CHAPTER 3
OPTIMIZATION OF PROCESSING CONDITIONS AND ELECTRIC BEHAVIOUR OF BISMUTH FERRITE

3.1 INTRODUCTION

In the process of advancement of materials, BFO is one of the few potential materials to be recognised as multifunctional multiferroics materials (Mf-MFm). But, physical properties of these materials is found to be very sensitive to processing conditions. In view of this, this material has also been synthesized by mechano-chemical activation technique as well as solid state route. The structural and electrical properties of the samples prepared by above methods have been optimized.

3.2 PREPARATION TECHNIQUES

3.3 MECHANOCHEMICAL ACTIVATION TECHNIQUE USING HIGH ENERGY PLANETARY BALL MILLING (HEPBM)

The reduction in size to nano scale improves the properties of these materials drastically. Mechano-chemical activation technique using high-energy planetary ball milling (HEPBM) is one of the many routes to synthesize the Nano Mf-Fm/Mf-MFm’s. In this process, energy is provided in powder mixtures in order to induce the necessary chemical reactions for phase formation. The ball milling of solid/liquid mixtures results in homogeneous dispersion of fine particles without changes being introduced in the starting phases. HEPBM has been widely used as a suitable method to obtain binary, mixed or nanocomposite materials. Simultaneously, it usually results in large density of crystal defects in the final samples which can, in turn, lead to unexpected magnetic properties of the nanostructured materials [52], [53].

BFO is well known material for its multiferroic properties due to existence of its ferroelectric and magnetic order simultaneously at room temperature. Magnetic properties of BFO can be tailored by controlling the particle size due to suppression of spin helical order(~64nm) [14]. This prompted the authors to enhance the magnetization by reducing the particle size using mechano-chemical activation technique. Hence, an attempt has been made to synthesize nanostructured bismuth ferrite using HEPBM. The details of preparation has been described in chapter2. In this section of thesis, the effect of milling duration on the microstructural, electrical and magnetic properties of bismuth ferrite has been discussed.
3.3.1 STRUCTURAL AND MICROSTRUCTURAL ANALYSIS

Fig. 3.1(a) compares the XRD patterns of the sintered pellets milled for different durations i.e. 10 h, 20 h, 30 h and 40 h (abbreviated as N10, N20, N30 and N40 respectively). The sample milled for 10 h showed phase formation after calcination for 1h at 700°C followed by same sintering condition whereas other samples showed phase formation just after milling. Thus, sample N10 has not been considered for general discussion throughout the text except where it is mentioned.

![Figure 3.1](image)

**Figure 3.1:** (a) X-ray diffraction patterns of the sintered pellets milled for different durations i.e. 20 h, 30 h and 40h (abbreviated as N20, N30 and N40, respectively) along with sample N10 (milled for 10h) for which phase formation occurred only after calcination for 2h at 700°C followed by same sintering condition and (b) the crystallite size calculated from the broadening of XRD peaks using the Scherrer’s formula (with shape factor k=1)

It is observed that the phase is closely matching with Bi$_{3.8}$Fe$_5$O$_{12}$ in accordance with the JCPDS File No. 01-086-0367. Thus, lattice parameters were calculated with the observed d-values using Powder-X (Table 3.1) [54]. The lattice parameters have been found to decrease with the increase in milling duration, leading to the formation of Fe$^{3+}$ instead of Fe$^{2+}$ ions as the ionic radii of Fe$^{3+}$ is smaller than Fe$^{2+}$ ions as shown in Table
3.1. The crystallite size, calculated from the broadening of XRD peaks using the Scherrer’s formula[48] (with shape factor k =1) for the studied specimens is shown in Fig. 3.1(b). The EDAX and RBS of N40 sample confirms the presence of constituent’s elements. (see Fig. 3.2).

Table 3.1: Parameters calculated from XRD, SEM and TEM

<table>
<thead>
<tr>
<th>Pre-sintering Processing Conditions</th>
<th>Sample</th>
<th>Crystallite size (Å) $t_{XRD} = \frac{k_0}{\beta_{W_1/2}}$</th>
<th>Lattice size (Å) $t_c = 4d_{400}$</th>
<th>Areal Grain size (µm²) $t_{SEM}$</th>
<th>Particle size (nm) $t_{TEM}$</th>
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</thead>
<tbody>
<tr>
<td>Milled, calcined</td>
<td>N10</td>
<td>10.7k</td>
<td>12.653</td>
<td>6.44</td>
<td>x</td>
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<td>Milled</td>
<td>N20</td>
<td>11.8k</td>
<td>12.688</td>
<td>4.57</td>
<td>x</td>
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<td>Milled</td>
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<td>12.683</td>
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</tr>
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<td>Milled</td>
<td>N40</td>
<td>10.5k</td>
<td>12.636</td>
<td>1.92</td>
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</table>

X: Data Not Available, * nearly 2D layered structure has been observed in TEM images

Figure 3.2: RBS and EDAX of milled bismuth ferrite, N40 (BIG dominated)
Fig. 3.3 shows the SEM images of the sintered specimens milled for different durations. The grains are cubical in shape for all these samples. The average areal grain size of the compound decreases from 6.44 µm² for N10 to 3.20 µm² for N40. It is well known that the reduction in the average grain size due to an increase in the milling time could be due to the decrease in the particle size [55] but in this particular case, it is not observed as the particle size is fairly constant (nearly 100 nm) even on increasing the milling duration as seen in TEM micrographs of N30 and N40 samples (Fig. 3.4).

