CHAPTER-6

THE INFLUENCE OF COBALT CONCENTRATION ON THE
STRUCTURAL, OPTICAL, HEMOCOMPATIBLE, MAGNETIC
AND ELECTROCHEMICAL PROPERTIES OF BISMUTH
FERRITE NANOSTRUCTURES

6.1. XRD ANALYSIS OF THE COBALT DOPED BFO

Cobalt (in various weight percentages of 8%, 12 % and 16%) doped BiFeO$_3$ nanopowders were characterized by the XRD analysis (Figure 6.1(a)). The pure BiFeO$_3$ diffraction peaks were given JCPDS values of BiFeO$_3$ in the XRD pattern reported by Maleki et al (2018). The Co doped BiFeO$_3$ samples clearly indicate the well crystalline and mixed phase of spinel and perovskite bismuth ferrite with rhombohedral structure formation reported by Liu et al (2005). We can clearly see that the Co concentration increased in the BFO, which induces structural changes in BFO to cobalt ferrite/bismuth ferrite from the XRD pattern, and also increased the secondary phases remarkably. Moreover, 16% Co concentration in the BFO powder caused diffraction peaks of 2θ values, such as $30.47^\circ$, $35.40^\circ$, $37.63^\circ$, $43.62^\circ$ and $53.71^\circ$ related to the cobalt ferrite respectively studied by Liu et al (2005).
Moreover, the gradually increasing peak at $2\theta = 27.75$ seen from Figure 6.1(b) on increasing the Co concentration, indicates the structural change of BiFeO$_3$ to Bi$_2$Fe$_4$O$_9$ or Bi$_2$O$_3$ due to the defects level induced by the dopants studied by Pradeep Reddy Vanga et al (2017). The other reason is that structural changes in the XRD diffraction may happen due to the ionic radius of Fe$^{3+}$ (0.64 Å) with larger sized Co$^{2+}$ (0.73 Å) ions in the BFO studied by Anju, et al (2017). As the Co concentration increases in BiFeO$_3$, the diffraction peaks in the XRD pattern slightly shift towards a lower angle (left side); this was due to the large size of Co ions. When lower angle shifts were observed in
the XRD, they indicate the compressive stress developed in the doped BFO samples.

Figure 6.1(b) : XRD patterns of JCPDS value of BiFeO$_3$, 8%, 12% and 16% of Co doped BiFeO$_3$ powder at 20°-35°.

6.2. EDX ANALYSIS OF THE COBALT DOPED BFO

The elemental composition and atomic weight percentage of Co doped BiFeO$_3$ powder samples are examined by the EDX analysis. The EDX pattern of pure, 8%, 12 % and 16% wt of Co doped BiFeO$_3$ powder is shown in Figure 6.2. For the pure BiFeO$_3$ sample, the atomic weight percentages of Bi, Fe and O element were 70.68 %, 17.81 % and 11.52 % respectively, in the EDX pattern. For the 8% Co doped BiFeO$_3$ sample, the atomic weight percentages of Bi, Fe, O and Co element
were 73.69 %, 17.01 %, 7.55 % and 1.75 %, respectively. For the 12% Co doped BiFeO$_3$ sample, the atomic weight percentages of Bi, Fe, O and Co element were 73.03 %, 16.94 %, 7.46 % and 2.57 %, respectively. Whereas, for the 16% Co doped BiFeO$_3$ sample, the atomic weight percentages of Bi, Fe, O and Co element were 73.91%, 14.82%, 7.61% and 3.66%, respectively. Based on the obtained EDX result, we can confirm the formation of the Co content incorporated in the BiFeO$_3$ samples.

