CHAPTER 6
STRUCTURAL AND ELECTRICAL BEHAVIOUR OF SAMARIUM AND TITANIUM CO-SUBSTITUTED BISMUTH FERRITE

6.1 INTRODUCTION
In the previous chapters, we have investigated structural, dielectric and conduction behaviour of ‘Ti’ substituted BFO and ‘Sm’ substituted BFO after synthesis by using conventional SSR method. It has been observed that with Ti and Sm substitution, an anomaly additionally occurring in comparison to BFO; which might be due to dipolar polarisation in both the systems BFTO and BSFO. It is sharp for Ti substituted BFO while for Sm substituted BFO, it is relaxor type. In R3c phase (for \( x \leq 0.12 \) in both the systems), variation in \( d_{33} \) with \( x \) shows opposite behaviour. Magnetisation increases in both systems but a significant rise in Sm substituted BFO is observed. In this chapter, we have investigated structural, dielectric and conduction behaviour of Sm and Ti co-substituted BFO system.

6.2 SYNTHESIS OF SM AND TI CO-SUBSTITUTED BFO
Highly pure powders of \( \text{Bi}_2\text{O}_3, \text{Fe}_2\text{O}_3, \text{TiO}_2 \) and \( \text{Sm}_2\text{O}_3 \) (Sigma Aldrich) were mixed in stoichiometric proportions to form samples with \( 0.04 \leq x \leq 0.20 \) in the system \( \text{Bi}_{1-x}\text{Sm}_x\text{Fe}_{1-x}\text{Ti}_x\text{O}_3 \). After calcination at 700 °C for 1h, the powder mixture was compacted into disk shaped pellets. These pellets were then sintered at the 830 °C for 2 h in air and characterised using XRD, VSM, piezo-meter, PL spectrometer etc. The dielectric and electric measurements were carried out in frequency range from 1 Hz to 10 MHz and temperature range from 300 K to 700 K using Novocontrol Impedance Analyser.

6.3 RESULTS
6.3.1 STRUCTURAL STUDIES
Fig. 6.1 shows the XRD patterns of various compositions \( x \) in \( \text{Bi}_{1-x}\text{Sm}_x\text{Fe}_1-x\text{Ti}_x\text{O}_3 \) system with \( x = 0.04 - 0.20 \) in steps of 0.04, abbreviated as Sm-Ti: BFO synthesized by solid state route. In XRD patterns, no characteristic peak of constituent oxides has been observed, but intensity of secondary phases has increased with the increasing Sm–Ti content in BFO. It is observed that with \( x \), amount and intensity of secondary phase increases with increasing \( x \). In order to further clarify these
observations, phase purity ($\varphi$) for R3c phase BFO has been determined using eqn. 3.2 and plotted (see Fig. 6.2). It is further noticed that with increasing $x$ the phase purity decreases. The data can be fitted with parabolic equation,

$$\varphi_{R3c}(x) \equiv 0.94 - 0.07x - 0.55x^2$$ .... (6.1)

The peaks (104) and (110) corresponding to $2\theta \sim 32^\circ$ are merging into a single peak with the increasing Sm-Ti content for $x > 0.12$. This disappearance of splitting of peak reveals phase change from rhombohedral R3c phase to some orthorhombic phase.

![X-ray diffractograms of compositions in the system Bi$_{1-x}$Sm$_x$Fe$_{1-x}$Ti$_x$O$_3$ with $x = 0.04 - 0.20$ in steps of 0.04]

Figure 6.1: X-ray diffractograms of compositions in the system Bi$_{1-x}$Sm$_x$Fe$_{1-x}$Ti$_x$O$_3$ with $x = 0.04 - 0.20$ in steps of 0.04
The XRD data have been refined using FULL PROF software package. Fig. 6.3(a) shows the Rietveld refined XRD patterns of Bi$_1$$_x$Sm$_x$Fe$_{1-x}$Ti$_x$O$_3$ (x = 0.04 - 0.20). In the refined patterns, the peak shapes were described by pseudo-Voigt functions. The lattice parameters and fitting factors are given in Table 6.1. The samples with x ≤ 0.12 have been fitted with R3c structural symmetry and a good agreement has been observed between the experimental and refined data. The agreement parameters ($\chi^2$) obtained after refinement are 1.67 for x = 0.04, 1.86 for x = 0.08 and 1.95 for x = 0.12 which lies within the acceptable limit of such structural symmetries. For the compositions with x ≥ 0.16, the diffraction data is fitted with R3c + Pn2$_1$a symmetries; where fitting parameters ($\chi^2$) are 1.76 for x = 0.16 and 1.16 for x = 0.20.