Fig 3.4 (a) shows the TEM micrographs of the specimen N30 and Fig. 3.4 (b) shows the TEM micrographs of N40 sample. The particles are appearing in the form of sheets and showing ductile like behaviour. With the increase in milling duration, crystallinity has been increased. Fig.3.4 (c) shows the change in contrast in the TEM images and multilayered sheet formation. The circle shows stacking faults that are a typical planar defect even visible in TEM images. This could possibly be the reason for increased crystallinity in the specimen N40 [56].

Fig. 3.4 (d) shows the selected area electron diffraction (SAED) patterns of the N30 sample and Fig.3.4 (e) shows the SAED patterns for N40 sample. In the diffraction pattern (DP) of N30, there is diffuse scattering due to short range ordering which at first appears random, sometimes circles with bright spots and sometimes spots between circles or there
are no circles [57]. In the DP of N40, spots are aligned in a line indicating high crystallinity of the specimen.

**Figure 3.4:** (a, b) TEM micrographs of the N30 and N40 samples respectively, (c) shows the change in contrast in the TEM images and multilayered sheet formation. The circle shows stacking faults that are a typical planar defect even visible in TEM images, (d, e) selected area electron diffraction (SAED) patterns of the N30 and N40 samples, (f) high-resolution transmission electron microscopy (HRTEM)-images of N40 sample. The domain bands are visible and thickness of these bands is ~ 3.2 Å i.e. interplanar spacing, d400.

Fig. 3.4 (e) shows the magnified selected area diffraction (SAED) pattern of 40 h milled sample, in which diffuse scattering has been observed. The extra spots indicated by arrow are caused by visible array of dislocations. Majority of the spots are in the form of doublets which is attributed to defects, especially if they interact with one another [58], indicating the presence of associated defects or defect clusters. Fig 3.4(f) shows the high-
resolution transmission electron microscopy (HRTEM) image of N40. The domain bands are visible and thickness of these bands is ~ 3.2 Å i.e. interplanar spacing, $d_{400}$. From the TEM micrographs [Fig. 3.4(c)] it is revealed that the particles are in the form of sheets rather spherical or ellipsoidal. Hence, the value of shape factor devised by Scherrer [48] could not be used as it was based on the spherical shape of particles. Also, the correction devised by Patterson [59] could not be used as it was based on ellipsoidal particles. Therefore, a correction for the shape factor, $k$, has been introduced (Table 3.1), which is calculated (Table 3.2) by equating crystallite size and lattice size as it is known that the crystallite size could not be smaller than the lattice size and should be near to integral multiple. In the present case, ratio of observed lattice size to crystallite size appears to be ~1. Hence, calculations showed that the value of shape factor is greater than 1 and compared with Scherrer’s constant for cubic lattice[60], given as:

$$K_{hkl} = \frac{6|\mathbf{h}|^3}{\sum_{h,k,l}h^2(6h^2-2|\mathbf{h}||\mathbf{k}|+|\mathbf{k}||\mathbf{l}|-|\mathbf{h}||\mathbf{l}|)} ....(3.1)$$

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lattice size (Å) $t_{d}=4d_{400}$</th>
<th>$(K_{hkl})_{avg}$</th>
<th>$k=t_d/t_\beta$</th>
<th>$t_{TEM}/t_d$</th>
<th>$t_{SEM}/t_d$</th>
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<td>x</td>
</tr>
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<td>1.07</td>
<td>2.14×10^4</td>
<td>x</td>
</tr>
<tr>
<td>N30</td>
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<td>1.10</td>
<td>1.11</td>
<td>1.77×10^4</td>
<td>9</td>
</tr>
<tr>
<td>N40</td>
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<td>1.10</td>
<td>1.20</td>
<td>1.38×10^4</td>
<td>*</td>
</tr>
</tbody>
</table>

X: Data Not Available, * nearly 2D layered structure has been observed in TEM images

### 3.4 CONVENTIONAL SOLID STATE REACTION METHOD USING MORTAR PESTLE

Microstructure of ceramics is very important to get desired properties e.g., a pore free microstructure with grain size $(t_{\text{grain}}) >>$ wavelength of electromagnetic (em) wave $(t_{\text{em}})$ or $t_{\text{grain}} < t_{\text{em}}$ may give electromagnetic transparency of corresponding em wave etc.,[1]. The microstructure depends on the processing conditions, especially the heat treatments. In solid state route, two step heating is involved, 1. First heat treatment (FHT), often referred as “Calcination”, which is originally defined as the process of subjecting a
substance to the action of heat, for the purpose of causing some changes in its physical or chemical constitution. The objects of calcination are usually: (a) to drive off water, present as absorbed moisture as "water of crystallization," or as "water of constitution"; (b) to drive off oxides of carbon, sulphur or other volatile constituent; (c) to oxidize a part or the whole of the substance and (d) diffusion of ions to form uniform lattice structure. Second heat treatment (SHT) after pelletization of sample generally referred as “Sintering”, which is originally defined as a method used to create an object from powders in the form of a product in a proper shape. It is based on mass diffusion, that occurs in any material at higher temperatures leading to the reduction in pore size and hence densification. In most sintering processes, the powdered material is held in a mould and then heated to a temperature below the melting point. The atoms in the powder particles diffuse across the boundaries of the particles, fusing the particles together and creating one solid piece for required application [61]. The heat treatments have two basic parameters temperature and time apart from surrounding atmosphere. There is huge literature available to explain the temperature dependent processing conditions, theoretically as well as experimentally, but time dependency is highly ignored, especially in the case of calcination; even after Avrami model [62]–[64] which explains time-temperature transformations.

