magnetization in the sample [181].

Table 4.3: Magnetic parameters for Bi$_{1-x}$Dy$_x$FeO$_3$ samples

<table>
<thead>
<tr>
<th>Compositions</th>
<th>$H_c$ (Oe)</th>
<th>$M_r$ (Oe)</th>
<th>$M_S$ (emu/g)</th>
<th>$H_c$ (emu/g)</th>
<th>$M_r$ (Oe)</th>
<th>$M_H$ (emu/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x = 0.03$</td>
<td>5.20</td>
<td>0.01</td>
<td>2.92</td>
<td>679.93</td>
<td>0.012</td>
<td>0.57</td>
</tr>
<tr>
<td>$x = 0.05$</td>
<td>62.47</td>
<td>0.27</td>
<td>3.32</td>
<td>1166.85</td>
<td>0.018</td>
<td>0.78</td>
</tr>
<tr>
<td>$x = 0.10$</td>
<td>56.06</td>
<td>0.45</td>
<td>5.51</td>
<td>987.66</td>
<td>0.131</td>
<td>1.32</td>
</tr>
</tbody>
</table>

4.3.3 ELECTRIC STUDIES

4.3.3.1 DIELECTRIC STUDIES

The room temperature frequency dependence of dielectric constant ($\varepsilon'$) and dielectric loss ($\tan\delta$) for Bi$_{1-x}$Dy$_x$FeO$_3$ nanoparticles are shown in Figure 4.9. It has been observed that all samples show decrease in both $\varepsilon'$ and $\tan\delta$ with increasing frequency from 100 Hz to 1 MHz. Low frequency dispersion in $\varepsilon'$ and $\tan\delta$ indicates the presence of dc conductivity in the samples [156]. In the low frequency range $\varepsilon'$ and $\tan\delta$ were found to decrease with increase in frequency, while at higher frequencies (>100 kHz), $\varepsilon'$ and $\tan\delta$ become almost constant. This variation of $\varepsilon'$ can be understood on the basis of Maxwell-Wagner model related to interfacial space charge relaxation. The space charge in the sample originates from oxygen ($V_{O}^{2+}$) and bismuth ($V_{Bi}^{3-}$)
vacancies that follow the applied electric field at low frequencies and contribute to the dielectric constant. At higher frequencies, they do not have time to follow rapidly changing applied field and undergo relaxation [182]. At lower frequencies the values of $\varepsilon'$ and $\tan\delta$ are larger for $x=0.03$ sample and decreases consequently for $x=0.05$ and 0.10 samples.

![Graph showing $\varepsilon'$ and $\tan\delta$ variation with frequency for Bi$_{1-x}$Dy$_x$FeO$_3$ nanoparticles at room temperature.]

*Figure 4.9:* Variation of $\varepsilon'$ and $\tan\delta$ with frequency for Bi$_{1-x}$Dy$_x$FeO$_3$ nanoparticles at room temperature.

The decreases in $\tan\delta$ with increasing Dy$^{3+}$ content indicates that Dy$^{3+}$ substitution is helpful in reducing the leakage current. The large value of $\varepsilon'$ for $x=0.03$ sample is mainly due to the creation of oxygen vacancies which is originated from the volatile nature of Bi$^{3+}$ ions. With increasing concentration of Dy$^{3+}$ ions in place of Bi$^{3+}$ ions, reduction in volatilization of Bi$^{3+}$ ions has been achieved which results in decrease in the value of $\varepsilon'$ [183]. The value of dielectric constant at 100 Hz for $x=0.03$, 0.05 and 0.10 samples are ~236, 139 and 87, respectively, and dielectric loss is small in all samples which is in agreement with previous reports [184-186]. The temperature dependence of dielectric constant ($\varepsilon'$) and dielectric loss ($\tan\delta$) for Bi$_{1-x}$Dy$_x$FeO$_3$ samples at frequencies 50 kHz, 100 kHz and 1 MHz are shown in *Figure 4.10* and *Figure 4.11*.
respectively. For $x = 0.03$ and $0.05$ samples, an anomaly has been observed in dielectric constant at temperature $\sim 160^\circ$C. This anomaly may be attributed to a transient reaction between oxygen ion vacancies and Fe$^{3+}$/Fe$^{2+}$ redox couple [187]. Catalan et al. reported that this anomaly is due to the charge defects and it is not intrinsic in type [100].