It has also been observed that the diffraction peaks shift towards lower angle with increasing concentration of Sm and Ti up to x ≤ 0.12 which can be attributed to the smaller size of substituent ions like the ionic radii of Ti$^{4+}$ (0.605Å) is less than that of Fe$^{3+}$ (0.64Å) [94]. After x > 0.12, the diffraction peaks shift towards the higher angle showing distortion in the lattice in a manner opposite to that of the compositions with x ≤ 0.12.
Figure 6.3: Rietveld refined diffraction patterns of Bi$_{1-x}$Sm$_x$Fe$_{1-x}$Ti$_x$O$_3$ compositions with $x \leq 0.20$, crystal structure for $x = 0.12$ and variation of microstrain with $x$. 
Table 6.1: Lattice Parameters, atomic positions and fitting parameters of Bi$_{1-x}$Sm$_x$Fe$_{1-x}$Ti$_x$O$_3$

<table>
<thead>
<tr>
<th>Samples</th>
<th>Symmetry</th>
<th>Lattice Parameters</th>
<th>Atoms</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>R-factors</th>
</tr>
</thead>
</table>
| x = 0.04 | R3c | a=b=5.5814Å, c=13.8338Å | Bi/Sm | 0     | 0     | 0     | $R_p = 2.3, R_{wp} = 2.16, R_{Bragg} = 8.11, R_F = 5.71, 
\chi^2 = 1.67$ |
|         |        |                    | Fe/Ti | 0     | 0     | 0.22368 |           |
|         |        |                    | O     | 0.49704 | 0.03922 | 0.95086 |           |
| x = 0.08 | R3c | a=b=5.5712Å, c=13.8247Å | Bi/Sm | 0     | 0     | 0     | $R_p = 2.93, R_{wp} = 2.76, R_{Bragg} = 14.5, R_F = 7.59, 
\chi^2 = 1.86$ |
|         |        |                    | Fe/Ti | 0     | 0     | 0.23235 |           |
|         |        |                    | O     | 0.46471 | 0.03047 | 0.95387 |           |
| x = 0.12 | R3c | a=b=5.5682Å, c=13.8014Å | Bi/Sm | 0     | 0     | 0     | $R_p = 3.25, R_{wp} = 3.02, R_{Bragg} = 15.5, R_F = 8.52, 
\chi^2 = 1.95$ |
|         |        |                    | Fe/Ti | 0     | 0     | 0.2365 |           |
|         |        |                    | O     | 0.55293 | 0.07 | 0.95391 |           |
| x = 0.16 | R3c | a=b=5.5388Å, c=13.701Å | Bi/Sm | 0     | 0     | 0     | $R_p = 4.94, R_{wp} = 3.56, R_{Bragg} = 11.4, R_F = 7.02, 
\chi^2 = 1.76$ |
|         |        |                    | Fe/Ti | 0     | 0     | 0.24417 |           |
|         |        |                    | O     | 0.22471 | 0.19902 | 0.32194 |           |
|          | Pn21a | a=5.6104Å, b=7.7868Å, c=5.4418Å | Bi/Sm | 0.00338 | 0.23821 | 1.00193 |           |
|         |        |                    | Fe/Ti | 0.04025 | 0 | 0.44432 |           |
|         |        |                    | O1    | 0.11873 | 0.35961 | 0.5123 |           |
|         |        |                    | O2    | 0.32532 | 0.15707 | 0.05413 |           |
|         |        |                    | O3    | 0.95438 | 0.63235 | 0.96866 |           |
|          | Pn21a | a=5.5304Å, c=13.6294Å | Bi/Sm | 0     | 0     | 0     | $R_p = 5.77, R_{wp} = 3.90, R_{Bragg} = 14.6, R_F = 10.7, 
\chi^2 = 1.16$ |
|         |        |                    | Fe/Ti | 0     | 0     | 0.26011 |           |
|         |        |                    | O     | 0.65102 | 0.14109 | 0.4614 |           |
|          | Pn21a | a=5.6013Å, b=7.8004Å, c=5.405Å | Bi/Sm | 0.00767 | 0.30543 | 1.02258 |           |
|         |        |                    | Fe/Ti | 0.00657 | 0 | 0.46238 |           |
|         |        |                    | O1    | 0.2362 | 0.34367 | 0.55024 |           |
|         |        |                    | O2    | 0.32532 | 0.15707 | 0.05413 |           |
|         |        |                    | O3    | 0.95438 | 0.63235 | 0.96866 |           |

The structural transformations are mainly caused by the displacement of atoms from their lattice positions due to different ionic radii of substituent ions than host ions and contribute to the lattice distortion, leading to the strained lattice. The microstrain can be calculated from XRD results by using the W-H model (explained in sec 4.2.1).