Bismuth ferrite is a well known multiferroic material at room temperature and is very prone to show secondary phases that nucleate at grain boundaries and impurities. It is difficult to synthesize BiFeO₃ in pure phase by solid state sintering method as BiFeO₃ is metastable, off-stoichiometric, having a low peritectic decomposition temperature, and its formation is affected by Bi₂O₃ evaporation[65], [66]. Due to all these factors, secondary phases of Bi₂₅FeO₃₀ and/or Bi₂Fe₄O₉ are usually observed [2]. Therefore, the synthesis parameters are optimized because it is important to achieve the pure phase formation of BFO by this method. In the present work, effect of calcination duration on phase formation and grain growth of bismuth ferrite, BiFeO₃ (BFO) bulk ceramics has been discussed in detail. The ferroelectric properties of these samples show the significant effect of calcination duration.

3.4.1 THERMOGRAVIMETRIC ANALYSIS (TGA)

TGA measurements of the homogeneous mixture of constituent oxides (preapared as mentioned in chapter 2) were carried out to determine the calcination temperature and structural stability. Fig. 3.5 shows the TGA and DTA measurements for precalcined
mixture of Bi$_2$O$_3$ - Fe$_2$O$_3$ powders. The mixture of powders was heated up to 840°C at the heating rate of 10°C/ min. It is observed that oxidation occurs in two stages. An initial loss of ~ 1% upto 100°C has been observed which is likely due to the evaporation of surface absorbed moisture. Another mass loss has been observed at 700°C and above which is due to the formation of BiFeO$_3$.

![TGA and DTA measurements for precalcined mixture of Bi$_2$O$_3$ - Fe$_2$O$_3$ powders](image)

**Figure 3.5**: TGA and DTA measurements for precalcined mixture of Bi$_2$O$_3$ - Fe$_2$O$_3$ powders

### 3.4.2 STRUCTURAL AND MICROSTRUCTURAL ANALYSIS

![XRD of pre-calcined and calcined sample at 700°C for different durations for 1h to 6h](image)

**Figure 3.6**: XRD of pre-calcined and calcined sample at 700°C for different durations for 1h to 6h (a1 to a6)
Fig. 3.6 compares the X-ray diffraction patterns of the powder samples calcined at 700°C for different durations i.e. 1 to 6 hours (abbreviated as a1, a2, a3, a4, a5 and a6 respectively) along with pre-calcined powder. The samples a1, a2, a3 and a6 are single phase where as ‘a4’ and ‘a5’ are formed with large number of secondary phases may be due to unfavourable temperature gradient inside the furnace. Hence, samples ‘a4’ and ‘a5’ could not be processed.

3.4.2.1 OPTIMIZATION OF SINTERING TEMPERATURE

Before optimization of the calcination duration, it was necessary to keep sintering conditions similar. Microstructure/grain size is crucial parameter which directly affects the physical properties of specimen. Thus, we have optimized sintering temperature for sample ‘a6’ while keeping the sintering duration for 2 h. Fig.3.7 shows the SEM micrographs of the specimen sintered at different sintering temperatures. The sample sintered at 750°C possesses smaller grains and a porous microstructure. On increasing the sintering temperature to 830°C, well developed grains with uniform distribution have been observed. Thus the calcined powders have been sintered at 830°C for 2 h.

![Figure 3.7: Effect of sintering temperature on gain size on 6 hr calcined sample](image)

3.4.2.2 OPTIMIZATION OF CALCINATION DURATION

In order to optimize the calcination duration, the calcined sample at different durations i.e., a1, a2, a3 and a6 were sintered at optimized sintering temperature. The sintered specimen now nomenclatured as A1, A2, A3 and A6 respectively. The structure of
the sintered samples has been analyzed by Rietveld analysis using FULL PROF software (Fig. 3.8(a)). Fig. 3.8(b) shows the Rietveld refinement of these sintered samples and refined parameters like Bragg R-factor, RF-factor and $\chi^2$ are mentioned in Table 3.3. It has been observed that sintered specimens show single phase formation with rhombohedral (R3c) structural symmetry. Fig. 3.8(c) shows \{111\} plane view of crystal structure of BFO (A1 sample).

