APPENDIX A
PRE-WORK SUMMARY (GRAPHS ONLY)

A.1 RE substituted BFO

![Graphs showing XRD patterns for BiRE\(_{0.08}\)FeO\(_3\) specimens](image)

**Figure A.1:** (a) XRD of specimens BiRE\(_{0.08}\)FeO\(_3\) (RE = La, Ce, Nd, Sm, Eu, Dy, Gd and Ho) (b) Rietveld refinement XRD pattern of La, Ce, Nd and Sm substituted BFO (c) Rietveld refinement XRD pattern of Eu, Dy, Gd and Ho substituted BFO with x = 0.08 for all samples.

Fig. A.1 (a) shows the XRD of specimens BiRE\(_{0.08}\)FeO\(_3\) (RE = La, Ce, Nd, Sm, Eu, Dy, Gd and Ho). All the samples have shown single phase formation. The XRD have been refined with Rietveld refinement using FULL PROF software package (Fig. A.1(b-c)). In the refinements, the peak shapes were described by pseudo-Voigt functions. The diffraction data is fitted with Rhombohedral (R3c symmetry) where fitting parameters (\(\chi^2\)) are within the acceptable limit of such structural symmetries.
A.2 AE substituted BFO

Figure A.1: (a) XRD of specimens BiAE_{0.08}FeO_{3} (AE = Ba, Sr and Ca) (b) Rietveld refinement XRD pattern of Ba, Sr and Ca substituted BFO with x = 0.08 for all samples.

Fig. A.2(a) shows the X-ray diffractograms of specimens BiAE_{0.08}FeO_{3} (A = Ba, Sr, Ca). All the samples have shown single phase formation. The X-ray diffractograms have been refined with Rietveld refinement using FULL PROF software package and the refined
parameters are mentioned in Fig. A.2 (b) In the refinements, the peak shapes were described by pseudo-Voigt functions. The diffraction data is fitted with Rhombohedral (R3c symmetry) where fitting parameters ($\chi^2$) are within the acceptable limit of such structural symmetries.
APPENDIX B
Gradient Core-shell microstructure in mixed valence multiferroic:
TM( Ti, Nb, W) substituted bismuth ferrite

B.1. INTRODUCTION

Multiferroics are noteworthy for the unique couplings of the ferroelectricity, ferromagnetism, and ferroelasticity [1]. BiFeO$_3$ (BFO) is one of the well-known multiferroic materials having ferro-electricity at room temperature. In spite of this, the incorporation of bismuth ferrite into practical memory devices has been hindered by leakage problems that led to low resistivity, presumably due to defects and non-stoichiometric related issues [2],[3]. The Fe$^{3+}$ ions in BFO like multiferroics provide an effective approach in creating a weakly ferromagnetic state in R3c ferroelectric phase. But, at the same time conventional weak ferromagnetism is symmetry forbidden in space group R3c. At $x = 0.08$, the modulated antiferromagnetic structure gives way to a weakly ferromagnetic state due to magnetoelastic interactions. In this magnetic phase, the linear magneto electric effect is allowed [4].

The volatile nature of Bi and presence of Fe$^{2+}$ ions induce defects in BFO. Thus aliovalent substitution may compensate the charge in sample and partial Ti$^{4+}$ substitution for Fe$^{3+}$ leads to charge compensation through oxygen nonstoichiometry. The aliovalent substitution in BFO matrix has been studied by several groups [4–10]. Most of these reports are consistent for magnetic properties while inconsistence for the electrical properties of aliovalent substitution [5]. Further, microstructural properties are rarely reported. In the report by Bernardo et al. [5], intrinsic compositional inhomogeneity is shown as the main factor to control electrical and magnetic properties in the bulk samples of Ti-doped BFO. In the present work, systematic microstructural variation of aliovalent substituents i.e., Ti (+4), Nb (+5) and W (+6) at 8 mole% substituted BFO has been analyzed. The intrinsic inhomogeneity model has been verified through impedance studies and compared.

A. About Core shell model (composite and dispersed)

Fig B.1 illustrates the different possible microstructures formed when two or more phases are simultaneously present in a system. The possible microstructures are core-shell and composite
microstructure. In the present case, as shown graphically, the microstructure of two phases can be seen separately in SEM or other high resolution image. Another possibility is the formation of solid solution and it can be formed in two ways and termed as (i) core-shell microstructure (ii) dispersed microstructure [11]. The comparison between the two models can be seen in later sections.

Figure. B. 1: Comparative illustration of (a) grain, grain boundary and electrode interface with secondary phase in composite and Core-shell microstructures during impedance study.(b) Core-shell (c) dispersed and (d) proposed gradient core-shell microstructure

A brief description, about the proposed model is given in the subsequent section. Fig. B.1 (a) compares composite and core-shell microstructure, where microstructural differences result in different dielectric/impedance response. Further, Fig. B. 1 (b) and (c) represent the core-shell form (second phase remains at the boundary of grain) and dispersed microstructure (second phase homogeneously dispersed throughout the grain and hence responsible for micro heterogeneity). Fig. B.1 (d) illustrates the special kind of possibility of mixed state of Core-shell and dispersed microstructure. Here, the concentration of second phase reduces on moving towards the core, even reverse possibility cannot be ruled out. In the present piece of work, an effort has been made
to establish a correlation between second phases observed in the XRD pattern of these modified bismuth ferrite compounds and their micro-structure using impedance analysis.