Fig.6.3(c) shows the variation of microstrain with x. It is observed that the value of microstrain shows two different regions. In region I, microstrain increases with x whereas in region II, it decreases. It can be attributed to the stress generated in the TiO$_6$ and FeO$_6$ octahedral. This leads to the changes in the phase from R3c to R3c.
+Pn2_1a with the substitution of Sm - Ti in BFO. This phase transition with x can further be understood with phase purity variation.

The phase purity (analytical) for R3c phase as per eqn. 6.1 has two kinds of dependence; one linear and other parabolic both represent decrease in phase purity with x. The behaviour of phase purity variation is quite different than that of individually Ti or Sm substitution. It may be due to complicated kinetics of materials caused by thermodynamic diffusion of dopants in to BFO matrix at high temperature. In contrast to analytical results, Rietveld refined data exhibits 100% phase purity for R3c symmetry up to x = 0.12. Thereafter, phase purity decreases drastically as new phase of Pn2_1a symmetry originates. Thus we have plotted a comparative plot for phase purity estimated by analytical relation (eqn. 3.2) as well as by Rietveld analysis (Fig. 6.4). The estimation for phase purity cannot be claimed to be very accurate as XRD data always shows some secondary phases.

![Figure 6.4: Comparative plot of phase purity for R3c phase in Sm-Ti co-substituted BFO](image)

**Figure 6.4: Comparative plot of phase purity for R3c phase in Sm-Ti co-substituted BFO**

### 6.3.2 DIELECTRIC STUDIES

#### 6.3.2.1 TEMPERATURE DEPENDENT DIELECTRIC BEHAVIOUR

The temperature dependent behaviour of the real part of permittivity (ε’) and dielectric loss (tan δ) of Bi_{1-x}Sm_xFe_{1-x}Ti_xO_3 (where x = 0.04 – 0.20) specimens has been studied in the temperature range 300 – 750 K over a frequency range of 1Hz - 10MHz. In order to have a better understanding of dielectric behaviour, the ε’ - T plots
at selected frequencies, i.e. 1 kHz, 10 kHz, 100 kHz and 1 MHz have been plotted and shown in Fig.6.5. It has been observed from these plots for all the compositions that there are few dielectric anomalies occur at different temperatures. In order to understand the features in detail, these plots have been divided into five temperature regimes: 300 - 330K, 330 - 440K, 440-500 K, 500 - 630K and above 630K, described as regime I, II, III, IV and V (as per Table 3.4) respectively and also shown in Fig. 6.5 for x = 0.04. Anomaly in ε’ in HTR II is not clearly seen for x = 0.04 while it is visible in tanδ Vs plots. A dielectric loss anomaly at temperature ~ 458 K may be correlated with Polomska transition as it is followed by a plateau [6, 8]. These permittivity peaks are broad and frequency independent. In regime HTR III-IV, another sharp dielectric peak is observed which is followed by a sharp rise in the ε’ in HTR V indicating conducting phase above this temperature.
Figure 6.5: Temperature dependent behaviour of the real part of permittivity ($\varepsilon'$) and dielectric loss ($\tan \delta$) of Bi$_{1-x}$Sm$_x$Fe$_{1-x}$Ti$_x$O$_3$ (where $x = 0.04 - 0.20$) specimens at few frequencies.

Almost similar behaviour has been observed for other compositions. In addition to all these observations, another anomaly has been observed in Region V, which is composition dependent i.e. observed at 700K for $x = 0.04$, 680K for $x = 0.08$, 610 K, 580 K and 550 K for $x = 0.12$, 0.16 and 0.20 respectively.