Further, in order to make the precise study of the effect of calcination duration on the structure of these compositions, we have carefully analysed the powder X-ray diffraction profiles.
Figure 3.8: (a) XRD of calcined at 700°C for different durations for 1h, 2h, 3h and 6h and sintered samples at 830°C for 2h (A1, A2, A3 and A6), (b) Rietveld refined patterns for A1, A2, A3 and A6, (c) Crystal structural of A1 sample (111) plane view
The intensity of the peak (110) at $\theta = 32.25^\circ$ decreases with the increase in calcination duration whereas intensity of the peak (104) at $\theta = 31.8^\circ$ increases with the increase in calcination duration. The peaks (102) and (104) firstly shift towards left in the sample A2 and on further increase in calcination duration the peak shifts towards right in the sample A3 and then shifts towards left in the sample A6. The lattice parameters of these samples were calculated using Reitveld refinement and given in Table 3.3.

**3.4.2.3 PHASE PURITY**

It is well known that Bi is highly volatile as the melting point of Bi$_2$O$_3$ is 817°C [2] and the formation of Bi gas is equally probable. Fig. 3.9 shows the variation of phase purity with the calcination duration of the sintered specimens. Hence in order to optimize the processing conditions, phase purity has been determined using the following relation:

$$\phi - purity = \frac{I_p}{I_p + 0.8I_S} \quad ....(3.2)$$

where $I_p$ is the intensity of the highest intense peak in pure phase sample and $I_S$ is the intensity of the secondary phase [67], [68]. It is observed in Fig. 3.9 that the sample A2 is highly phase pure and A4 sample is least phase pure. Here, it is noticeable that A6 sample,
is showing highest phase purity but Intensity of peaks (104) and (110) in this sample is weak.

Figure 3.9: Variation in phase purity with calcination duration

3.4.2.4 GRAIN SIZE

Figure 3.10: SEM images of calcined (lower small blocks) and sintered (upper big blocks) specimens
Fig. 3.10 shows the SEM images of the calcined and sintered specimens. Well developed grains with lower porosity are observed for the sample calcined for 1 h and grains with higher porosity are observed in the sample calcined for 6 h. In higher calcination duration, a partial melting and formation of another phase has also been observed. Areal grain size has been calculated and its variation is shown in Fig.3.11. It is observed that after sintering, areal grain size is higher for the sample calcined for 6 h.

3.4.2.5 Experimental Density

In the bulk samples, optimization of sintering temperature is usually being done by measuring the density of the sample. Fig.3.12 shows the variation of bulk density with the calcination duration. A1 sample is showing the maximum experimental density as compared to other samples.
In order to see the effect of density variation (due to calcination duration) on the electrical properties, the electrical properties of the specimens has been studied in the following section.

### 3.4.3 DIELECTRIC BEHAVIOUR

Fig. 3.13(a-b) shows the frequency dependence of dielectric constant and dielectric loss (\(\text{tan} \delta\)) at room temperature in the frequency range of 100 Hz to 1MHz. The dielectric constant has been found to decrease with frequency for all the samples and it is maximum for A3 at frequency \(< 100 \text{ kHz}\). The dielectric loss, also, has been found to decrease with frequency for A1 sample. Such type of behaviour is not observed in higher calcined samples. However, for other sample, tangent loss curve showed a broad hump at frequency \(\sim 100 \text{ kHz}\). The observed behaviour of dielectric loss is attributed to the Debye relaxation [69].
3.4.4 FERROELECTRICITY

Fig. 3.14 (a-b) shows the P-E hysteresis loops for the samples with different calcination duration at room temperature at 50 Hz and 1kHz. Nearly unsaturated loop have been observed for all these samples.

Figure 3.13: Frequency dispersion curve of dielectric constant and tangent loss for specimens

Figure 3.14: PE hysteresis loops of specimens at (a) 50 Hz and (b) 1kHz.
There are two major effects of grain boundary on polarization. In the samples with lower grain size, there is large number of grain boundaries [70] and it is well known that grain boundary is a low permittivity region; hence these samples should show poor ferroelectric characteristics. Also, it is well known that there is polarization discontinuity between grain boundary and grain surface which reduces the remanent polarization. Both these factors deteriorate the ferroelectric characteristics, as indeed observed in the present work. All these features observed indicate loops observed for A2 and A3 samples are artefacts while A6 is showing antiferroelectric behaviour. The fact is already supported with bulk density variation which shows that bulk density of sample except for A1 is very low. However, this artefact-ness reduces slightly as we move out to space polarization regime. It is seen in Fig. 3.14(b) where FE loops at 1kHz has been plotted. It is observed that all loops observed are now symmetrical with respect to y-axis. Lossy PE loops in BFO are very common. Some of uncommon loops might be observed due to mis-matching of RC combination of Sawyer-Tower circuit with the materials as these materials especially A3 (misplaced PE loop) has lowest density and phase purity. Thus most leaky sample is A3 in comparison to A1 keeping RC combination constant.

Polarization reversal of a ferroelectric domain is much easier inside a larger grain compared to that in a smaller grain [71], [72]. As it is well known that the ferroelectric properties depend on the microstructure, density and nature of substituent etc.; hence, the above observed behaviour can be due to the calcination duration.

