3 Chapter 3

Sutural, Dielectric, Magneto-dielectric and Multiferroic properties of (Yb, Co) co-doped Bismuth ferrite

3.1 Introduction

In order to exploit the device prospects of multiferroic BiFeO$_3$, we need to resolve certain challenges like how to improve the magneto-electric coupling, ferromagnetic and dielectric properties at room temperature[265, 266]. There could be many ways to manipulate these challenges by doping and co-doping, nanostructures, and nanocomposites. The doping into the host lattice of BiFeO$_3$ was found to be a very effective approach which helps to overcome the above-mentioned challenges. The doping in BFO can be single site doping (either at A site or B site) or on both sides simultaneously [156, 171, 267-273]. The advantage of simultaneous doping on both sites is expected to enhance the magnetic and ferroelectric properties and reduce in the leakage current [156, 274, 275].

Here, the structural, magnetic, ferroelectric, dielectric properties and magneto-dielectric properties of Yb and Co-substituted BFO powder prepared using the Sol-gel method are systematically investigated. The structural studies confirm the single-phase polycrystalline rhombohedral structure with R3c space group. The co-substitution studies revealed that electrical, ferromagnetic and ferroelectric properties of BFO significantly enhanced as compared to pure BFO samples. Furthermore, the Bi$_{0.95}$Yb$_{0.05}$Fe$_{0.95}$Co$_{0.05}$O$_3$ (BYFCO) samples show strong magneto-electric coupling at the room temperature.

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1 Some parts of the work presented in this chapter are published in Physica Scripta 94, 065802 (2019).
3.2 Experimental details

Multiferroic BiFeO$_3$ and Bi$_{0.95}$Yb$_{0.05}$Fe$_{0.95}$Co$_{0.05}$O$_3$ were synthesized using sol-gel method. We used Bi(NO$_3$)$_3$5H$_2$O, Yb(NO$_3$)$_3$5H$_2$O, Fe(NO$_3$)$_3$9H$_2$O (Aldrich, >98%), and Co(NO$_3$)$_2$6H$_2$O (Sigma Aldrich, >98%) as starting reagents to obtain the precursor powders. The precursor solution was kept overnight at 80°C on a magnetic hot plate for proper solubility and dry. The resultant xerogel powder was grinded using AGATE mortar and pestle. In order to obtain the pure phase the resultant powder was annealed in air at 400°C for 4 hours. For electrical measurements the powders were compressed using hydraulic pressure with 5.0 Ton to get pellets and sintered in air at 400°C for 2 hours. The diameter and thickness of pellet for pure BFO were 10.0 mm and 1.41mm, respectively. The mass of the sample was 0.86283 gm. For co-doped sample, the diameter and thickness of the pellet was 9.0 mm and 1.83 mm. The mass of the sample was 0.90088 gm. The electrical contact was made by silver epoxy. And, magnetic measurements were performed on powder samples. For magnetic measurements the sample was wrapped in Teflon tape. The magnetic field was varied from -10000 Oe to 10000 Oe. The mass for pure and co-doped BFO samples was 0.0145gm and 0.0158gm, respectively. The structure analysis was carried out by Rigaku Minifexl-II X-ray diffractometer using CuKα radiation with wavelength of 1.54 Å. XRD data was collected at a slow rate (0.02° per second). The dielectric measurement was recorded in the frequency range 100 Hz -10MHz using Nova control Alpha-A high-performance Frequency analyser. Temperature dependent dielectric measurements were carried out at a few selected frequencies in between 100Hz to 10MHz in the temperature range from 300K to 700K. The magneto-dielectric measurements were performed using a variable electromagnet (magnetic field up to 1.5 Tesla). The magnetic measurements were performed using PPMS VERSALAB vibrating sample magnetometer (VSM) at room temperature. The ferroelectric hysteresis loops (P-E) and leakage current (J-E) for the ceramics samples were measured at 100 Hz using RADIANT PRECISION TECHNOLOGY INC. under electric field of 20 kV/cm.
3.3 Results and Discussion

3.3.1 Structural Analysis

![XRD Pattern Graph](image)

Figure 3-1: XRD pattern of Pure BFO and BYFCO samples, respectively.