6.3.2.2 TEMPERATURE DEPENDENT VARIATION WITH COMPOSITION

Fig. 6.6 shows the variation of real part of permittivity and dielectric loss with temperature at 10 kHz frequency for all the compositions. A nearly constant region of
\( \tan \delta \) (a plateau) is observed at the same temperature showing signature of Polomska transition. In Regime IV i.e. 500 – 630 K, a peak has been observed at ~ 500 K; which is marginally temperature dependent. The temperatures of peak position decreases with \( x \) in R3c phase (\( x \leq 0.12 \)) and then saturated in R3c+Pn2\(_1\)a phase (\( x > 0.12 \)). Further, with the increase in \( x \), sharpness of peak decreases and corresponding peaks are also seen in tangent loss plots. After this, a peak has been observed at < 700K which is varying with Sm-Ti composition. Then there is increase in the value of \( \varepsilon' \) and \( \tan \delta \) after 700 K.

![Figure 6.6](image)

**Figure 6.6**: Temperature dependent behaviour of the real part of permittivity (\( \varepsilon' \)) and dielectric loss (\( \tan \delta \)) of Bi\(_{1-x}\)Sm\(_x\)Fe\(_{1-x}\)Ti\(_x\)O\(_3\) (where \( x = 0.04 - 0.20 \)) specimens at 10 kHz frequency

### 6.3.3 IMPEDANCE AND MODULUS ANALYSIS

The impedance-modulus bode and Nyquist plots have been plotted for a few compositions and shown in Fig. 6.7-6.9. For \( x = 0.04 \), it has been observed from bode plots of impedance at different temperature (Fig. 6.7a) that \( Z'' \) decreases with increasing frequency and dispersion is observed only in low frequency region; while in the high frequency region \( Z'' \) becomes temperature independent. Modulus bode plot
(Fig. 6.7 b) shows peak which shift towards high frequency with increasing temperature. These peaks are broader at low temperature and with increasing temperature it becomes sharper. This behaviour may be an indication for two dielectric processes at low temperature, whereas at high temperature only single dielectric process takes place. Therefore, at low temperature localised hopping cannot be ruled out. Modulus plots reveal that the relaxation time decreases with the increase in temperature. Nyquist plots of impedance (Fig. 6.7 c) are not resolvable, confirming the dominance of diffusive (grain) mechanism i.e. Warburg type behaviour [75]. Further modulus Nyquist plots (Fig. 6.7 d) reveal two semi circular arcs at low temperature and single at high temperature, which also support dielectric behaviour. Almost similar behaviour of impedance and modulus have been observed from bode and Nyquist plots for x = 0.12 (Fig. 6.8) and 0.20 (Fig. 6.9).

**Figure 6. 7:** Bode and Nyquist plots of $Z''$ and $M''$ for x = 0.04 in Bi$_{1-x}$Sm$_x$Fe$_{1-x}$Ti$_x$O$_3$ system.
Figure 6.8: Bode and Nyquist plots of $Z''$ and $M''$ for $x = 0.12$ in $\text{Bi}_{1-x}\text{Sm}_x\text{Fe}_{1-x}\text{Ti}_x\text{O}_3$ system

Figure 6.9: Bode and Nyquist plots of $Z''$ and $M''$ for $x = 0.20$ in $\text{Bi}_{1-x}\text{Sm}_x\text{Fe}_{1-x}\text{Ti}_x\text{O}_3$ system
6.3.4 RESISTIVITY BEHAVIOUR

Fig.6.10 shows the variation of resistivity as a function of temperature for Bi$_{1-x}$Sm$_x$Fe$_{1-x}$Ti$_x$O$_3$ (x ≤ 0.20) system at 1 Hz. From these plots, it is found that resistivity (ρ) decreases with increasing temperature indicating semiconducting behaviour with negative temperature coefficient of resistance (NTCR).

![Figure 6.10: Variation of resistivity (at 1Hz) with temperature](image)

This resistivity data has also been divided in five different temperature regimes as per the dielectric plots. Although, no distinct features are visible in ρ Vs. T plot, across these regions, except a few anomalies observed at intermediate temperature (regime IV). Even though, data has been analysed in all these regimes and correlated with dielectric behaviour in detail.