**Figure 4.10:** Temperature dependence of dielectric constant ($\varepsilon'$) for Bi$_{1-x}$Dy$_x$FeO$_3$ nanoparticles at different frequencies

A similar behavior has also been reported in Sr and Ti codoped BFO [188]. The disappearance of anomaly at $\sim 160^\circ$C for $x=0.10$ sample is direct indication of suppression of charge defects/oxygen vacancies with increasing Dy concentration. Replacement of some volatile Bi$^{3+}$ ions with non volatile Dy$^{3+}$ ions is helpful in suppressing oxygen ion vacancies which stabilizes the valence fluctuation of Fe$^{3+}$/Fe$^{2+}$ ions in BFO.

An anomaly has also been observed in dielectric constant ($\varepsilon'$) and dielectric loss near Neel temperature ($T_N$). Landau–Devonshire theory of phase transition predicted this type of dielectric anomaly in magnetoelectrically ordered system as a consequence of vanishing magnetic order on
electric order. This type of anomaly in $\varepsilon'$ and $\tan\delta$ near antiferromagnetic Neel temperature demonstrates the occurrence of magnetoelectric coupling (ME) in all the samples.

**Figure 4.11:** Variation of dielectric loss ($\tan\delta$) with temperature for Bi$_{1-x}$Dy$_x$FeO$_3$ nanoparticles at different frequencies

### 4.3.3.2 CONDUCTIVITY STUDIES

To further study the conduction behavior of the samples, temperature dependent ac conductivity measurement was carried out. Temperature dependent ac conductivity at frequency 10 kHz is shown in **Figure 4.12**. The value of ac conductivity can be calculated using an empirical relation:

$$\sigma_{ac} = \varepsilon_0 \varepsilon_r \omega \tan \delta$$  \hspace{1cm} (4.3)

where $\omega$ is the angular frequency, $\varepsilon_0$ is vacuum permittivity, $\varepsilon_r$ is dielectric constant and $\tan\delta$ is dielectric loss. The value of $\sigma_{ac}$ was found to decrease with decreasing temperature and increasing Dy$^{3+}$ concentration in BFO. The increase in conductivity with increasing temperature
may be ascribed to the increase in oxygen vacancy mobility. Oxygen vacancies are mobile charges and play an important role in the conduction process of oxide. The decrease in oxygen vacancies with increasing Dy$^{3+}$ concentration results in reduction of ac conductivity. The activation energy $E_a$ (which depends on a thermally activated process) can be calculated by using the relation:

$$\sigma_{ac} = \sigma_0 \exp\left(-\frac{E_a}{k_B T}\right)$$  \hspace{1cm} (4.4)

where $k_B$ is Boltzmann constant and $\sigma_0$ is pre exponential factor. The values of $E_a$ at high temperature range (335-445ºC) are calculated as 0.36, 0.39, 0.44 eV for $x = 0.03$, 0.05, 0.10 samples. However, in the low temperature range (40-110ºC), the values of $E_a$ are found to be

Figure 4.12: Variation of a.c. conductivity with inverse of temperature at 10 kHz for Bi$_{1-x}$Dy$_x$FeO$_3$ samples.
0.13, 0.14, 0.21 eV for x=0.03, 0.05 and 0.10 samples, respectively. The overall ac conductivity may arise due to hopping of oxygen vacancies between the multivalent oxidation states of Fe$^{3+}$/Fe$^{2+}$ ions and presence of bismuth vacancies and oxygen vacancies. The value of activation energy at higher temperature clearly indicates the contribution of short range movement of oxygen vacancies to the conduction process [149].

4.3.4 OPTICAL STUDIES
4.3.4.1 UV-VIS DIFFUSE ABSORPTION STUDIES

In the past few years, numerous research works has been carried out on structural, electric and magnetic properties of BFO. Whereas very few works has been done to study the optical properties of BFO. In addition, BFO nanoparticles have exhibited potential application in photocatalytic activity of organic compounds. Therefore, in order to explore detailed optical properties of Bi$_{1-x}$Dy$^x$FeO$_3$ nanoparticles, UV-visible diffuse reflectance spectra (DRS) of all the samples were recorded. UV-visible diffuse reflectance spectra for Bi$_{1-x}$Dy$^x$FeO$_3$ nanoparticles are shown in Figure 4.13. It can be seen that all the compositions can absorb visible light in the wavelength range of 450-600 nm. Optical band gap of the compositions was calculated from the tangent line in the plot of $(\alpha h\nu)^2$ versus $h\nu$ according to classical Tauc's approach [189].