Fig. 3.1 shows the room temperature XRD profiles of pure BFO and BYFCO powder. It is clear from the XRD patterns that the diffraction peaks are very intense which suggest a good crystalline nature of the samples. The diffraction pattern was compared and indexed with PCPDFWIN card number 74-2493. XRD pattern reveals rhombohedrally distorted BFO structure with R3c symmetry. The structural properties of Bi$_{0.95}$Yb$_{0.05}$Fe$_{0.95}$Co$_{0.05}$O$_3$ (BYFCO) powders are found to be identical to those of pure BFO. For co-doped sample, the XRD peak appears at 27.6° and 33.5°, respectively perhaps associated with the traces of impurity phases corresponding to Bi$_{25}$FeO$_{40}$ and Bi$_2$Fe$_4$O$_9$, respectively. These peaks represent the secondary phase of traces of impurity which is generally formed because of highly volatile nature of bismuth [276]. The XRD peak due to secondary phase of traces of impurities has also been reported in La and Gd co-doped BFO system [277]. Note that these secondary phases due to
impurities (i.e. Bi$_2$Fe$_4$O$_9$ and Bi$_{24}$FeO$_{40}$) are paramagnetic which do not significantly contribute to the magnetic properties [278-280].

The diffraction peak at (104) and (110) in the XRD pattern for BYFCO sample shifted towards a higher angle as compared to pure sample. The shift in peak profile towards higher angle indicates a compressive lattice distortion could be due to co-doping[281, 282]. This could be due to the smaller cation ionic radii Yb$^{3+}$ (0.868 Å) and Co$^{3+}$ (0.545Å) as compare to Bi$^{3+}$ (1.03Å) and Fe$^{3+}$ (0.65Å), respectively [283, 284]. Note that the estimated Goldschmidt tolerance factor for co-doped samples is found to be less than 1. This indicates that the driving force for the octahedral rotation increases and consequently Fe-O and Bi-O bonds may be under compression and tension strain, respectively [145, 284, 285].

3.3.2 Dielectric properties

Figure 3.2 (a) and (b) shows the dielectric constant (ε) and tangent loss (tan δ) of pure BiFeO$_3$ and Bi$_{0.95}$Yb$_{0.05}$Fe$_{0.95}$Co$_{0.05}$O$_3$, respectively recorded at room temperature as a function of frequency. In both samples the dielectric constant decreases monotonically in the frequency up to 10 MHz [Fig3.2 (a)]. The dielectric constant values for the co-doped BFO sample are found to be higher as compared to the pure BFO sample. The rate of change in the dielectric constant with frequency in the co-doped sample is faster than the pure BFO sample. The decrease in dielectric constant value with increase in probe frequency may be due to dielectric relaxation[31, 286]. The tangent loss for pure BFO and BYFCO shows opposite behaviour up to the frequency ~22 kHz as shown in Fig 3.2(b). Further, both the samples show smooth decay in the tangent loss as the frequency increases. The BYFCO sample exhibits a significant improvement in the value of dielectric constant as compared to pure BFO sample. The enhancement could be due to the presence of fewer charge defects in BYFCO as compared to BFO sample. To the best of our knowledge, the value of the dielectric constant of
pure BFO is found to smaller than the many another reports on BFO thin films and ceramics[287, 288].

![Graph 1](image1.png) ![Graph 2](image2.png)

Figure 3-2: (a) The variation dielectric constant with frequency at room temperature for Pure BFO and BYFCO samples, respectively. (b) The variation of tangent loss with the frequency at room temperature Pure BFO and BYFCO samples, respectively.