**B.2. EXPERIMENTAL**

Highly pure powders of Bi$_2$O$_3$, Fe$_2$O$_3$ and TiO$_2$ / Nb$_2$O$_5$ / WO$_3$ (M/s Aldrich) were mixed in stoichiometric (with 5 mole% extra Bi$_2$O$_3$) proportions to form BiFe$_{0.92}$TM$_{0.08}$O$_3$ by solid state route. The powder mixture was then calcined at 700°C for 1 hour in an alumina crucible. The calcined mixtures were ground and admixed with polyvinyl alcohol (PVA) as a binder and then pressed at 150 MPa into disk shaped pellets. The pellets were then sintered at 830°C for 2 hours in air as reported in Ref. [12]. Phase development in these samples was monitored at each step of calcination and sintering using X-ray diffractometer (RIGAKU 6000) with Cu-Kα radiation (λ = 1.5405Å) with a scanning rate of 1°/min. Scanning Electron Microscope (SEM, Hitachi S3700) was used to study the grain size and surface morphology. The parameters of SEM settings used in the present work are Accelerating Voltage – 25 kV, Probe Current - 40 nA, Working Distance – 16.46 mm. The sintered pellets were polished and coated with silver paste on both sides and cured at 325°C for 1/2 h. Impedance analyzer (Novocontrol, Alpha - AT) has been used for dielectric measurements.

**B.3. RESULTS AND DISCUSSIONS**

**B.3.1. STRUCTURAL STUDIES**

Fig. B.2 (a) compares the X-ray diffraction (XRD) patterns of the transition metal substituted BFO samples with x = 0.08 in the system BiFe$_{1-x}$Tm$_x$O$_3$, where Tm = Ti, Nb and W, abbreviated as BFTO, BFNO and BFWO respectively. All these samples have been synthesized at optimized processing conditions for BFO. The substituent elements are supposed to occupy the Fe-site and order of ionic radii are R$_{Fe}$ (0.645 Å) ~ R$_{Nb}$ (0.64 Å) > R$_{Ti}$ (0.605 Å) ~ R$_{W}$ (0.60 Å), more importantly the relative variation of ionic radii for Ti, Nb and W is 6.25%, 0% and 5.47% respectively. Thus, according to Hume - Rothery rule, at least the size of substituent should not hinder the solid solution formation. But, contrary to this, these samples have shown some second phases (marked with •) along with R3c phase. The results are very surprising, especially in view of the fact that such extra peaks are nearly absent in rare earth and alkaline earth substituted BFO
with \( x = 0.08 \). Also, it is contrary to previous reports [10], which claim single phase formation. However, most of the reports [5–8], show minute or noticeable impurity peaks. To recheck our results, we have varied the sintering temperature in both directions i.e. from 750°C to 950°C, but no single phase formation has been obtained. However, the EDX results confirm elemental composition; details are discussed in later section.

Figure. B. 2: (a) XRD pattern, (b) phase purity (%), (c) SEM images, (d) EDX of Nb substituted BFO at grain boundary, (e) EDX positions marked at grain(G) and grain boundary (GB) in SEM micrograph, (f) atomic distribution of constituents atoms at grain (G) and grain boundary (GB) using EDX data and (g) Difference in atomic percentage at grain and grain boundary of transition metal (TM = Ti, Nb, W) substituted BFO.

It is observed that the second phase is closely matching with \( \text{Bi}_{3.5}\text{Fe}_5\text{O}_{12} \) in accordance with the JCPDS File (No. 01-086-0367) i.e. garnet phase as obtained in our milled samples [12–14]. The highest intensity peak for second phase, corresponding to the reflection (400), belongs to the garnet phase. The XRD patterns have also been refined using Reitveld refinement by Full Prof Suite package. The XRD patterns have been fitted with R3c, R3c + Pnma, R3c + Pn\(_2\)Ia and
R3c + I41a. Our observations show quite good fitting with R3c symmetry only. However, phase purity (shown in Fig. B.2(b)) for R3c phase has been calculated using the following relation[15],[16]:

\[
\phi_{purity} = \frac{I_P}{I_P + 0.8I_S}
\]

Where \(I_P\) and \(I_S\) are the intensities of the highest intensity peak in pure phase and secondary phase respectively. More interestingly, the intensities of XRD peaks of second phase have been found to increase with aloe-valency (i.e., Ti\(^{+4}\) to W\(^{+6}\)) and hence, a gradual (nearly linear) decrease in phase purity with the substituents of excess charge is observed (not shown here). Further, no such correlation can be made with tolerance factor. It indicates that the size of substituent ions is not vital here rather; the excess charge plays a key role for the structural/microstructural alteration. It is further observed in BiFe\(_{1-x}\)Ti\(_x\)O\(_3\) system that the peak intensity of second phase maxima has been found to increase with increasing \(x\) i.e., concentration of Ti.