$$\alpha h\nu = A(h\nu - E_g)^n$$

(4.5)

with $n = 1/2$ since BFO is a direct band gap material. The band gap of the samples was calculated by extrapolating the linear portion of the curve to the x-axis. The band gap of the nanoparticles was estimated to be 2.12, 2.20 and 2.22 eV for x=0.03, 0.05 and 0.10 respectively, which is in good agreement with the earlier reported values on BFO nanoparticles [190, 191]. The decrease in the band gap of Bi$_{1-x}$Dy$^x$FeO$_3$ nanoparticles may be attributed to the rearrangement of molecular orbital and distortion induced in the FeO$_6$ octahedra. The bump around 370 nm is attributed to the ligand to metal and metal to metal charge transfer [192]. The absorption band around 750 nm is associated with the crystal field transitions [193].

The prominent blue shift in the absorption spectra of Dy doped BFO samples shows the change in band structure of the nanoparticles. The reason for the observed blue shift may not be
related to quantum confinement as in our case particle size is larger than 10 nm and therefore, the increase in band gap may be attributed to the presence of dopants atoms which alter the electronic structure of the nanoparticles.

![UV-Visible absorption spectra and Tauc’s plots](image)

**Figure 4.13:** (a) UV-Visible absorption spectra and (b) – (d) Tauc’s plots for Bi$_{1-x}$Dy$_x$FeO$_3$ nanoparticles

### 4.3.4.2 FTIR STUDIES

Infrared spectroscopy has been a powerful tool to characterize the materials for the bond formation. The Fourier transform infrared (FTIR) spectrum represents a finger print of a sample containing peak which correspond to the frequencies of bonds vibration of the atoms present in the material. As every material has unique combination of atoms therefore, no two materials have similar IR spectrum. By using FTIR spectroscopy, we can identify the bond formation between different atoms present in the material. The FTIR spectra of all samples were recorded using KBr pellet. **Figure 4.14** shows the room temperature FTIR spectra for Bi$_{1-x}$Dy$_x$FeO$_3$ samples in the
wave number range 400-1000 cm\(^{-1}\). It is clear that there are two vibration bands at \(\sim 550\) cm\(^{-1}\) and \(\sim 443\) cm\(^{-1}\). These bands are assigned to Fe-O stretching and bending vibration, respectively, present in FeO\(_6\) octahedral unit. BiO\(_6\) octahedral structure unit also exhibits absorption bands around \(\sim 530\) cm\(^{-1}\) and \(\sim 450\) cm\(^{-1}\) [194]. Therefore, the appeared broad nature of vibration bands is due to occurrence of FeO\(_6\) octahedra and BiO\(_6\) octahedra absorption peaks.

![FTIR transmittance spectra for Bi\(_{1-x}\)Dy\(_x\)FeO\(_3\) nanoparticles](image)

**Figure 4.14:** FTIR transmittance spectra for Bi\(_{1-x}\)Dy\(_x\)FeO\(_3\) nanoparticles

nearly at the same wave number. The third peak at \(\sim 573\) cm\(^{-1}\) corresponds to the out of phase vibrations of basis atoms of oxygen normal to (111) plane of the rhombohedral BFO [195]. The formation of the perovskite structure can be confirmed by the formation of metal-oxygen bond. The Shift in FTIR spectra may be attributed to nano sized grains in which arrangement of atoms are different at grain boundaries than that of bulk crystal which results in disorder in both length as well as co-ordination. This degradation in symmetry is responsible for the shifting in FTIR spectra.
To calculate the metal oxide bond length and effect of Dy doping on bond length, the Gaussian peak fitting was carried out in the wave number range 500 cm\(^{-1}\) to 620 cm\(^{-1}\) as shown in Figure 4.15 (a-c). It is observed from the graphs that mode at 533.14 cm\(^{-1}\) shifts towards 528.16 cm\(^{-1}\) and mode at 548.16 cm\(^{-1}\) shifts towards 552.60 cm\(^{-1}\) with the substitution of Bi\(^{3+}\) ions by Dy\(^{3+}\) ions. The vibrational frequency of Bi/Dy-O and Fe-O bonds can be determined by using the relation:

\[
\nu = \frac{1}{2\pi c} \sqrt{\frac{K}{\mu}}
\]  