The peak in the tangent loss represents relaxation time of charge carriers. It means that the charge carriers in BYFCO relax faster than pure BFO (the peak may be out of probe frequency). To the best of our knowledge, the BFO tangent loss data never gave loss peak from 1Hz to 1MHz at room temperature (the relaxation time is inverse of probe frequency). It means the mobility of charge carriers in BYFCO is faster than BFO.
In the lower frequency range \( \varepsilon \) show a large dispersion. In general, the dielectric relaxation in BFO can be due to mainly two contributions such as (1) intrinsic, and (2) extrinsic. The intrinsic contribution originated from the off-centering of positive and negative ion in crystals. While, the extrinsic contribution originated from various factors such as finite conductivity, defects dipoles, accumulation of charge carriers, interface between electrode and sample grain boundaries in crystalline materials [289-292]. Among them, the interfacial and dipolar polarization play a major role in dielectric measurement because in the high-frequency range, the dielectric constant becomes saturated. In sub-infrared range of frequency, dipolar polarization or oriental polarization contributes to the dielectric[293]. The polarization corresponding to this mechanism occurs at a frequency range \( 10^{3}-10^{6} \) Hz at room temperature [293]. The interfacial polarization dominates when mobile charge carriers are impeded by a physical barrier that inhibits charge migration. The charges pile up at the barrier producing a localized polarization of the materials[294]. Therefore, for our samples, the dielectric behaviour perhaps associated with dipolar as well as interfacial polarization[293].

Fig 3.3 (a) and (b) shows the variation of dielectric permittivity (\( \varepsilon \)) for pure BFO and BYFCO as a function of frequency at different temperatures. The value of \( \varepsilon \) monotonically decreases as frequency increases for all temperatures. The frequency response of dielectric constant at the smaller frequency the space charges can follow the applied field whereas at high frequencies they find extremely narrow time limit to build up space charge and thus unable to undergo relaxation process. The behaviour of dispersion of dielectric constant with frequency can be explained by the space charge polarization model of Maxwell Wagner model [295-297]. At low temperature, dipoles freezes due to space charge relaxation process at the interface which causes decrease in polarization that results a smaller value of dielectric constant. Further, the space charge polarization is controlled by available free charges which are across the applied field. The gradual increase of dielectric constant as the temperature
increases particularly in the lower frequency region could be due to thermally activated charge carriers (i.e. space charge, charge defects, and associated defects) [31, 298, 299].

![Dielectric Constant vs Frequency](image)

Figure 3-3: (a) the variation of dielectric constant with the frequency at different temperature for pure BFO. (b) The variation of dielectric constant with the frequency at different temperature BYFCO sample.

The dielectric dispersion can also be explained by Koop’s theory since atoms in the dielectric media do not immediately respond to the applied field they need some time to align themselves along the applied field direction. As the frequency of the electric field increases, a point is reached when the charge carriers of dielectric media do not exactly follow the applied frequency of the electric field, therefore the value of \( \varepsilon \) decreases. The decrease in dielectric constant could be due to the hopping of the electrons from Fe\(^{2+}\) to Fe\(^{3+}\) ions. At lower frequency, the electric field is not strong enough to provide sufficient energy to the electron for hopping from Fe\(^{2+}\) to Fe\(^{3+}\) ions. But, as the frequency increases the electric field provides sufficient energy to the electron for hopping transport. The dielectric behaviour of BYFCO might be understood on the basis of oxygen vacancy and displacement of Fe\(^{3+}\) ions. The
structure of BFO can be characterized by two distorted perovskite blocks connected their body diagonal to build a rhombohedral unit cell. The ferroelectric state is realized by a large displacement of the Bi-ions relative to the FeO$_6$ octahedral [12, 25].