Fig. 3. 15 shows the variation of remanent polarization, maximum polarization and back-switching parameter i.e. $P_r/P_s$ with frequency for different calcination duration. It is necessary to mention we have used notion $P_s$ for maximum polarisation. The decreasing trend in the value of $P_r$ and $P_s$ (with the increase in frequency) is observed. $P_r$ and $P_s$ are maximum at 50 Hz for the sample calcined for one hour duration; while at 1kHz, $P_r$ and $P_s$ values are low. Whereas $P_r/P_s$ ratio is nearly constant for the sample calcined at one hour in comparison to samples processed at higher calcined duration.
Figure 3.15: Variation of remanent polarization, maximum polarization and back-switching parameter i.e. Pr/Ps with frequency for the sintered specimens calcined for different durations

3.4.5 PIEZOELECTRIC CONSTANT

The piezoelectric constant (d_{33}) is plotted as a function of calcination duration and shown in Fig. 3.16. It has been observed that with increase in calcination duration value of piezoelectric coefficients decreases initially up to A3 (calcined for 3h) but for higher calcination duration i.e., A6 (calcined for 6h), the value of the coefficients again increases. This can be understood as follows. There are two major contributions to the piezoelectric coefficients: extrinsic and intrinsic. Influence of grain size, preferred orientation and the MPB conditions determine the intrinsic component of the piezoelectric constant in a specimen [73]. The extrinsic contribution is related to domain wall motion in the specimen [74]. As discussed earlier the variation of grain size in the SEM micrographs may be correlated with the increase in d_{33}; which is relatively high due to large grain size.
Synthesis and electrical characterization of bismuth ferrite

On the basis of comparative analysis, we have chosen conventional solid state route for further sample preparation, and all the samples are prepared at optimized condition i.e., calcined at 700°C for 1h and sintered at 830 °C for 2h. Now, we will focus on the electrical behaviour of BFO.

3.5 ELECTRICAL BEHAVIOUR

In Chapter 1, we have mentioned about the dielectric anomalies present in BFO. In the present part of chapter, the dielectric studies on BFO sample prepared at optimised conditions have been carried out. The behaviour of dielectric and resistivity of the sample around the two anomalies namely the ghost anomaly at 458 K i.e., Polomska transition and other at ~643 K i.e., Neel temperature have been keenly observed. Apart from the dielectric studies, we have focused on the conduction behaviour of this sample.

3.5.1 DIELECTRIC BEHAVIOUR

The Temperature dependent behaviour of the real part of permittivity ($\varepsilon'$) and dielectric loss (tan $\delta$) of BiFeO$_3$ specimen has been studied in the temperature range 300 – 700 K over a frequency range of 1Hz - 10MHz. In order to have a better understanding of dielectric anomalies, the $\varepsilon'$ - T plots at selected frequencies, i.e. 1kHz, 10 kHz, 100 kHz and 1MHz have been plotted (see Fig.3.17(a)). It is observed that there is an anomaly in $\varepsilon'$ appearing with a dip at temperature 350K, thereafter, it increases with increasing temperature followed by a plateau. These plateau is, further followed by steep rise in $\varepsilon'$. As the plateaus are shifting towards higher temperature, thus steep rise is only appearing for low frequency data. Dielectric loss data (see Fig.3.17(b)) gives better understanding as it clearly shows the variation in slope at temperature < 500K and till this temperature insulating character of BFO is observed as the value of dielectric loss is small ($\leq 1$). An anomalous rise in tan $\delta$ has been observed in temperature range 500 – 630 K; which indicates conducting phase. However this rise gets slower with increase in frequency. For $T > 600$, tan $\delta$ becomes independent to temperature at lower frequency.

In order to verify the observation that $\varepsilon'$ and tan$\delta$ shows a dip at ~ 350 K, sample is further heated on next day and cooled, the corresponding dielectric loss data is plotted (Fig. 3.17(c)). It shows the variation of dielectric loss with temperature at 10 kHz frequency in multiple heating and cooling processes. On day 2 heating, the decrease in tan$\delta$ is less
prominent as compare to day 1 heating and it disappears in cooling data on day 2, indicating, the anomaly is due to extrinsic factors and has nothing to do with sample itself.

The vertical dotted line has been drawn to identify another anomaly, i.e., polomska transition, which was earlier understood due to defects. No observable variation is appearing in cooling data along this vertical line.

3.5.2 IMPEDANCE AND MODULUS BEHAVIOUR

Impedance spectroscopy (IS) is a handy tool to probe the nature of different electro active regions. Thus, with proper selection of formalism out of four (Z, C, M and Y) various microstructure-electric property correlation can be understood [69], [75]. Bode plot and Nyquist plot are the two ways to represent the IS. We have started with, impedance formalism, but the Nyquist plots of impedance are not resolvable, confirming the dominance of diffusive (grain) mechanism i.e. Warburg type behaviour [69]. Almost similar feature is observed in permittivity or capacitance Nyquist plots. It is the Modulus

![Figure 3.17: Temperature dependent behaviour of (a) real part of permittivity ($\varepsilon'$), (b) dielectric loss (tan $\delta$) and (c) tan $\delta$ on day 1 for heating ($^1H$) and on day 2 heating ($^2H$) and cooling ($^1C$) for BiFeO$_3$](image)
(1/ε) Nyquist plot which is found to be resolvable. However, in order to understand origin of relaxation, it is necessary to have impedance bode plots along with modulus bode plot.