So, as discussed above, in prima fascia, impurity phase appears to be present in these samples. These impurity peaks neither belongs to constituent oxides, nor other derived compounds, and therefore it may be due to the composite nature of the resulting compound. Surprisingly, these impurity phases are found to be similar to what obtained in milled pure BFO sample [12–14]. In Ref [12-14], authors have mentioned another technique i.e. mechanochemical activation technique to synthesis pure BFO but pure phase BFO was not achieved. As this second phase is garnet phase, it means this second phase in not due to substituents i.e., their untreated/unwanted derived compounds. It may be due to the chemical pressure exerted by these substitution elements as we have seen that pressure has changed thermodynamics while synthesis in high energy planetary ball milling [12]. But simultaneously it is reported that Ti –substitution introduces microstructural alteration[17]. Thus microstructural analysis is carried out in following section.

**B.3.2. MICROSTRUCTURAL STUDIES**

SEM images do not show any composite like structure (Fig. B.2 (c)), neither could we see significant presence of impurities. As mentioned earlier in the structural studies, there is increase
in the % volume of second phase with aliovalency, as revealed by XRD data. Hence, micro heterogeneity in these samples cannot be overruled. Thus the point remains to testify that whether microstructure of grain boundary and grain is distinctly or similar. In order to clarify this, EDX has been taken at a point on the grain boundary as well as in the grains close to grain boundary. Fig. B.2 (d) shows EDX graph for Nb at grain boundary. Fig.B.2 (e) shows the different positions of EDX i.e. at grain and grain boundary. Fig.B.2(f) shows the EDX analysis for different element at different regions which reveals that element’s % atomic distribution, is not uniform within the grain (G) and at the grain- boundary (GB). The relative atomic concentration is different from an inner (core/G) and outer regions of the grain, considered as a shell around the grain. It is seen that ‘O’ is concentrated in the core in BFTO and BFNO samples; while in BFWO, ‘O’ is more concentrated at GB i.e., shell! But other elements show reverse pattern i.e. Ti and Nb are more concentrated at the shell, whereas in BFWO, ‘W’ is more concentrated in the core. To avoid confusion, here we have defined concentration gradient as, \( \Delta c \equiv c_g - c_{gb} \) (Fig.B.2(g)). In magnitude, \( \Delta c \) is largest for ‘O’ and smallest for TM’s. It is obvious that ‘O’ is the lightest element, hence the diffusion rate will be faster and it can easily escape from GB, therefore higher \( \Delta c \) for ‘O’. For ‘Bi’, we observe \( \Delta c \) is negative in BFTO and with alio valency, magnitude of \( \Delta c \) decreases (even become positive for BFWO). Nearly similar variation is observed in case of Fe, TM’s. As TM’s occupy the Fe-site, variation between these is complementary. The observational summary of EDX result is as follows:

(i) All the samples exhibit micro heterogeneity.

(ii) The concentration gradient between G and GB is not same for all these constituents. % \( \Delta c \) is large for volatile constituent i.e. ‘O’ and ‘Bi’.

(iii) For small variation in ionic radii of substituent, there should be homogeneous distribution of substituent ions and \( \Delta c \) should be small for \( \text{Fe}^{3+} \) ions. EDX support the fact. But variation in \( \Delta c \) for W in reference to Fe (in BFWO) is noticeable and reverse to the BFTO and BFNO

(iv) In BFTO and BFNO, concentration of \( \text{Fe}^{3+} \) ions is nearly same in the grain. While in BFWO, it seems that W has influenced the diffusion process significantly. The variation is very different (almost reverse) except in concentration.
These observations may be interpreted as, if \( \varphi_1 \) and \( \varphi_2 \) represents a main phase of BFO and second phase BIG along with other isomorphic compound to BFO respectively. Then in BFTO and BFNO, \( \varphi_1 \) is at grain and \( \varphi_2 \) at grain boundary and reverse in the case of BFWO (core-shell micro structure). But concentration of ‘Bi’ is almost same at grain in all the samples showing the existence of dispersed phase as supported by presence of continuous grain in SEM images (See Fig. B.1(b)).

The inhomogeneity in these samples occurs due to complex diffusion process during sample preparation. In case of aliovalent substitution, the driving force on the charge species is essential, electrochemical potential gradient \(^{11}\). As in the present case for \( x = 0.08 \) the charges on the substituted species is different and is maximum for W, therefore electro-chemical potential gradient must be present. This explains the different microstructures observed in SEM and variation in EDX results which is giving rise the signature of core-shell microstructure.