There are always some oxygen vacancies in un-doped BFO, which result in relatively high conductivity and less dielectric constant [276, 285, 300]. The presence of a large number of oxygen vacancies makes the perovskite phase of BFO less stable. The small amount of Yb$^{3+}$ doping is expected to reduce the oxygen vacancy in BFO. Therefore the Yb$^{3+}$ doping may stabilize the perovskite structure of BFO. In Bismuth Ferrite, Bi, Fe, and Co cations possess mixed valance states, it changes various valance states due to the presence of oxygen vacancies in the crystal, and it rapidly changes with a change in probe temperatures and frequencies. The change in the magnitude of dielectric constant and large dielectric dispersion with doping may be due to the crystal distortion brought by a large amount of oxygen vacancies and mixed valance states of cations. The free charge carriers develop pseudo polarization (Maxwell–Wagner polarization) in the crystal which in turns originate large dielectric dispersion and large dielectric constant due to the local charge imbalance caused by the oxygen non-stoichiometry[301].
Figure 3-4: (a) Temperatures dependence variation of dielectric constant of Pure BFO at different frequencies. (b) The variation of dialectic constant for BYFCO sample at different frequencies as a function of temperature.

Fig 3.4 shows the variation of \( \varepsilon \) as a function of temperature for pure BFO [Fig3.4 (a)] and BYFCO [Fig3.4 (b)] at different frequencies. The temperature dependent feature of \( \varepsilon \) at different applied frequency show anomalous behaviour at \( \sim 415 \) K and \( \sim 675 \) K, respectively in pure BFO sample. The dielectric constant increases gradually with temperature almost up to 415 K for all samples. Such behaviour could be due to thermally activated dipoles as the more and more dipoles participated towards polarization and with increasing temperature[31, 32]. Whereas, the anomalous feature in BYFCO appears at a lower temperature as compared to pure BFO. As the frequency increases the anomalous feature slowly disappears. This type of dielectric anomaly nearby the antiferromagnetic–paramagnetic transition temperature (Neel
temperature, $T_N$) signifies usually strong coupling between magnetic and electric order parameters[302, 303]. In many literature, it is reported that the anomaly near $T_N$ is due to Landau-Devonshire Theory of phase transition[170]. The observation of an anomaly in the dielectric constant at the magnetic transition temperature is taken as evidence of multiferroic magneto-electric coupling [15, 304, 305]. The peaks appeared at ~415 K in pure BFO sample associated with unknown phase transition[301]. These peaks can be attributed to the dielectric relaxation process superimposed on electrode interface polarization.

### 3.3.3 Magneto-dielectric properties

Figure 3.5 (a) and (b) shows the variation of a magneto-dielectric constant as a function of frequency at room temperature for pure BFO and BYFCO samples, respectively. The co-substitution of Yb and Co in BFO shows six time enhancements in dielectric constant as compared to pure BFO samples. The magneto-dielectric constant decreases as frequency increases for both the samples. The applied static magnetic field reduces the magneto-dielectric constant as compared to the values of a magneto-dielectric constant in zero magnetic field.
Figure 3-5: (a) Frequency response of magneto-dielectric constant for pure BFO at room temperature. (b) Frequency dependence magneto-dielectric constant BYFCO at room temperature.

Figure 3.6 (a) and (b) shows the frequency dependent magneto-tangent loss at different applied static magnetic field recorded at room temperature for pure BFO and BYFCO samples, respectively. The nature of variation of magneto-tangent loss for pure BFO decreases as frequency increases. Whereas, a magneto-tangent loss for BYFCO initially decreases as frequency increases (up to ~700 Hz) and a further increase in frequency results in a peak in the magneto-tangent loss profile. The change in magneto-dielectric properties with the applied magnetic field is attributed to the presence of strong magneto-electric coupling in the materials.
Figure 3-6: (a) Frequency dependence Magneto-tangent loss for BFO sample at room temperature. (b) Frequency dependence Magneto-tangent loss for BYFCO sample at Room temperature.

The magneto-electric coupling in multiferroic materials may be attributed to simultaneously presences of electric and magnetic order[300]. Applied magnetic field induces spin in the lattice which modulates the polarization in the materials. This modulation ultimately causes the observed magneto-dielectric coupling in the samples[170, 306]. Shalini et al., also reported the magneto electric coupling in (Nd, Mn) co-doped BFO system which is consistent with our observation[307]. The quantitative measurement of magneto-dielectric coupling (MDC) in term of magneto-dielectric constant $MD\%$ and magneto-tangent loss $ML\%$ defined as [285, 291, 307]
\[
MD(\%) = \frac{\varepsilon(H) - \varepsilon(0)}{\varepsilon(0)} \times 100
\]