![EDX spectra of 8%, 12% and 16% of Co doped BiFeO$_3$ powder.](image)

Figure 6.2: EDX spectra of 8%, 12% and 16% of Co doped BiFeO$_3$ powder.
6.3. FE-SEM ANALYSIS OF THE COBALT DOPED BFO

We carefully examined the surface morphology of the pure and Co doped BiFeO$_3$ nanostructures; pure BiFeO$_3$ shows spherical morphology and all the doped samples have mixed morphology like tiny spherical/broken red bricks (as shown in Figure 6.3). The particle shape of the broken red bricks increased with increasing Co content in the BiFeO$_3$ due to the increased particle grain growth. The average particle sizes are found to be ~95, 89, ~85 and ~80 nm for the pure, 8%, 12% and 16% Co doped BFO samples.

Figure 6.3 : FE-SEM images of pure, 8%, 12% and 16% of Co doped BiFeO$_3$ nanopowders.
6.4. TEM ANALYSIS OF THE COBALT DOPED BFO

Figure 6.4 (a-c) : TEM images of 8%, 12% and 16% of Co doped BiFeO₃ nanopowders.

Figure 6.4 (a-c) shows the Co doped BiFeO₃ samples. From the TEM images, the average particle sizes were measured to be ~ 89, ~
85 and ~ 80 nm for 8%, 12% and 16% Co doped bismuth ferrite, which is comparable with the obtained SEM results. A schematic formation of Co doped BiFeO$_3$ nanoparticles are shown in Figure 6.4 d. We can clearly see that the increased particle grain growth may be due to the Co incorporated in the BFO nanoparticles.

![Schematic formation of Co doped BiFeO$_3$ nanoparticles](image)

Figure 6.4 (d): Scheme of the formation of Co doped BiFeO$_3$ nanostructures.

### 6.5. UV-VISIBLE ABSORPTION SPECTRA ANALYSIS OF THE COBALT DOPED BFO

The tuning of optical absorption and optical band gap of pure and Co-doped BFO nanoparticles under the influence of Co dopant can be tested with the help of UV-visible spectra. From the UV-visible spectra Figure 6.5 (a), of the pure and Co-doped BFO samples strong
absorption peaks were seen in the visible region. Generally, optical absorption of pure and doped BiFeO₃ nanoparticles was observed in the visible region. Moreover, we can clearly see that it is very difficult to find the exact direct optical band gap of the obtained pure and Co-doped BFO samples from the UV-visible absorption spectra due to the multiple absorption edges. We can calculate the exact optical band of the obtained BFO samples by using Tauc plot.

Figure 6.5 (a) : UV-visible spectra of pure, 8, 12 and 16 wt% Co doped BFO nanoparticles.
Figure 6.5 (b): The optical band gap ($E_g$) calculated from the Tauc plot.

Figure 6.5 (c): The optical band gap ($E_g$) and particle size (nm) values of pure and Co-doped BFO versus Co concentration (wt %).
The optical band gap energies were calculated by using the Tauc plot (extrapolating the linear portion of the \((\alpha h\nu)^2\) versus \(h\nu\) curve, as shown in Figure 6.5 (b). The optical band gap can be calculated from the optical absorption data by using the equation 6.1:

\[
(\alpha h\nu)^2 = B (h\nu - E_g) \tag{6.1}
\]

Where, \(h\nu\) - photon energy, \(\alpha\) - absorption coefficient, \(B\) - constant relative to material, and \(E_g\) - energy gap.

The optical band gap energies are estimated to be ~1.89, 1.78, 1.75 and 1.72 eV for pure BFO, 8%, 12% and 16 wt% Co doped BFO nanoparticles, respectively. With an increase in the Co content the optical band gap edge shifts towards a longer wavelength, which can be ascribed to the decreasing optical band gap of the BFO sample due to the density of states in the valence band, which would lead to a move in the optical absorption toward the narrow photon energy and the additional sub-band-gap energy levels that are induced by the abundant surface and interface defects in the doped samples. Moreover, the obtained optical band gap values of pure and Co doped BFO samples, are comparable with the previous report of the optical band gap values of pure and doped BFO samples by Wang et al (2001). The decreasing optical band gap and increasing particles size values with increasing Co content in BFO are shown in Figure 6.5(c).
6.6. HEMOCOMPATIBILITY ANALYSIS OF THE COBALT DOPED BFO