### B.3.3. Dielectric Loss and Warburg plot, Modulus plot

Grain and grain boundary effects can be probed using Impedance spectroscopy. Thus various Nyquist and bode plots at RT have been drawn. Bode plots of tangent loss (Fig. B.3(a)), show a peak in each compound, corresponding to the immobility of space charge species. The peaks are fitted with Gaussian symmetry (Fig. B.3(b)) to evaluate the relative broadening (FWHM). It is found that in all cases it is less than or just above 1.414 decades of frequency (Hz), indicating Debye like relaxation, occurs due to single polarization process \(^{18}\). It seems to be due to the homogeneous bipolar species present in the bulk or grain of BFO sample.
Figure. B. 3: (a) Bode plots (b) normalized tanδ Bode plots and (c) Permittivity Nyquist plots for Ti, Nb, W substituted BFO

Figure. B. 4: Bode plots (a) real and (b) imaginary part of Warburg function. (c) PE loops and (d) MH loops for BFTO, BFNO and BFWO systems at room temperature.
The Nyquist permittivity plots (Fig. B.3(c)) hints for dominant diffusion mechanism as the value of the slope is close to 1 (Warburg type impedance) or in general CPE (constant phase element)\(^{18}\). It has been observed that Impedance Nyquist plots (\(Z' - Z''\)) are not resolvable (not shown). Hence, bode plots of Warburg functions i.e., \(\ln Z'\sqrt{f} \equiv w'\) and \(\ln Z''\sqrt{f} \equiv w''\) have been drawn and shown in Fig. B.4(a-b). In Fig. B.4(a) \(w'\) almost remains uniform up to \(f < 10\) kHz, thereafter it decreases. While, \(w''\) bode plots show a continuous and almost linear however distinct slope which falls just after a few hundred Hz. In BFTO, a relaxation hump is observed for \(w'\), otherwise it is almost similar to BFNO. It may be due to complex dipolar species. The fact is supported by comparison of PE loops (Fig B.4(c)). The P-E loops observed are not saturated as these are elliptical shape. In case of BFWO, it has higher value of both real and imaginary Warburg impedance at low frequency. It is necessary to mention that, \(w''\) does not show any plateau for BFWO like it shows for others, while \(w'\) starts falling nearly a decade earlier on frequency scale as compared to others indicating the presence of diffusive elements [18] as chain. These observations indicate some dissimilarity between BFWO and others.

**Figure. B. 5:** Modulus Nyquist plots for Ti, Nb, W substituted BFO. Inset shows possibility of different microstructure within grain may be like as proposed gradient core shell.
As impurity phases are magnetic in nature, therefore magnetism should increase as we go from Ti to W, but nothing like this is seen. The Warburg plots and almost identical M-H loops (Fig B.4(d)) rule out any contribution to the magnetism because of the impurities in these samples. In order to extract more information about the microstructure, modulus Nyquist plots have been studied (see Fig.B.5).

Unlike impedance Nyquist plot, Modulus- Nyquist plots are well resolvable (Fig. B.5) which is a signature of dispersed medium phase\textsuperscript{11}. To analyze it further, the modulus plot has been decomposed in two asymmetric peaks for all the three samples as it can be seen in insets of Fig. 5.B. For BFTO and BFNO, the two decomposed peaks lie within the bulk contribution; while for BFWO a very small peak outside the bulk contribution has been observed (see inset for BFWO).

![Figure B. 6: Arrhenius variation for Schottky pinning energy co-efficient for Ti, Nb, W substituted BFO.](image)

Generally electrode effect gets suppressed in modulus plot. But our observation with various samples shows that at the temperature where Schottky pinning energy coefficient, $S = \frac{d\phi_B}{d\phi_M} \equiv 1/ (\{1 + 0.1(\varepsilon-1)\})$ is maximum, electrode effect appear in modulus plot. Here $\phi_B, \phi_M$
and $\varepsilon_{\infty}$ represent barrier height, metal work function and permittivity at high frequency respectively [19].

Thus, in order to understand the origin of the small hump outside the main curve in BFWO, we studied temperature variation of S. It can reflect, whether electrode effect is strong enough to appear in modulus plots (at room temperature). The Arrhenius plot of S for these three samples has been plotted (Fig. B.6 (a)). It is observed that BFWO shows maxima in the low frequency range at $\sim 285$ K near to RT. Hence small peak/ hump may be due to electrode contribution (see Fig. B.6 (a)). Thus, claim to the existence of two kinds of phases within the grain is supported.

**B.3.4. POLOMSKA TRANSITION: INDIRECT SUPPORT TO THE EXISTENCE OF MULTILAYER**

Polomska transition is supposed to occur due to spin wave propagation and such features should be observed in high quality thin crystals only. However, we have observed this phenomenon to occur in BZT substituted BFO ceramics [20]. But pure bismuth ferrite does not show such type of transition. Moreover, spin wave propagation can be feasible in ultra thin multilayer structures [21] and therefore, it can be realized if microstructure of the sample is multilayered. Thus, we can assume a typical microstructure which is made of nano-sized spherical layers i.e., a gradient core-shell microstructure as shown in Fig. B.1 (d). Hence forming a self assembled bicomponent magnonic crystal [22].

**B.3.5. COMPARISON OF PROPOSED MODEL WITH BERNARDO’S MODEL [5]**

**Similarity:**

- Both model hint for intrinsic inhomogeneity in bulk sample.
- In both models, each microstructure contains several nano structures
- Microstructure distribution in both models is homogenous.
- The electrical and magnetic properties are affected in substituted BFO due to nano-structuring.
Dissimilarity:

- The present model assumes dispersed medium, but gradually converting into core shell medium. It is contrary to Bernardo model, in which core-shell nano-structure allow to redistribute homogeneously.
- Present model almost explains why Polomska like transition dominates in Ti-substituted BFO ceramics,

With lot of similarity and little dissimilarity, in results, this model nearly supports the Bernado’s model. We can conclude that intrinsically, dispersed like microstructure can contain core-shell like nanostructure. It can affect both electrical and magnetic properties. However, more specific and advance study requires to verify, how these nano-structures redistribute in microstructure in gradient way or else.