\[
ML(\%) = \frac{Tan\delta(H) - Tan\delta(0)}{Tan\delta(0)} \times 100
\]

where \(\varepsilon(H)\) and \(\varepsilon(0)\) are the dielectric constant with and without a magnetic field, respectively. And, \(Tan\delta(H)\) and \(Tan\delta(0)\) are the tangent loss with and without magnetic field, respectively [285, 291, 307]. The \(MD(\%)\) and \(ML(\%)\) are calculated at 1 kHz using above formula for pure BFO is found to be -7.15\% and -5.57\%, respectively at magnetic field 1.5 T. Whereas, MD and ML values for BYFCO are found to be -1.14\% and -7.21\%, respectively [291, 307].

3.3.4 Magnetic properties

![Graphs showing magnetic properties](image)

Figure 3-7: (a) Field dependence of magnetization measured at room temperature for Pure BFO. (b) Field dependence of magnetization measured at room temperature for BYFCO sample.
Figure 3.7 (a) and (b) show the room temperature $M$-$H$ hysteresis loop for pure BFO and Bi$_{0.95}$Yb$_{0.05}$Fe$_{0.95}$Co$_{0.05}$O$_3$ (BYFCO), respectively. The pure BFO sample exhibit anti-ferromagnetic nature. While the co-doped sample shows a strong ferromagnetic behaviour. The details about quantitative analysis of $M$-$H$ hysteresis looss curve is given in Table1.

Table 3-1 : The calculated values of magnetization at maximum applied field ($M_{\text{max}}$), Remnant magnetization ($M_r$), Magnetic coercivity ($H_c$), Spontaneous polarization at maximum applied field ($P_{\text{max}}$), Remnant polarization ($P_r$) and ferroelectric coercivity ($E_c$), respectively for Pure and Yb and Co Co-doped samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Magnetic Parameters</th>
<th>Ferroelectric Parameters</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>$M_{\text{Max}}$ (emu/g)</td>
<td>$M_r$ (emu/g)</td>
</tr>
<tr>
<td>Pure BFO</td>
<td>0.08325</td>
<td>0.00518</td>
</tr>
<tr>
<td>BYFCO</td>
<td>2.1715</td>
<td>0.44545</td>
</tr>
</tbody>
</table>

The parent compound BFO is G-type antiferromagnetic due to the local spin ordering of Fe$^{3+}$ at room temperature. The spin ordering is further modulated by a cycloidal spin structure with a period of wavelength 62 nm [28, 308]. The ferromagnetism in BFO is restricted due to long-range order since the moment gets averaged out. But, a small residual magnetic moment is observed due to the canting of Fe-O-Fe spin structure [28].
Ferromagnetic nature can also be observed by altering the spin structure from helical to the linear. Modulation of the spin structure thereby increase the canting angle between Fe-Fe sub lattices in BFO can be explained regarding Dzyaloshinskii-Moriya (DM) interaction. Furthermore, the rotation of the oxygen octahedral is responsible for the variation in DM vector[104]. Therefore, any change in Fe-O octahedral and rotation of the oxygen octahedral strongly affect the magnetic properties. The bending of the angle between Fe-O-Fe in FeO₆ octahedral phase is very important because it controls both the magnetic exchange and orbital overlap between Fe and O which essentially determines the magnetic ordering[22]. Whereas, in the co-doped samples, the dilution of the spin cyclicity and the decreases in the bond lengths (Bi-O), bond angles (Fe-o-Fe) are due to the distortion created by Yb³⁺ and Co³⁺ [281]. The enhancement in the magnetization is perhaps due to the change in oxide system that influences magnetic properties via super-exchange interaction.