For this purpose, the modulus and impedance bode plots at different temperatures have been plotted and shown in Fig. 3.19. It is observed from these plots that the peaks in impedance and modulus plots do not coincide with each other indicating the possibility of short range hopping process, and decrease in the relaxation time decreases with increase in temperature. On the other hand, the bulk (grain) and the grain boundary contributions are clearly resolved in Modulus bode plots (Fig. 3.18) at 300K and 325 K. However at higher temperature, only bulk contribution is appearing.

3.5.3 RESISTIVITY BEHAVIOUR

Fig.3.19(a) shows the variation of resistivity as a function of temperature at 1 Hz for BiFeO₃. The resistivity has been found to decrease with increasing temperature showing NTCR behaviour. The resistivity of this sample varies from high value (~ 10¹⁰ Ω/cm of insulating nature) at room temperature to a low value (~ 10³ Ω/cm in almost semiconducting state) at 700 K. We have categorised resistivity plot in to five different
temperature regimes on the basis of transition/anomalies already marked in literature as discussed in previous chapter. It is reported [76]–[78] that up to 230 - 330 K, BFO shows polaronic behaviour with activation energy 125 eV, thus first regime, for < 330 K (regime I). Second regime is marked just before polomska transition i.e., 330 K - 440 K (regime II). 

![Figure 3.19: Resistivity Vs. temperature on semi log scale (a) at 1Hz (b) at 1kHz to 1MHz](image)

Third regime is marked at 500 K, from where steep rise is observed in dielectric loss data 440 K - 500 K (regime III). Finally, the regime IV is just before T_N (500 K - 630 K) and above this temperature as regime V. It is broadly divided in low temperature regime (LTR) and high temperature regime (HTR) as shown in Table 3.4. This
classification is considered as the base for all temperature dependent analysis of various dielectric and electrical behaviour in this thesis. Fig. 3.19 (b) shows dispersion in ac resistivity with temperature at frequencies of 1kHz to 1MHz. It is observed that with increase in frequency the resistivity remain almost constant before 458K marked by dotted vertical line (LTR and HTRII). It notable that the difference in resistivity is almost constant (~ by order of 10 for I decade of frequency interval). In HTR III, variation in value of resistivity is appearing with frequency and dispersion in resistivity decreases in this regime; this dispersion vanishes at Neel temperature and beyond (HTR V).

<table>
<thead>
<tr>
<th>Temperature Range</th>
<th>Broad Division</th>
<th>Temperature Regime</th>
<th>Nomenclature</th>
<th>Feature</th>
<th>Effect on conductivity</th>
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<td>I</td>
<td>LTR I</td>
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<td>Insulating behaviour[76]</td>
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<td>II</td>
<td>HTR II</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>440-500K</td>
<td></td>
<td>III</td>
<td>HTR III</td>
<td>Polomska transition at ~ 458 K[13]</td>
<td>Spin wave propagation[33], [34]</td>
</tr>
<tr>
<td>500-630K</td>
<td></td>
<td>IV</td>
<td>HTR IV</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>&gt;630K</td>
<td>V</td>
<td>HTR V</td>
<td>AFM transition at ~643K[2]</td>
<td>Increases till transition and get stabilize after $T_N$</td>
<td></td>
</tr>
</tbody>
</table>

### 3.6 DATA ANALYSIS

In this section, we will analyse the results obtained in order to (i) identify the origin of various anomalies/transitions observed (ii) to find activation energies (iii) for polaronic conduction mechanism.

#### 3.6.1 DIELECTRIC ANOMALIES/TRANSITIONS
3.6.1.1 FERROELECTRIC TRANSITION IN BFO

In order to find the phase transition temperature ($T_m$), we have used the phenomenological relation [79] similar to the Curie-Weiss law based on established materials having low $T_c$. As BFO is reported to have $T_c$ at 1103 K, it is not possible to have dielectric measurements up to 1200 K for this material. For this, data of $1/\varepsilon$ (modulus) at 100 kHz for BFO has been plotted as a function of temperature and data has been extrapolated to find $T_m$ which is found to be 1120 K. For the confirmation of $T_m$, $1/\varepsilon$ ($\equiv M$) vs. $T$ has also been plotted for BaTiO$_3$ (BTO) as shown in Fig. 3.20. The value of $T_m$ estimated by extrapolating these curves is found to be $\sim$1120 K and $\sim$ 395 K respectively for BFO and BTO, which are well in accordance with literature [2], [12], [72].

![Figure 3.20: Temperature dependent variation of $M (= 1/\varepsilon)$ for BiFeO$_3$](image)
3.6.1.2 POLOMSKA TRANSITION

In section 3.5.3, we have seen that there is almost no variation observed in the dielectric or resistivity data around 458 K. Although, the variation in the slope of temperature derivative of tanδ has been clearly observed (see Fig. 3.21), which strongly suggests the presence of an anomaly. The exact reason of this anomaly is not yet clear, however this feature was firstly noticed by Polomska[13].