B.4. CONCLUSION

Dielectric analysis and EDX studies give an idea of the new rather mixed kind of microstructure different from Core-shell model and dispersed medium Model. This multilayered microstructure is gradually changing analogously to Graded Index fiber. Hence gradient core-shell modeling has been proposed in these systems. This also supports the observation of Polomska transition in bismuth ferrite based ceramics. The results will trigger research related to a new kind of insulated barrier layer devices apart from basic study on the magnonic crystal formation and the spin wave propagation mechanism in bismuth ferrite based materials.
REFERENCES:


8. Murari NM, Thomas R, Melgarejo RE, Pavunny SP, Katiyar RS. Structural, electrical, and magnetic properties of chemical solution deposited BiFe$_{1-x}$Ti$_x$O$_3$ and BiFe$_0.9$Ti$_0.05$Co$_0.05$O$_3$ thin films. *J Appl Phys*. 2009;106(1):-. doi:http://dx.doi.org/10.1063/1.3158556.


APPENDIX C

Diffuse phase ferroelectric vs. Polomska transition in (1-x) BiFeO$_3$ - (x) Ba Zr$_{0.025}$Ti$_{0.975}$O$_3$ (0.1 ≤ x ≤ 0.3) solid solutions

C.1. INTRODUCTION

Current research on materials for the storage and process information is focused towards charge-based to spin-based technologies [1, 2]. BiFeO$_3$ (BFO), has opened up a new possibility of making room-temperature devices that rely upon spin wave propagation. This is a well known multiferroic which shows ferroelectricity and magnetism of G-type antiferromagnetic (AFM) order above room temperature. The compositional instability and leakage current lead to high dielectric loss and hinder its potential applications [3]. In stoichiometric BFO, many dielectric anomalies have been observed [4] and most of them are attributed to the defects rather than intrinsic phase transition (PT) barring anomalies at 1118 K (α - β PT) and 643 K (AFM - PT) [3]. Whereas transition around 458 K has been treated as a ghost transition [3], which rules out to be ferroelastic as the phase is rhombohedral on both sides of the transition temperature [5]. Recently, a surface phase transition has been referred to as a Polomska transition in thin films of BFO [6, 7] and is attributed to the long range spin wave propagation at high temperature [6]. Contrary to earlier understandings of the extrinsic origin like defects, it is now proposed that the origin of this transition in BFO might be surface-generated [3, 8]. However, it is still unanswered, whether the origin of this Polomska transition is (i) intrinsic or extrinsic, (ii) associated with thin films only [6, 8] or it is universal, and (iii) bulk effect or skin effect [8]?

In order to increase magneto-electric coupling, one needs to reduce the temperature difference between electric and magnetic transitions. It is also known that the solid solution of BFO with other ferroelectric perovskites results in dielectric anomalies with the reduction in ferroelectric phase transition temperature ($T_{\text{ft}}$) [9, 10]. An extensive literature survey shows that chemical doping leads to the reduction in $T_{\text{ft}}$ with substitutions [11]. In case of type I multiferroics (ABO$_3$ - BiFeO$_3$) [12], the dielectric anomaly corresponding to magnetic transition is observed at temperature ~ 645 K [9, 10, 13-15]. However, there is hardly any mention of the ferroelectric transition in these solid solutions [10, 15].

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Ba (Zr$_{0.025}$Ti$_{0.975}$) O$_3$ (BZT) has been chosen as a ferroelectric material in order to study these dielectric anomalies. Earlier, we reported solid solution formation for the entire range of composition, i.e. (1-x) BiFeO$_3$- (x) Ba Zr$_{0.025}$Ti$_{0.975}$O$_3$ (0.0 ≤ x ≤ 1.0) [16]. It was observed that there is structural transformation from rhombohedral to tetragonal with increasing x and the results are in accordance with the earlier reports on similar type of solid solutions [10, 13 and 17]. Weak ferromagnetic order (FM) has been reported in these solid solutions instead of the AFM order in pure BFO [14, 18].

In the present work, an attempt has been made to identify the nature of the dielectric anomaly observed at temperature ~ 458 K. Simultaneously, an effort has been made to investigate the ferroelectric to non-ferroelectric (FE - NFE) phase transition and its correlation with Polomska transition using dielectric, Differential Scanning Calorimetry (DSC) and ac conductivity for x = 0.1, 0.2 and 0.3 in (1-x) BFO – (x) BZT system.