6.3.5 ROOM TEMPERATURE MULTIFUNCTIONAL STUDIES

6.3.5.1 PIEZOELECTRIC STUDIES

Fig.6.11 shows the variation of piezoelectric coefficient as a function of x (x = 0.04 - 0.20) in the system Bi$_{1-x}$Sm$_x$Fe$_{1-x}$Ti$_x$O$_3$. It has been observed that value of piezoelectric coefficient (d$_{33}$) is almost constant up to x = 0.08 and thereafter increases and becomes maximum for x = 0.16; which is found to be in correlation with structural transformation in this system. The high value of piezoelectric coefficient can be attributed to the existence of interface region with two structural symmetries referred as morphotropic phase boundary (MPB).
6.3.5.2 MAGNETIC HYSTERESIS

Fig. 6.12 shows M-H hysteresis curves as a function of x in the system Bi$_{1-x}$Sm$_x$Fe$_{1-x}$Ti$_x$O$_3$. For x = 0.0 (pure BFO), the loop is antiferromagnetic in nature. With the increasing x, loops tend to become more of ferromagnetic character i.e. AFM character is suppressing. This can be attributed to the breaking of Fe-O-Fe bonds due to Ti substitution at Fe-site. The remanent magnetization (M$_r$) increases with x (Fig. 6.13). It has been found that up to x = 0.12 and thereafter, M$_r$ become almost composition independent. From this, it is understood that structural distortion caused by substitution of Sm and Ti up to x = 0.12 relaxes by transforming the structure locally. For higher x, distortion originates Pn2$_1$a symmetry and hence existence of R3c + Pn2$_1$a symmetry for x $\geq$ 0.16 cannot be ruled out.
Figure 6.12: M-H hysteresis curves as a function of $x$ for $\text{Bi}_{1-x}\text{Sm}_x\text{Fe}_{1-x}\text{Ti}_x\text{O}_3$

Figure 6.13: Remanent magnetization with Sm, Ti co-substitution

6.3.5.3 PHOTOLUMINESCENCE

Fig.6.14 shows the photoluminescence (PL) curves for Sm-Ti co-substituted BFO samples for composition with $x \leq 0.20$. PL excitation for pure BFO resulted in an intense blue emission, which is clearly visible. The absorption spectra show three strong emissions at 421 nm, 459 nm and 484 nm, similar to Ti substituted BFO samples or Sm substituted BFO samples. However, the sharpness of the peaks has
been found to be changed. A strong emission at 459 nm lying in the blue region can be assigned as a band to band transition with a band gap of 2.67eV. The well known fact is that pure BFO has the intrinsic emission arising from a band edge to band edge transition only. With the increasing $x$, the intensity of these peaks has been reduced indicating the suppression of oxygen vacancies, which is in agreement with the observed dielectric data (Fig. 7.5) where loss decreases with increasing $x$.

![Photo-luminescence curves for pure BFO and Sm-Ti co-substituted samples](image)

**Figure 6. 14:** Photo-luminescence curves for pure BFO and Sm-Ti co-substituted samples

### 6.4 DATA ANALYSIS

In this section, an attempt has been made to analyse the dielectric anomalies observed in Fig.6.5 in correlation with resistivity behaviour in Fig. 6.10. In Fig.6.5, one shoulder, at 458 K, is observed; peaks are observed in two regimes: one composition independent and other frequency and composition dependent. To analyse the nature of peak, we have plotted differential derivative of $\ln\rho V.s.1/T$ curve i.e., $\delta \equiv d(\ln\rho)/(d(T^{-1}))$ with respect to temperature shown in Fig. 6.15. It is to be noted that $\delta$ is measure of activation energy. The anomalies have been further verified by pyroelectric current measured for $x = 0.12$ shown in Fig. 6.16. In Sm-Ti co-substituted
system, for $x \leq 0.12$, we have observed a broader dip; which splits into two peaks for $x \geq 0.16$. This

![Figure 6.15: Variation in (modified) activation energy with temperature](image)

may arise due to structural heterogeneity caused by co-substitution. This might be due to the charge ordering as observed for Ti substituted BFO. But, broadness in the curves, which start to split with $x$, indicates that the peak observed for $x > 0.12$, is in fact associated with peaks even with $x < 0.12$. This fact is further confirmed in

![Figure 6.16: Pyroelectric coefficient for $x = 0.12$ with temperature](image)
pyroelectric behaviour for $x = 0.12$, where two strong ferroelectric type peaks are observed. It is corresponding to the dip and peak seen for $\delta$- variation along with a small peak at $\sim 458$ K.