The obtained pure and Co-doped BFO nanoparticles are mixed with human blood and thus samples are collected in test tubes like Sodium Heparin coating at low temperature (4 °C) by using the blood compatibility experiment analysis. Initially, mixing of BFO nanoparticle samples with human blood were sterilized for 1 h under UV radiation of 365 nm using the Jasco V-760 UV-Vis Spectrophotometer. Then, the sterilized samples were mixed with 1 mL of saline solution in 5 mL centrifuge tubes and were incubated for one day at room temperature. After that, the saline was extracted from the centrifuge tubes and the samples were incubated at room temperature for 10 min. 2 mL of sterile saline was added into the above samples and they were incubated for 1 h further. The tubes were centrifuged at 750 rpm for 10 min with the help of the Remi R8C Centrifuge Machine. The serum was taken and collected in individual tubes. The positive control and the human blood with 2 mL saline solution acts as the negative control. The optical density (OD) values of the positive control (human blood with 2 mL of distilled water) and negative control (human blood with 2 mL saline solution) were detected with the help of the Jasco V-760 UV-Vis Spectrophotometer at wavelength (545 nm). We can calculate the percentage of hemolysis as obtained in the pure and Co-doped BFO samples from the optical density values.
The percentage of hemolysis formula is given below;

\[
\% \text{ of hemolysis} = \frac{\text{OD Value of the test sample} - \text{OD Value of the negative control}}{\text{OD value of the positive control} - \text{OD value of the negative control}} \times 100
\]

Figure 6.6: Hemocompatibility test for pure and Co-doped BFO samples.

If the samples’ percentage of hemolysis was below 5%, between 5-10% and 20%, they can be referred to be highly hemocompatible, hemocompatible and non-hemocompatible, respectively studied by Ramana Ramya et al (2014), as confirmed by the Standard American Society for Testing and Materials (ASTM) values. The BFO and Co-doped BFO nanoparticles samples shown in Figure 6.6 revealed less
than 5% hemolysis representing a highly hemocompatible nature, which is consistent with the ASTM and it would be used for biomedical applications.

6.7. VSM ANALYSIS OF THE COBALT DOPED BFO

The tuning of the hysteresis loops, magnetic saturation, and magnetic phase of BiFeO$_3$ under the influence of Co doped is presented in the VSM analysis from Figure 6.7 (a). The pure and 8 wt% Co doped BiFeO$_3$ sample reveals weak ferromagnetic behavior as shown in the inset in Figure 6.7(a).

![M-H curve of pure, 8, 12 and 16 wt% of Co doped BFO powders.](image)

Figure 6.7 (a) : M-H curve of pure, 8, 12 and 16 wt% of Co doped BFO powders.

On increasing the Co concentration (12 and 16 wt %) in the BiFeO$_3$ samples (refer inset M-H curve), the weak ferromagnetic
behavior changed to strong ferromagnetic behavior with broad hysteresis loops, as observed in the VSM analysis.

The magnetic saturation (Ms) and coercivity (Hc) values of BiFeO$_3$ increased on increasing the Co concentration percentage as shown in Figure 6.7 (b).

![Figure 6.7 (b) : The magnetic saturation (Ms) and coercivity (Hc) values of pure and Co-doped BFO versus Co concentration wt %.](image)

The Ms and Hc values are listed in Table.6.1. Khan et al (2015) have reported similar behavior of pure and Co doped BiFeO$_3$ nanostructures. In addition, Mohammadi et al (2015) and Philip et al (2015) have also observed the same phenomena of pure and Gd doped BiFeO$_3$ nanostructures. Moreover, the magnetic saturation values increased on increasing the Co content in the BiFeO$_3$; this may be due to two reasons: (i) exchange of Co ions and Bi ions in the ferrite oxide, and
(ii) increasing of oxygen vacancy defects as studied by Manjula et al (2018). The difference in the magnetic property should come from the increasing of the Co content. Moreover, the 8 and 12 wt % of Co incorporated in the BiFeO₃ caused the soft magnetic behavior and it can be used for temporary magnets. However, the 16 wt% of Co content in the BiFeO₃ sample caused the hard magnetic behavior and it can be used for permanent magnets. Based on the above magnetic studies, the higher percentage the Co doped BiFeO₃ samples has better magnetic properties compared to the 8 and 12 wt % Co doped BiFeO₃ samples.