3.6.2 ELECTRICAL CONDUCTION BEHAVIOUR

3.6.2.1 DC CONDUCTION ACTIVATION ENERGY ANALYSIS

The activation energies have been estimated using the data of relaxation time (Fig. 3.22) and resistivity (Fig. 3.19) at different temperature. The relaxation time $\tau_M$ has been extracted from peak positions in the bode plots of $M''$ at various temperatures in the range 350-450 K using $\omega = 2\pi f$ and $\tau$ is relaxation time. From these plots, activation energy has been estimated according to linear Arrhenius relation $\sigma = \sigma_0 \exp\left(\frac{-E_a}{k_BT}\right)$.

It has been observed that modulus relaxation time plot (Fig. 3.22) follow Arrhenius relation over the complete temperature range studied. However, the resistivity plots do not show one linear region, rather having different slopes in different temperature regimes.
In the present case, the activation energy is estimated as 0.44 eV. While, the activation energy values estimated from resistivity plots, are 126 meV in LTR and ~ 0.98 eV in HTR (II- V). In LTR, the activation energy is close to the order of energy associated with polaronic conduction i.e. 75 meV [80] whereas, in HTR the estimated activation energy is almost equivalent to the energy value required for oxygen vacancy (Table 3.5). It is well understood that the polarization and conduction mechanisms are, generally, different [69]. In order to understand ac conduction behaviour, Arrhenius variation of resistivity data has been studied at few frequencies from 1 kHz – 1 MHz.

3.6.3 AC CONDUCTION

\( \ln(\rho_{ac}) \) vs. 1000/T at a few frequencies with interval of ~ 1 decade (1kHz - 1MHz) are shown in Fig.3.23. The features observed in these plots are explained below.

At low frequencies, say for 1 Hz (<10 kHz) resistivity decreases monotonously with temperature as seen in Fig. 3. 19. We will discuss its Arrhenius variation in later section. But at higher frequency, where space-charge contribution is negligible. The resistivity curve shows a steep fall in resistivity with singular temperature which may be either due to Polomska (al low frequency) or possible charge order transition (T_{co}) (at high
Beyond $T_N$, it becomes almost frequency independent. The resistivity plots support the fact that regimes (I-III) up to 500 K represent insulating phase while regime V is a conducting phase.

![Arrhenius plot for ac resistivity](image)

**Figure 3.23:** Arrhenius plot for ac resistivity

### 3.6.4 POLARONIC CONDUCTION

In the previous section, it is seen that peaks of $M''$ and $Z''$ in frequency dependent plots (bode plots) do not coincide. The mismatch of maxima positions in bode plots occurs usually due to the short range polaronic conduction [75], [81].

In order to verify the polaronic conduction, logarithmic graph between the relaxation frequency and corresponding conductivity (dc) at different temperatures has been plotted (see Fig. 3.24) where relaxation frequencies are obtained from the peak positions of modulus bode plots (Fig.3.18), which is linear with good agreement of least square fitting parameters ($R^2 >> 0.99$). Thus, polaronic conduction cannot be overruled in these materials [37], [39], [69].

To order to verify the conduction mechanism, we have used the statistical best fit method, after plotting logarithmic resistivity ($\ln \rho$) with $1/T^p$, for $p = 1, \frac{1}{2}$ and $\frac{1}{4}$ (Fig. 3.27). For BFO, it is found that data is best fitted for $p = \frac{1}{4}$ (see Fig 3.27(a)). We have mentioned in chapter 1 that the density of state is not constant for BFO where $p = \frac{1}{2}$ i.e., Efros-Shklovskii (ES) VRH mechanism may be dominating. Therefore, Arrhenius and ES plots for ($\rho$) and $\rho/T$ are studied and shown in Fig.3.27(b,c). From these plots, it can be observed that thermal activation energy, $E_a$ (0.98 eV) is less than NNH energy (1.06 eV).
The ES plot of ln (ρ/T) gives best linear fit as compared to Arrhenius resistivity plot in HTR. The hopping energy, \( \epsilon_{\text{hop}} = \left( \frac{1}{2} \right) k_B \left( T_0 T \right)^{1/2} \) can be estimated using characteristic temperature (\( T_0 \)).

These energy values for BFO are tabulated in Table 3.5. From this table, it is clear that the hopping energy being much larger than thermal fluctuation (~ 25 meV) energy which rules out the possibility of long range hopping and allowing only short range hopping process. These observation may be correlated with localization length estimation as per section 1.11 in chapter 1.

**Table 3.5:** Various Energies in different temperature regime for BFO

<table>
<thead>
<tr>
<th>LTR</th>
<th>HTR</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>II</td>
</tr>
<tr>
<td>Thermally activated energy, ( E_a ) (eV)</td>
<td>0.12(6)</td>
</tr>
<tr>
<td>Nearest neighbour hopping energy, ( E_{\text{NNH}} ) (eV)</td>
<td>0.16(9)</td>
</tr>
<tr>
<td>Hopping Energy, ( E_{\text{hop}} ) (eV) at Temperature</td>
<td>300 K</td>
</tr>
<tr>
<td>1.08</td>
<td>10.21</td>
</tr>
</tbody>
</table>

*Figure 3.24: ln conductivity Vs. ln relaxation frequencies*
The localization length ($\xi$) can be estimated from characteristic temperature using equation 1.11. The variation with respect to temperature is plotted in Fig. 3.26. The value of $\xi$ is less than effective donor bohr radius for BFO i.e., $a^* = d(BFO)/4$. It undergoes
transition from Mott insulating phase to metallic phase around polomska transition temperature [79]. Thus, there is sudden increase in dielectric loss value beyond 500 K. Therefore, after polomska transition, leakage current may be considered as intrinsic behaviour of BFO.