![Figure 6.17: Variation of c/a ratio and $T_{ft}$ temperature with x](image)

The FT/MIT temperature ($T_{ft}$) is seen to be composition dependent. To analyse, c/a ratio and $T_{ft}$ (estimated from different measurement techniques) has been plotted with $x$ (see Fig.6.17). It is observed that $T_{ft}$ decreases with the increasing $x$ as c/a ratio. It may be explained as the Ti-O bonds (672.4 KJ/mol) are stronger than Fe-O bonds (407 KJ/mol), hence the Ti$^{4+}$ ions can be substituted at lower temperature for phase formation, and hence the phase transition temperature is reduced.

### 6.4.1 TEMPERATURE REGIME WISE ENERGY ANALYSIS

The electrical resistivity behaviour has been mentioned in results section. It has been observed that with increase in temperature resistivity decreases sharply. But, the variation is not appearing linear for the whole temperature range. Moreover, a few anomalies are also visible. The discussion in LTRI has been ignored as data is scattered in most of the samples and now focused on HTR only. Firstly, we have
estimated the thermally activated energy \( (E_a) \) using Arrhenius relation (eqn.1.5) and then nearest neighbour hopping energy \( (E_{\text{NNH}}) \) using relation (eqn.1.6).

![Figure 6.18: Arrhenius plot of resistivity of various compositions (x) at 1 Hz in Bi_{1-x}Sm_xFe_{1-x}Ti_xO_3 system](image)

**Table 6.2:** Temperature regime-wise activation and nearest neighbour energy for Sm-Ti co substituted BFO

<table>
<thead>
<tr>
<th>Composition (x)</th>
<th>LTR</th>
<th>HTR</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>I</td>
<td>II</td>
</tr>
<tr>
<td>Thermally activated energy. ( E_a ) (eV)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0</td>
<td>0.126</td>
<td>0.98005</td>
</tr>
<tr>
<td>0.04</td>
<td>--</td>
<td>1.02</td>
</tr>
<tr>
<td>0.08</td>
<td>--</td>
<td>1.06</td>
</tr>
<tr>
<td>0.12</td>
<td>--</td>
<td>0.92</td>
</tr>
<tr>
<td>0.16</td>
<td>--</td>
<td>0.93</td>
</tr>
<tr>
<td>0.20</td>
<td>--</td>
<td>0.86</td>
</tr>
<tr>
<td>Nearest neighbour hopping energy. ( E_{\text{NNH}} ) (eV)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0</td>
<td>0.169</td>
<td>1.05774</td>
</tr>
<tr>
<td>0.04</td>
<td>--</td>
<td>0.97</td>
</tr>
<tr>
<td>0.08</td>
<td>--</td>
<td>1.18</td>
</tr>
<tr>
<td>0.12</td>
<td>--</td>
<td>0.93</td>
</tr>
<tr>
<td>0.16</td>
<td>--</td>
<td>0.81</td>
</tr>
<tr>
<td>0.20</td>
<td>--</td>
<td>0.94</td>
</tr>
</tbody>
</table>
The Arrhenius plots for all the compositions are shown in Fig. 6.18. In HTR, data could be fitted linearly in HTRII-III and HTRV; while in HTR IV an anomaly is observed. Therefore regime wise, thermally activated energy has been estimated. Similarly, nearest neighbour hopping energy has also been estimated. These two energies for all composition in different temperature regime is given in Table 6.2. It is found that most of the time, \( E_a \) is less than \( E_{\text{NNH}} \). It means thermally activated energy is not sufficient for feasibility of NNH.

![Arrhenius plots for ac resistivity](image)

**Figure 6. 19:** Arrhenius plots for ac resistivity

If we focus on regime wise energy variation with composition, it is observed that in HTRII-III, thermally activated energy almost decreases with \( x \) for \( x \geq 0.08 \); while in HTRV decreases with \( x \). However, the NNH energy is also decreasing in all three regime if we exclude \( x = 0.04 \) and 0.20. As the energy, estimated in HTRII-III, is found to be in the range of 1.11 to 0.85 eV, it hints for presence of doubly ionised oxygen vacancies. Whereas in HTR V, the energy range is 0.82 to 0.57 hinting for singly ionised oxygen vacancies.
The variation in ac resistivity with temperature indicates polaronic conduction till 458 K, and then the resistivity decreases sharply, with increasing temperature. The phase transition is also observed in regime HTRIV at low frequency while it disappears at high frequency ~ 1MHz. It indicates possibility of dipolar polarisation similar to Ti substituted BFO system.