In BFO, Yb and Co ions interact with Fe ions via super-exchange interaction[309]. The magnetic orderings of Fe–O–Fe, Fe–O–Co, and Co–O–Co super-exchange interactions strongly depend on 3d orbital configuration and can be explained in terms of Goodenough–Kanamori rules [309-312]. Due to super exchange interaction of Fe-Co coupling and the collapse of the cycloid spin structure by Co doping the ferromagnetic behaviour is expected to enhance[173]. The possible mechanism for the enhanced ferromagnetic due to Yb and Co co-doping perhaps relates to (1) the destruction of the space modulated antiferromagnetic state through structural distortion, and (2) the increases of the ferromagnetic super exchange interaction between Fe³⁺ and Co³⁺ ions[136, 171, 313]. Another factor that may be responsible for the enhancement of magnetization is the presence of Yb and Co in co-doped BFO. Note that the presence of Co-ions not only affects the formation of Fe²⁺ they also control Fe²⁺ to Fe³⁺ charge fluctuation and it also favours the creation of oxygen vacancy[265, 281, 314, 315]. The enhanced ferromagnetic properties could be due to the substitution of Yb³⁺ ions at Bi³⁺ site where the interaction between the spins of the 4f electrons of Yb³⁺ ions and 3d of Fe³⁺ ions, which, to some extent, decouples the antiferromagnetic interactions between the
Fe$^{3+}$ ions[316, 317]. Therefore, the observed enhancement in the magnetization in BYFCO is believed to be due to co-doping in BFO samples.

### 3.3.5 Ferroelectric properties

![Graphs of P-E hysteresis loops for BFO and BYFCO samples](image)

Figure 3-8: Room temperature P-E hysteresis loops for pure BFO sample (a) and for BYFCO samples (b), respectively recorded at 100Hz.

Figure 3-8 (a) and (b) show the room temperature ferroelectric hysteresis loop (P-E) for pure BFO and BYFCO samples, respectively recorded at 100 Hz. The samples exhibit the unsaturated ferroelectric behaviour with lossy loop characteristics. The lossy behaviour of the loop can be attributed to the leakage current where the anion vacancies or fluctuations of valance electron of metal ions leads to electronic conduction[175]. Ferroelectric properties of Bi$_{0.95}$Yb$_{0.05}$Fe$_{0.95}$Co$_{0.05}$O$_3$ are found to be enhanced as compared to pure BFO [175]. The spontaneous polarization ($P_s$), remnant polarization ($P_r$) and the coercive field ($E_c$) of pure BFO and Bi$_{0.95}$Yb$_{0.05}$Fe$_{0.95}$Co$_{0.05}$O$_3$ (BYFCO) samples are given in table1.

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Figure 3-9: The variation of leakage current density for Pure BFO (a) and for BYFCO (b), respectively, as a function of electric field recorded at room temperature.

The room temperature plot of leakage current density (J) as a function of the electric field (E) of the pure BFO and BYFCO, respectively is recorded at 100Hz is shown Fig 3.9 (a) and (b). BYFCO sample shows a large leakage current as compared to pure BFO. The value of leakage current density recorded at electric field (~20kV/cm) for pure BFO and BYFCO (~15kV/cm) sample is found to be $3.9189 \times 10^{-4}$A/cm$^2$ and $2.329 \times 10^{-3}$, respectively. The high leakage current in BFO is mostly due to the defects such as secondary phases or oxygen vacancies[265] which can be due to the substitution of Yb$^{3+}$for Bi$^{3+}$ [318]. The material with better ME properties is necessary for many device applications due to its ability to simultaneously manipulate the magnetic and ferroelectric properties of BFO by the co-doping
method. Therefore our study suggests that the co-doping method could be a very efficient technique to manipulate the magnetic and ferroelectric properties of BFO.

3.4 Conclusions

The pure and (Yb, Co) co-doped BFO were successfully synthesized by using the Sol-gel method. The structural investigations of these samples confirm the single-phase polycrystalline rhombohedra perovskite structure with R3c space group. The BYFCO samples show larger ferromagnetism as compared to pure BFO. Furthermore, our study revealed that the Yb and Co co-doping effectively improve the dielectric properties of the samples. Both BFO and BYFCO exhibit a magneto-dielectric coupling effect at room temperature.