![Localization length Vs. Temperature.](image)

**Figure 3.26:** Localization length Vs. Temperature.

Generally, in most of the solids, polaronic conduction occurs below room temperature [35], [37]; whereas in the present case polaronic conduction appears well above the room temperature. Thus, the feasibility of polaronic conduction above room temperature is needed to understand. In order to understand this mechanism, the critical temperature ‘T\textsubscript{h}’ has been estimated according to the approximation for perovskites as per equation 1.14, i.e., \( \frac{\varepsilon_{ij}}{k_B T} - \left(\frac{c}{\xi T}\right)^{1/2} + 2\frac{r_{ij}}{\xi} = 0 \). In the present case for BFO with \( a_{Fe} = 0.60 \) Å, \( \varepsilon_{ij} = 300 \) meV, \( r_{ij} = 1.44 \) Å, the estimated value of \( T_{h} \) (upper most temperature) is ~726 K. While, with \( \varepsilon_{ij} = 128 \) meV, \( T_{h} \sim 320 \) K. Thus, polaronic conduction may occur up to 726 K in BFO; provided the ratio, \( \varepsilon_{ij}/r_{ij} \) should not decrease with temperature. In LTR, the activation energy is \( \sim 128 \) meV, hence VRH is quite acceptable. But in HTR, polaronic conduction is due to oxygen vacancy as explained in following section.

### 3.6.5 BAND CONDUCTION MODEL

In order to verify above, we have taken the help of Photo-luminiscence (PL) study. Fig. 3.27(a) shows the band model based on band structure given by Clark et. al., [28].

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[Image of localization length vs. temperature graph]

**Figure 3.26**: Localization length Vs. Temperature.
Figure 3.27: (a) Energy distribution between lower p orbital and upper d-orbital energy state with density of state [28] (b) PL-Energy spectrum and (c) Modification in (a) due to oxygen vacancies and energy states Model at Metal – Insulator Interface.

Fig. 3.27(b) shows normalized PL spectra for BFO excited with laser light with wavelength of 350 nm at 295K. PL Spectra peaks are marked as $E_1$, $E_2$, $E_3$, $E_4$ and $E_5$ in increasing order of energy. Spectra ($E_5$) reveals the band gap of BFO is 2.94eV, which is in agreement theoretically [28] but slightly greater than experimental value reported [2]. As PL intensity ($I_\varepsilon$) is due to photon intensity, thus, it is proportional to number density at given energy level $E$ i.e., $N(\varepsilon)$. On careful analysis of these spectra, it is observed that $E_{43}$ ($\equiv E_4-E_3$) ~ 127 eV , which is same as observed from conductivity data for LTR which belongs to the polaronic conduction. Thus, it seems to have certain degree of correlation between high number density and 3D polaronic conduction in BFO. The strongest peak ($I_{\varepsilon_3}$) in PL spectra at RT, further supports the fact that polaronic conduction is main conduction mechanism. Moreover, $E_{51}$ ~ 1 eV, may be linked to the doubly ionize oxygen vacancies. It may need vacancy channel to move across grain boundary at higher temperature [82]. Other transitions have energy gap in between 0.2-0.7 eV, which may be due to localized hopping along Fe$^{2+}$- O - Fe$^{3+}$ network [83]. The activation energy, observed in PL study is in well accordance with the dielectric study. Thus, based on our studies, we are able to present a band model modification as compared to Fig. 3.26(a).
This modification is shown in Fig. 3.27(c) with an labelled Metal-Insulator-Interface (MIIF). This model shows formation of impurity band due to vacancies (typically Oxygen). Thus, band filling MIT occurs in present case through oxygen vacancies which seems to be the signature of charge order MIT, observed in derivative of loss curve (Fig. 3.21).

3.7 CONCLUSIONS

First, BFO has been prepared by HEPBM, the calcination duration has been optimized at 700°C which is found to be 1 h with sintering temperature 830°C. The milling duration has reduced the particle size and phase has been converted to garnet phase. The major phase has been found to be garnet phase. The FM character increases and simultaneously, there is a decrease in FE character. Thus, for further study, we opted for conventional SSR as compared to HEPBM.

The studies on electrical behaviour of BFO samples show signature of Polomska transition. The Impedance – Modulus Bode plots reveal SRH in this sample. In LTR (> 330 K) the thermally activated energy is 126 meV, while in HTR it is 0.98 eV. In all regimes/sub regimes, NNH energy is found to be greater than activation energy. Energy analysis reveals that Mott 3D VRH mechanism is dominant in BFO, thus e-e interaction is absent. Efross-Shklovskii model, applied to the present system that the critical temperature limit is ~ 726K up to which the polaronic conduction can be expected in present sample. The LTR results are verified by PL study and found in accordance with the reported literature. In HTR, the polaronic conduction is due to band filling by oxygen vacancies.