**Table 6.1: The magnetic saturation (Ms) and coercivity (Hc) values of pure and Co-doped BiFeO₃ (BFO).**

<table>
<thead>
<tr>
<th>Samples</th>
<th>Magnetic saturation (Ms) (emu/g)</th>
<th>Coercivity (Hc) (Gauss)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure BFO</td>
<td>0.10</td>
<td>650.07</td>
</tr>
<tr>
<td>8% doped BFO</td>
<td>0.38</td>
<td>676.71</td>
</tr>
<tr>
<td>12% doped BFO</td>
<td>0.39</td>
<td>812.57</td>
</tr>
<tr>
<td>16% doped BFO</td>
<td>4.77</td>
<td>1009.1</td>
</tr>
</tbody>
</table>

6.8. CV ANALYSIS OF THE COBALT DOPED BFO

The electrochemical properties of pure BFO and CFO/BFO samples are examined by the CV curves. Figure 6.8 (a&b) shows the CV curves of the pure BFO and CFO/BFO samples electrode at a scan
rate 20 mV·s\(^{-1}\) in the voltage range between 0 and 1.7 V. It is clearly seen that the pair of reduction and oxidation (redox) peaks observed during the anodic and cathodic sweeps for both samples, confirm the faradic and non-faradic reactions due to the contribution of the pseudocapacitive mechanism by Khajonrit et al (2018).

Figure 6.8: CV curve of (a) BFO and (b) 16% Co doped BFO nanoparticles.

In addition, the anodic peak current density is observed to be 0.49 and 0.80 for pure and CFO/BFO, respectively. The pure BFO and CFO/BFO samples can be used for rechargeable Li-ions batteries.
6.9. PL SPECTRA ANALYSIS OF THE COBALT DOPED BFO

The PL emission spectra of the Pure BFO and 16% Co doped BFO samples under excitation wavelengths (350 nm) are presented in Figure 6.9 (a & b).

Figure 6.9: PL emission spectra of (a) BFO and (b) 16% Co doped BFO nanoparticles.

For the pure BiFeO\textsubscript{3} sample it was observed in the visible emission peaks such as 420,447,470,486, 540,565, 601, 628, 652, 663 and 694 nm with lesser PL intensity. However, 16% Co concentration in the BiFeO\textsubscript{3} sample caused broad visible emission peaks such as 416, 450, 495, 514, 544, 592, 617, 643, 672 and 695 nm with high PL intensity. 16% Co doped BiFeO\textsubscript{3} sample was observed in the visible emission region with slightly shifted longer wavelength, which is comparable with the PL emission spectra of the pure BFO sample. The visible emission peaks indicate that, this may be due to the oxygen vacancy defects studied by Wang et.al (2012). 16% Co doped BiFeO\textsubscript{3}
sample revealed the increasing oxygen vacancy defects in the PL emission spectra. The presence of higher oxygen vacancy defects of the 16% Co doped BiFeO$_3$ can be used for advanced optoelectronic devices. Moreover, Wang et.al (2012) has reported PL emission spectra of pure and Zr doped BFO samples observed in the range of the visible region (425-775 nm). Mishra et al (2016) have reported the PL emission of pure and Ni doped BiFeO$_3$ observed in the visible emission region (650-750 nm). The above PL emission spectra literature of pure and doped BiFeO$_3$ samples is different from our PL emission results. Based on the above PL analysis, it is seen that higher Co content (16%) incorporated in the BiFeO$_3$ sample has better photoluminescence properties compared to the pure BiFeO$_3$ sample.