C.2. EXPERIMENTAL

The polycrystalline samples were prepared by the solid state reaction method by using high purity BaCO$_3$, TiO$_2$, ZrO$_2$, Bi$_2$O$_3$ and Fe$_2$O$_3$ (Sigma - Aldrich) in their stoichiometric proportions. Details of sample preparation, structural and multifunctional properties have been reported elsewhere [16]. Impedance analyzer (Novocontrol, Alpha - AT) has been used for dielectric measurements. DSC measurement has been carried out in the temperature range 300 – 673 K and PE loop tracer has been used to get temperature dependent polarization.

C.3. RESULTS AND DISCUSSIONS

C.3.1 DIELECTRIC BEHAVIOR

Temperature dependent behavior of the real part of permittivity ($\varepsilon'$) and dielectric loss (tan $\delta$) of these 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 anomalies, the $\varepsilon'$ - T plots at selected frequencies, i.e. 1, 10 and 100 kHz have been studied (see Fig.C.1). It is noticeable that anomalies in the regime I, remain unnoticed because of colossal behavior in regime II (see magnified view of regime I in inset a, b and c of Fig.C.1). These anomalies may be due to some important physical features.

It is observed that the value of permittivity ($\varepsilon'$) for x ≤ 0.30 increases gradually with temperature to a maximum value ($\varepsilon'_m$) up to temperature $T_1$ and then decreases (regime I),
Figure C.1: (a) The temperature dependence of the real part of permittivity ($\varepsilon'$) for $x = 0.3$ in the temperature range 300 – 750 K (measured at 1 kHz), (b) The temperature dependence of the real part of permittivity ($\varepsilon'$) and dielectric loss (tan $\delta$) for $x = 0.1$, 0.2 and 0.3 in region I i.e., 300 – 500 K.

followed by a colossal rise in $\varepsilon'$ up to temperature $T_2$ (regime II) and a small increment in temperature $T_3$ (regime III). Up to 600 K, almost similar behaviour has been observed for $x = 0.1$ and 0.2 (not shown). Further, it is also evident that $\varepsilon'$ is observable above a particular temperature, i.e. 600 K for frequencies $f < 10$ kHz. However, for $f \geq 10$ kHz, $\varepsilon'$ could not be observed for all these samples. Moreover, an anomalous rise in tan $\delta$ has been observed at temperatures $> 520$ K. It indicates conducting phase between regime II and III.

In regime I, the value of dielectric loss is small ($\leq 1$) (see Fig. C.1 (inset a', b' and c')). Permittivity and dielectric loss peaks are broad and marginally frequency dependent, more importantly; these peaks coincide on the temperature scale ($T_1$). This shows that regime I is an insulating phase and FE - NFE transition occurs at $T_1$ (i.e. $T_f$). An important observation for emphasis is the plateau between $T_1$ and 475 K, before onset of loss tangent in tan $\delta$ vs. T plots. It is a signature of Polomska like transition [6, 8].
C.3.1.1 MODULUS -TEMPERATURE PLOT

In order to find $T_{ft}$ using a phenomenological relation [19], $1/\varepsilon$ (modulus) has been plotted as a function of temperature (see Fig. C. 2 (a)) and data has been extrapolated to find $T_{ft}$.

![Figure C.2: Temperature dependent variation of (a) normalized $\varepsilon^{-1}$ in temperature range 300 – 750 K for $x=0.1$, 0.2 and 0.3, (b) pyrocurrent with temperature region I for $x=0.1$ and 0.3, (c) heat flow and $\varepsilon^{-1}$, (d) $\varepsilon'$ and $\varepsilon''$ and (e) diffusivity plots for $x=0.1$, 0.2 and 0.3 in region I.](image)

C.3.1.2 PYROELECTRIC STUDY

The pyroelectric coefficient relates the variation in electrical displacement with temperature, i.e. spontaneous polarization ($P_s$) with $T$ [20]. The first derivative of $P_s$ w.r.t. $T$ ($dP_s/dT$) passes through a maximum at a temperature $T_m \leq T_{ft}$. Thus, $T_{ft}$ (observed in regime I) has been estimated through $dP_s/dT$ vs $T$ curves (see Fig. C.2 (b)). This temperature nearly coincides with the temperature at which a hump is observed in modulus vs. temperature plots. It implies that both Polomska and FE - NFE transitions are occurring simultaneously in the system.
C.3.1.3 CALORIMETRIC (THERMAL) STUDY

The phase transition temperature for \( x = 0.3 \) has also been confirmed from DSC in the temperature range 300 - 673 K (see Fig. C.2 (c)). In the DSC curve, three endothermic peaks at 375 K, 440 K and 640 K have been observed. The peak observed at 640 K (region III) is due to magnetic transition temperature [10, 15], whereas the peak at 375 K is due to moisture as this anomaly disappears with repeated measurement with temperature (see Fig. C. 2 (b)). The endothermic peak at 440 K, nearly coincides with the temperature, \( T_{ft} \) obtained from the extrapolation of modulus vs. temperature plot as well as \( \varepsilon' - T \) for \( x = 0.3 \). Thus, the endothermic peak appears to be due to FE - NFE transition.