6.4.2 POLARONIC CONDUCTION

In order to verify the polaronic conduction, logarithmic graph between the relaxation frequency and corresponding conductivity at 1 Hz (σ_{dc}) at different temperatures has been plotted (see Fig.6.18) where relaxation frequency at each temperature is obtained from the peak positions of modulus bode plots (Fig. 6.7(b)). All plots are linear with good agreement of least square fitting parameters (R^2 >> 0.99), indicating polaronic conduction in these materials [102].

![Figure 6.20: ln conductivity vs. ln relaxation frequency plot](image)

To verify the conduction mechanism, we used the statistical best fit method, after plotting logarithmic resistivity (lnρ) with 1/T^p, for p = 1, ½ and ¼ (graph not shown). It is found that data is best fitted for p = 1/2, hence ES- VRH mechanism is dominating in HTR. Thus, Arrhenius and ES- plots for resistivity are studied (Fig.6.20 and 6.21). From these plots, it can be observed that thermal activation energy (E_a) is less than NNH energy. E_{NNH} is not exactly same for whole temperature range (Table 6.2) which indicates the occurrence of multiple conduction phenomenon [38], [41].
Figure 6.21: Efros-Shklovskii plot for resistivity

The localization length has been estimated from eqn.1.14. Fig. 6.22 shows contour plot for localization length with temperature for Sm-Ti substituted BFO system. It can be seen that, in LTR behaviour is almost same for all x. In HTR I, a colossal decrease in value of localization length is observed (nm to tens of pm). This variation is sharper for low and high concentration of Sm-Ti, however for $0.04 < x < 0.16$, variation is a bit slower. A small variation promoting up to HTR II-V, get diminishes with the rise in temperature. It is noticeable that the variation is appearing just before the temperature, where polomska transition is reported. It is noticeable that localization length much smaller than the donor Bohr radius for BFO (~ 1 nm) and stabilizes after HTRIII.
6.5 CONCLUSION

The effect of Samarium (Sm$^{3+}$) and Titanium (Ti$^{4+}$) co-substitution at the Bi$^{3+}$ and Fe$^{3+}$ sites in BFO on the structural, electrical and magnetic properties has been investigated. The structural phase transition is observed from rhombohedral (R3c) with $x \leq 0.12$ to co-existence of two phases i.e., rhombohedral (R3c) and orthorhombic (Pn2$_1$a) phase for $x \geq 0.16$. M-H hysteresis loop has revealed anti ferromagnetic behaviour to ferromagnetic behaviour with increasing $x$. Moreover, remanent magnetization has been found to be enhanced significantly for $x \geq 0.12$ thereafter it almost saturates. The value of piezoelectric coefficient ‘d$_{33}$’ increases up to $x = 0.16$, thereafter decreases. Electrical behaviour has been investigated in the details. Data has been analysed in four temperature regimes: 330-440 K (HTRII), 440-500 K (HTRIII). 500-630 K (HTRIV) and $> 630$K (HTRV). Dielectric behaviour has revealed three dielectric anomalies; (i) in HTRII, around 460 K and it is composition independent but behaviour is frequency dependent, (ii) in HTRIII & HTRIV, it is temperature and frequency independent but varies with composition and (iii) occurring at magnetic transition temperature ($T_N$). From impedance and modulus analysis, it is revealed that up to HTRIV, two dielectric processes occur. Resistivity, in these samples, is showing NTCR behaviour. The analysis of resistivity data along with dielectric and pyroelectric studies reveals that the anomaly $\sim 460$ K appears to be suppressed with co-substitution. The anomaly in HTRIV belongs to a special kind of behaviour may be attributed to MIT caused by the charge ordering in these samples.

The resistivity analysis has also been used to find out conduction mechanism. Conductivity-relaxation frequency plot on log scale appears as straight line indicating polaronic conduction, in these samples. Thus, the data has been fitted for various conduction models. Both Mott and Efros-Shklovskii VRH models have been applied. Either of them is not able to fit for entire temperature range. Although value of $R^2$ in both the cases is close to 1, but it is ES- VRH model that edges out Mott-VRH. Also, the PL spectra of these compositions is similar to BFO, hence we assume similar band structure. Band structure of BFO hints that density of state is not constant and this fact again supports ES- VRH for this system. Further, the localisation length has been estimated, which is less than the donor Bohr radius and variation stabilizes after 460 K, indicates Mott metallisation.