(4.6)

Figure 4.15: Fitted FTIR absorption spectra in the wave number range 500-620 cm\(^{-1}\) for Bi\(_{1-x}\)Dy\(_x\)FeO\(_3\) nanoparticles.
where, $\nu$ is the wave number, $c$ is the velocity of light, $K$ is average force constant of the Bi/Dy-O bond and Fe-O bond. Also, $\mu$ is the effective mass of the bond which can be obtained by using the by the relation:

$$\mu = \frac{M_o \times \left[xM_{Bi} + (1-x)M_{Dy}\right]}{M_o + \left[xM_{Bi} + (1-x)M_{Dy}\right]}$$

and

$$\mu = \frac{M_o \times M_{Fe}}{M_o + M_{Fe}}$$

(4.7)

where, $M_o$, $M_{Bi}$, $M_{Dy}$ and $M_{Fe}$ are the atomic weights of O, Bi, Dy, and Fe respectively. Force constant (K) can be related to the average Bi/(Dy) – O and Fe-O bond lengths (r) by the equation:

$$K = \frac{17}{r^3}$$

(4.9)

The values of effective mass, force constant and bond lengths as calculated from the above equations are shown Table 4.4. It can be seen that the variation of the bond lengths in all the samples is consistence with the results obtained from Rietveld refinement of the XRD patterns.

Table 4.4: Wave number, effective mass, force constant and bond lengths calculated from FTIR spectra for Bi$_{1-x}$Dy$_x$FeO$_3$ nanoparticles

<table>
<thead>
<tr>
<th>Parameters</th>
<th>0.03</th>
<th>0.05</th>
<th>0.10</th>
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<td>Wave number (cm$^{-1}$)</td>
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<td>550.43</td>
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<tr>
<td></td>
<td>(Bi-O)</td>
<td>533.14</td>
<td>531.56</td>
</tr>
<tr>
<td>Effective mass $\mu$ (10$^{-26}$Kg)</td>
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<td>2.080</td>
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<tr>
<td></td>
<td>(Bi-O)</td>
<td>2.485</td>
<td>2.484</td>
</tr>
<tr>
<td>Force constant $K$ (Ncm$^{-1}$)</td>
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<td>2.491</td>
</tr>
<tr>
<td></td>
<td>(Bi-O)</td>
<td>2.218</td>
<td>2.237</td>
</tr>
<tr>
<td>Bond Lengths (Å) (FTIR)</td>
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</tr>
<tr>
<td></td>
<td>(Bi-O)</td>
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<td>1.896</td>
</tr>
<tr>
<td>Bond Lengths (Å) (Rietveld)</td>
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<tr>
<td></td>
<td>(Bi-O)</td>
<td>2.402</td>
<td>2.467</td>
</tr>
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4.4 CONCLUSIONS

In this chapter, we have successfully synthesized Bi$_{1-x}$Dy$_x$FeO$_3$ nanoparticles with $x = 0.03$, 0.05, and 0.10 by sol-gel method using tartaric acid route. Effects of Dy substitution on structural, magnetic, dielectric, optical and vibrational properties of BiFeO$_3$ were studied. The rhombohedral phase to orthorhombic phase transformation for $x=0.10$ sample has been confirmed from XRD and Raman studies. The observed spin-two phonon coupling predicted the oxygen octahedral rotation which is critical for weak magnetic nature. The distortion in spin cycloid structure and the ferromagnetic coupling between Dy$^{3+}$ ions Fe$^{3+}$ ions have been attributed for enhanced magnetization in the samples. Dielectric studies revealed that the addition of Dy$^{3+}$ ions improve dielectric properties of the materials. The band gap of nanoparticles varies from 2.12 eV to 2.22 eV for $x = 0.03$ to $x = 0.10$ samples which indicates its potential application in photocatalytic activity and optoelectronic devices. The FTIR spectra showed the presence of various theoretically predicted peaks associated with the formation Bi-O and Fe-O bonds and the calculated bond lengths are consistent with that obtained from Rietveld analysis.