Fig. C. 2 (d) shows the variation of \( \varepsilon' \) and \( \varepsilon'' \) with the temperature at frequency 1 kHz. At 440 K, \( \varepsilon' \) and \( \varepsilon'' \) curve crossover, the same temperature at which DSC curve (see Fig. C.2 (c)) shows a hump indicating PT at this temperature. Beyond this point \( \varepsilon'' \) increases sharply and becomes almost temperature independent after 600 K. In Fig.C. 2 (d) there is a hump in \( \varepsilon' - T \) curve. This hump is lying in the temperature range where a dip has been observed in DSC plot and corresponds to the magnetic phase transition (~ 640 K) [15]. It is also observed that \( \varepsilon' \) and \( \varepsilon'' \) overlap with each other in the temperature range 400 – 450 K. It means that \( \tan \delta = \varepsilon''/\varepsilon' \) should be constant, hence plateau is observed on the loss curve before onset (see Fig. C.1 (a)). This is showing another mechanism (Polomska) [6], which does not allow the usual rise or fall in \( \tan \delta \) near FE - NFE transition.

C.3.1.4. DIFFUSE PHASE TRANSITION

In order to describe the diffuseness of PT, a modified Curie-Weiss law [21] i.e., \( 1/\varepsilon' - 1/\varepsilon'_m = (T-T_m)^\gamma /C' \) has been applied. In this equation, \( C' \) is Curie constant and \( \gamma \) is regarded as a measure of the diffuseness of the phase transition. Value of \( \gamma \) for these compositions has been calculated from slope of \( \ln(1/\varepsilon' - 1/\varepsilon'_m) \) vs. \( \ln(T-T_m) \) plots (see Fig.C.2 (e)). A systematic increase in \( \gamma \) (1.24 to 1.65) with \( x \) indicates the contribution of BZT in diffuse phase transition (DPT) at \( T_1 \).

For the confirmation of \( T_{ft} \), \( 1/\varepsilon \) (≡ M) vs. T has been plotted for BFO and BaTiO\(_3\) as shown in Fig.C. 3. The value of \( T_{ft} \) has been estimated by extrapolating these curves and is found to be ~1120 K and ~ 395 K respectively, which are well in accordance with literature [3].
Additionally, Fig. C.2 (a) shows humps at 475 K, 450 K and 440 K for x = 0.1, 0.2 and 0.3 respectively, similar to BFO (~ 458 K) (see Fig.C.3) and might refer to Polomska transition [7].

![Image](image_url)

**Figure C.3:** Temperature dependent variation of $\varepsilon^{-1}$ for BiFeO$_3$ and BaTiO$_3$.

### C. 3.2. CONDUCTIVITY (AC) BEHAVIOR

As discussed above, the unconventional FE - NFE transition can be attributed to the simultaneous occurrence of another anomaly (Polomska transition); which is in fact, magnetic in nature [6]. Therefore, conductivity ($\sigma_{ac}$) around Polomska transition is expected to show some behavioral changes like another magnetic transition at $\sim$ 640 K (Neel temperature) [3]. Thus, $\ln\sigma_{ac}$ is plotted with $1000/T$ at a frequency interval of $\sim$ 1 decade (1Hz - 10MHz) (see Fig.C.4 (a, b, c)). The features observed in these plots are:

For $x = 0.30$, at low frequencies say for 1 Hz (<10 kHz) conductivity increases with temperature up to $T_1'$. The conductivity curve shows a dip at $T_2'$ followed by a sharp two step rise in conductivity i.e. $T_3'$ for first step and $T_4'$ for the second step, respectively. Beyond $T_4'$, it becomes almost frequency independent and at high frequencies say 1 MHz (> 10 kHz) ac conductivity shows nearly step like behavior. It is also observed that conductivity is temperature independent till $T_3'$ and onset temperature ($T_3'$) varies (marginally) with frequency (see Fig. C.4 (b)). The variation at $T_2'$ appears to be suppressed or completely lost.
followed by a sharp rise up to temperature $T_4'$ thereafter, it nearly flattens. It is also observed that conductivity up to $T_3'$ (i.e. 520 K) is of the order of $10^{-10}$ S/cm and changes to $10^{-4}$ S/cm at $T_4'$. Thus pure insulator to conductor transition appears at ~ 520 K and not at phase transition temperature ($T_{ft}$).

**Figure C.4:** (a) Arrhenius conductivity plots at 1 Hz for $x = 0.1$, 0.2 and 0.3, (b) Arrhenius conductivity plots at different frequencies for $x = 0.3$, (c) Arrhenius conductivity plots at 1 MHz for $x = 0.1$, 0.2 and 0.3, (d) Arrhenius fitting for $x = 0.3$ and (e) Mott fitting for $x = 0.3$. 

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In view of the above, Arrhenius - conductivity plots (see Fig.C.4 (a, c)) at 1 Hz are classified in five regions (marked at bottom of temperature scale): region A₁ (RT – T₁ʹ), region A₂ (T₁ʹ - T₂'), region B₁ (T₂' - T₃'), region B₂ (T₃' - T₄') and region C > T₄'. It is noticeable that conductivity classification is roughly in accordance with permittivity regimes as A, B and C resemble with regime I, II & III, and IV respectively. The conductivity plots support the fact that regime II, III and IV are representing conducting phase while region I is an insulating phase at least in the high frequency regime. In the dielectric plots, we observed broad peaks at all frequencies both in the ε' and tan δ curves and the same have been reflected in conductivity plots.

In region A₁, for x = 0.1, the order of \( \sigma_{ac} \) observed is \( \sim 10^{-11} \) S/cm, but from Nernst-Einstein (NE) equation, this should be of the order of \( 10^{-13} \) S/cm. This huge difference suggests that conductivity is not purely ionic in nature, but possesses contributions from electronic/polaronic as well [11]. The space charge contribution becomes negligible at high frequency region. Moreover, in regions B and C, \( \sigma_{ac} \) (at 1Hz) is almost composition independent.

In region A₁, at low frequency \( \sigma_{ac} \) is changed by a factor of 10 as x varies from 0.1 to 0.3, nearly following the NE equation (ignoring the electronic/polaronic contribution). This can further be correlated to systematically increase in diffusivity with x, which indicates that ionic conduction is due to the presence of BZT and thus, pertaining to the two phonon mode behavior observed in these solid solutions [16].

In order to understand the conduction/hopping mechanism, the Arrhenius (Fig C.4 (d)) and Mott (Fig C.4 (e)) variations of \( \sigma_{ac} \) (at 1Hz) have been plotted. The values of activation energies in various linear regions have been determined using Arrhenius relation. It reveals that, in region A₁, variable range hopping (VRH) like conduction occurs. It is not polaronic as estimated energy is \( \sim 700 \) meV while for polaronic hopping, energy should be \( \sim 75 \) meV (\( \equiv E_{ap}^p \)) [22]. It is noticeable that estimated energy gets close to \( E_{ap}^p \) with increasing frequency.

It is well known that VRH usually occurs at low temperature (< 300 K) in most of the materials and generally referred as a Mott type transition in magnetic materials [22, 23]. Being a multiferroic material, role of magnetism (e-spin and correlated motion, i.e. spin wave propagation) is expected for VRH mechanism. Such behavior may be due to the combination
of e (charge) -motion and structural change which is inducing the FE-NFE phase transition. Moreover, e-spin generated motion may also be referred as Polomska like transition [6]. In the recent studies on thin films of BFO, Polomska transition has been treated as skin effect [8] i.e. surface dependent transitions. This has been verified with Magnon study using low frequency Raman analysis [6]. In these solid solutions too, similar surface dependent dielectric behavior has been observed. The observations of spin relaxation in other bulk samples [24] and spin wave emission by magnetic multilayer [25] support the fact that transition observed in BZT-BFO bulk sample may be due to spin wave propagation. Thus, the observation of Polomska transition should not be limited to thin films only and can be associated with spin wave.

C.3.3. MAXWELL-WAGNER ARTIFACT OR POLOMSKA (SURFACE PHASE) TRANSITION

MW relaxation occurs when there is a conductivity difference between grain/grain boundaries or grain boundary/electrode. At low frequency and high temperature, such difference between conductivity is easy to happen and hence MW can be accounted for high values of ε' in region II and III. But in region I/A, at low frequency ε' and conductivity are much smaller and therefore, the contribution due to MW should be absent.
Figure C.5: Modulus Nyquist plots for x= 0.3 in the temperature range 350 – 500 K

Modulus study (as electrode effect gets suppressed and bulk effect dominated) is a suitable tool to verify surface phenomena in ceramics and avoid the possibility of Maxwell-Wagner (MW) like artifacts [3, 26]. Thus, in order to verify, whether Polomska transition is confined at bulk boundary or not, Modulus Nyquist plots have been studied close to 450 K in temperature range 350 - 500 K (see Fig. C.5). A small semicircular arch at the high frequency side along with a prominent semicircle (due to bulk) is observed at 350 K. The semicircular arch gets suppressed up to 450 K thereafter disappears at 500 K. This systematic disappearance of semicircular arc (at the high frequency end) for T > 458 K, occurrence of VRH (Mott) mechanism at high frequency and similarity of observed plateau pattern (in dielectric loss vs. temperature plots) with thin films [6, 8] suggests that it is due to skin layer of BFO but not due to grain boundary.

Thus, the origin behind the disappearance of small modulus semicircular arc (at the high frequency end) might be intrinsic and from the surface of bulk only. However, mechanism of Polomska transition in ceramics needs further attention.

C.4. CONCLUSION

In this study, an unusual kind of diffuse phase FE - NFE transition has been observed at temperature ~ 458 K. This has been associated with the surface dependent magnetic transition and appears to be Polomska transition. The FE transition is due to the dipolar contribution of BZT while Polomska transition is due to BFO justifying two phonon mode behavior of solid solutions. The Modulus Nyquist plots suggest that this FE/Polomska transition is a surface phase transition and is different from normal grain -grain boundary interface effect which occurs due to impurity or insulating grain boundary layer. This study will be a step ahead in the unfolding mystery of Polomska transition, but further investigation is needed to confirm our belief that it is a true skin effect irrespective of the nature of the material (thin film or ceramic). This may help in understanding the spin wave propagation mechanism and hence, the realism of spintronics devices along with the development of a surface dependent piezo-sensors.
REFERENCES:


