CHAPTER 1
INTRODUCTION

The stone, bronze and iron ages have been created and in recent years, perhaps the materials age is on the verge of creation. In the process of advancement of materials, many new ferroic materials named ‘advanced materials” have been synthesized and investigated. These materials have outperformed conventional materials with superior properties such as high electrical or magnetic or mechanical strength. If material possesses more than one functional properties including optical to the above three with one ferroic character, known as multi-functional ferroic material (Mf-Fm) and with more than one ferroic character, known as multi-functional multiferroic material (Mf-MFm). They possess novel properties including the ability to recognise and respond to shape and/or sense changes in the environment. The development of these materials can even lead to design of completely new products including medical implants, miniature energy storage devices, display devices, etc.

Bismuth Ferrite is one of such materials, which shows multifunctional behaviour apart from being multiferroic. But, it is customary to introduce the host material and the basic terms involved in thesis, before problem statement. In the following sections, a brief history of bismuth ferrite along with a brief description of associated terms/mechanism is presented.

1.1 CERAMICS

Ceramics in general can be defined as solid compounds that are formed by the application of heat and/or pressure and comprising at least any one combination (i) a metal and a non-metallic element solids or (ii) two non-metallic elemental solids [1]. There are several way to classify the ceramics, viz., bulk or nano size materials, single and poly crystalline materials, pellets and thin films. Thin films are different from ceramics because of its extensive and more applicable form. Now-a-days materials are further classified as ceramics (in pellet form, provided above condition is satisfied) and thin films. Thus bismuth ferrite, chemically BiFeO₃ (BFO), being an oxide is ceramic. The Fig. 1.1 shows SEM/FESEM images of different form of BFO.
Figure 1.1: SEM/FESEM of thin film, single crystal (dendrite form) [2] and polycrystalline BFO

1.2 MULTIFUNCTIONAL PROPERTIES AND FERROICITY

Multifunctional properties as mentioned in introduction is about to possess more than one functional properties (illustrated in Fig. 1.2). The physical properties are concerned with the variation of basic form of energy viz., mechanical, electric, magnetic, light, thermal etc. Thus, for material to be a functional, it is necessary that it shows significant variation in at least one physical property with variation of a physical parameter (like pressure, temperature, current etc.), e.g., variation in dimension of metallic rod (mechanical) with application of pressure (by hammering, mechanical), variation in magnetic moment for magnetic material (magnetic) with magnetic field (magnetic) etc. Now the material can be termed as multifunctional, if it shows more than one functionality e.g., variation in dimension of wire with application of temperature (thermal) in addition to pressure, variation in magnetic moment of magnetic materials with applied electric field (electrical) in addition to magnetic field etc.

Ferroic materials deal with the special feature of hysteresis as compare to other functional materials (as illustrated in Fig. 1.3). Thus, it can be used for memory devices. Historically, it appears ‘ferroicity’ word is generated in the nineteenth century because of magnetic hysteresis of iron ore (ferrous oxide). With application of alternative magnetic field, the variation in magnetization had been shown hysteresis, hence named as M-H hysteresis curve. This is how, the concept of ferromagnetism was generated. Later, with the invention of the transformer, application of this hysteresis and significance of its hysteresis shape is clearly understood.

Ferroelectric materials possess another type of ferroic property due to application of alternative electric field and hence the concept of ferroelectricity. The terms used in ferroelectricity are analogous about a century older, ferromagnetism with major difference is that magnetic moment here is replaced with dipole moment and magnetic field with an electric field, thus polarization (P) - electric field (E) hysteresis curve. With the different
Figure 1.2: Illustration for multi functionality [3]

Figure 1.3: Illustration for multiferoicity
state of dipole moment and its behaviour with temperature and electric field, the different terms are developed as paraelectric, dielectric, ferroelectric, ferri-electric, anti ferroelectric properties etc. similar to ferromagnetism.

Ferro-elasticity is another type of ferroic properties that deals with piezoelectricity and stress-strain variation. The concept of piezoelectricity developed a few decades earlier to ferroelectricity and independent to both Magnetic and electric ferroic properties. The stress-strain hysteresis shape is different than earlier mention hysteresis curves. However, ferro-elasticity is closely linked with ferroelectricity. The fourth ferroic property, toroidicity is latest in addition to ferroicity[4]. With this addition, the possible four type of materials based on space-time symmetry invariance is now approached. Now, if any material possesses more than one ferroic property than it is termed as multiferroic material and hence is the phenomenon of multiferroicity.

![Figure 1.4: Space –time symmetry[5], d^j-ness and ferroicity](image)

The space-time symmetry invariance and d^j-ness are interlinked as suggested by N.A. Hill [6] (Fig. 1.4). Thus, this makes rarity for multiferroic materials. Generally, for ferroelectric materials, their d-shell should be empty i.e. j = 0, as in barium titanate, lead titanate etc., while for magnetism, it is necessary to have unpaired d –shell electron i.e. j ≠ 0 or 10. The occurrence of these two opposite features in a single material rarely happen; especially keeping this in mind that d-orbital contained by transition metal (TM) and, most of the time ferroelectricity is due to TM e.g., BaTiO₃, where ferroelectricity is due to off-centring of d-electron of Ti⁴⁺ ions. Thus only materials in which ferroelectricity is not due to TM e.g., origin in Pb based perovskite is lone pair and TM – ion now, can possess d-
electron without losing its ferroelectric properties. Similar logic can also be applied for Bi based perovskites. Therefore, in such materials, long awaited magnetoelectric coupling can be possible.

Thermodynamically, the magnetoelectric effect can be understood within the Landau theory framework, approached by the expansion of free energy for a magnetoelectric system, i.e.

\[ F(E, H) = F_0 - P_i^i E_i - M_i^i H_i - \frac{1}{2} \varepsilon_0 \varepsilon_{ij} E_i E_j - \frac{1}{2} \mu_0 \mu_{ij} H_i H_j - \frac{1}{2} \beta_{ijk} E_i H_j H_k - \frac{1}{2} \gamma_{ijk} H_i H_j E_k = \ldots \ldots \] 

\[ \ldots (1.1) \]

where \( F_0 \) is the ground state free energy, subscripts (i, j, k) refer to the three components of a variable in spatial coordinates, \( E_i \) and \( H_i \) the components of the electric field \( E \) and magnetic field \( H \), respectively, \( P_i^i \) and \( M_i^i \) are the components of spontaneous polarization, \( P^i \) and magnetization, \( M^i \), \( \varepsilon_0 \) and \( \mu_0 \) are the dielectric permittivity and magnetic susceptibility of vacuum, \( \varepsilon_{ij} \) and \( \mu_{ij} \) are the second-order tensors, \( \beta_{ijk} \) and \( \gamma_{ijk} \) are the third-order tensor coefficients and most importantly, \( \alpha_{ij} \) is the components of tensor \( \alpha \) which is designated as the linear magneto-electric co-efficient, which corresponds to the induction of polarization by a magnetic field or a magnetization by an electric field. The rest of the terms in the preceding equations correspond to the high-order magnetoelectric effects parameterized by tensors \( \beta \) and \( \gamma \) [4].

1.3 BISMUTH FERRITE

Ferroelectricity and superconductivity are electrical phenomenon but always tried to couple with magnetism and hence search for magnetoelectric materials[7]-[9]. Attempts to combine the dipole and spin orders into one material system started in the 1960s with borates including boracites (\( \text{Ni}_3\text{B}_7\text{O}_{13}\text{I}, \text{Cr}_3\text{B}_7\text{O}_{13}\text{Cl} \)), fluorides (\( \text{BaMF}_{4}, M = \text{Mn, Fe, Co, Ni} \)), magnetite \( \text{Fe}_3\text{O}_4 \), (\( \text{Y/Yb} \)) \( \text{MnO}_3 \) and BiFeO\(_3\) [4].

Bismuth ferrite (BFO) is one of these materials on which lot of research has been carried out in recent decade, though studies on BFO pioneered by Smolenskii’s group in 1958 [10]. It is an important and interesting material not only because of occurrence of many ferroic properties simultaneously, hence labelled as multiferroic materials [11] but also because of its ambiguous multifunctional properties, which many times shake the present state of fundamental knowledge/science [12].
Prior to describing its some feature, it would be better to see historical journey of BFO, which can be divided into two eras as follows:

**Survival era (1958-2003):** This was period in which, studies on bismuth ferrite was nominal, because of its difficulty in synthesis and various ambiguities in its properties. However, this was period in which many distinguished features for BFO were observed e.g., observation of dielectric anomalies by Polomska’s group [13], its spiral magnetic structure by Sonowskii’s group [14], its structure clarity by Kubel and Schimd [15] etc. But all this was appearing to be in vain as expected high value of remanent polarization is very far from reality due to poor quality of sample and leakage current. But, again this was era in which lots of new features about the Physics of multiferroicity has been established e.g., Dzyloshinskii-Morya (DM) [16][17], KNB model[18], electrical current cancelation model [19] etc. The effect of new finding on multiferroicity also affected the studies on BFO. However, it was Science paper [20] in 2003 which gave rebirth to BFO by reporting high value of remanent polarization.

**Revival era (2003-2015):** After 2003, throughout the globe, a huge amount of work has been done on these materials and its derivatives. Various synthesis methods have been tried in order to improve the quality of samples, consequently, liquid phase sintering has been found to be a promising method [21]. Photo catalytic activity under visible light has been revealed for BFO [22]. Its piezoelectric value gets enhanced by a few typical rare earth substitutions viz., Sm [23]. Various doping strategies have been used to improve the multiferroicity, reduce leakage current and its multi functionality. More or less every possible combination, now have been tried. If, one looks out to number of publications in last decades it is easy to conclude that lots of research has been carried out. So, BFO related research work is now approaching to saturation. But, most of these works was done for multiferroic properties of BFO. A few attempts have been made to understand the Physics of BFO which many times put existing understanding in doubt. Understanding of dielectric, conductivity, magnetic behaviour was very little in survival era, but in this era all the three concerned behaviour has been readdressed with a mixture of successes and failure [12]. We will discuss these in later sections.

### 1.3.1 CRYSTAL STRUCTURE

BFO has rhombohedral, distorted perovskite structure with space group R3c at room temperature. It can be indexed in hexagonal form with \( a = b = 5.58 \, \text{Å}, \ c = 13.90 \, \text{Å} \)
\( \alpha = \beta = 90^\circ \) and \( \gamma = 120^\circ \) [24]. Fig. 1.5(a) shows lattice structure of BFO ceramic [24]. It consists of six formula unit of BFO in one unit cell.

Figure 1.5: Lattice structure of BiFeO\(_3\) [3], [24]

Its lattice parameters, in case of perovskite –type unit cell, is 3.965 Å and angle is 89.3-89.4°. Fig. 1.5(b) shows two connected unit cell along [111] direction [3]. However, its structure, in thin film samples particularly, remains controversial whether it monoclinic or phase coexistence (rhombohedral and orthorhombic) [12].

1.3.2 BAND STRUCTURE

The optical band gap of BFO, is a subject of which need more attention, as (i) its reported values from theoretical calculations are in range of ca.1.9 – ca.3.6 eV, (ii) many claims its direct band gap, mean while there are a few reports which, hint for additional indirect band gap 0.4-1.0 eV (iii) even the experimentally estimated value of band gap is in range of 2.1 to 2.9 eV [12]. The band gap in BFO, is highly dependent on its microstructure and hence processing conditions, typically for nano-sized microstructure [25].

Primarily, coulomb gap and exchange interaction are main factors in calculation of band gap. Experimentally, it is observed that microstructure [25], size of particles, oxygen defect [26], microstrain and shelling (to BFO (core) [27] also influence the band gap. Fig. 1.6 shows band structure and density of states calculated on the basis of LSDA+U for BFO using screen exchange formalism by Clark et.al [28] and as per this report, the band gap is ca.2.8 eV.
1.4 FERROIC AND ELECTRICAL PROPERTIES

BFO is one of the few multiferroics with both ferroelectricity and magnetism at and above room temperature; apart from this it also possess many dielectric anomalies. Recently, metal to Insulator transition (MIT) has been also reported for it. All these properties, has been briefly described below.

1.4.1 FERROELECTRICITY

The polarization in BFO prefers to align along the [111] direction, as shown by the arrow. The ferroelectric Curie point (Tc) is ~1103K [2]. The high ferroelectric Curie point usually refers to a large polarization since other typical ferroelectrics with such Curie points have a remanent polarization (P_r) up to ~100 μC/cm² [12]. However, for BiFeO₃
single crystals, the measured $P_r$ along the [001] direction at 77K was ~3.5 μC/cm$^2$, indicate a possible $P_r$ of only 6.1 μC/cm$^2$ along the [111] direction, as reported in earlier work [29]. For polycrystalline samples, the expected value of $P_r$ should be smaller. The reason for this small polarization is possibly due to the high leakage current as a result of defects and the non-stoichiometry of the test materials [12].

### 1.4.2 FERROMAGNETISM

BFO shows G-type anti ferromagnetism (AFM) (Fig. 1.7(a, b)) with Neel temperature at ~643K. But, the observed results show weak ferromagnetism. It is accounted due to DM interaction as FE polarization breaks centre of symmetry and hence induces canting. Addition to this, there is another ferroelectrically induced spin cycloid (Inverse DM interaction), which in commensurate and have a wavelength of 64 nm, which average out the canting magnetism (Fig. 1.7(c)) [30].

![Figure 1.7: (a) G-type AFM, (b) [111] plane generating AFM and (c) Average outing of canting due spin cycloid [30]](image)

### 1.4.3 DIELECTRIC ANOMALIES

BFO shows numerous dielectric anomalies, out of which a few are recognised at ~140 K, ~200 K, ~458 K and ~643K apart from ferroelectric transition at 1118 K. In following sections these anomalies are discussed.
Dielectric anomalies at ~140K and 200K: The anomalies, observed in BFO (see Fig. 1.8) are supposed to be because of coupled spin reorientation similar to ortho-ferrite as revealed by magnetic resonance study[12]. But, it is contradictory to the fact that, in ortho-ferrites, the spin reorientation occurs due to rare earth ion, which is magnetic; while in BFO, Bi$^{3+}$ is non-magnetic [12].

b) Dielectric anomalies at ~458K: The transition around 458 K has been treated as a ghost transition [12], It shows change in slope for resistance as shown in Fig. 1.9.

It rules out to be ferro-elastic as the phase is rhombohedral on both sides of the transition temperature [32]. Recently, a surface phase transition at this temperature has been referred to as a Polomska transition [13] in thin films of BFO and is attributed to the long range spin wave propagation at high temperature [33], [34]. 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 [12], [33], [34]. However, it is still unanswered, whether the origin of this Polomska transition is (i) intrinsic or extrinsic, (ii) associated with thin films only [33], [34] or it is universal, and (iii) bulk effect or skin effect [34]?

c) **Dielectric anomalies at ~643K**: This dielectric anomaly is for AFM-PT as mentioned earlier, and thus, temperature is Neel temperature. It shows change in slope for log conductance (1/R) as shown in Fig. 1.10.

![Figure 1.10](image)

**Figure 1.10**: Anomaly ~ 370 °C or 643 K appearing in modified resistivity curve [12]

### 1.4.4 METAL INSULATOR TRANSITION

A recent issue of metal insulator transition (MIT) in BFO has been taken into consideration. In general, MIT can be induced in two ways (i) band controlled- MIT (BC-MIT) and (ii) filling controlled- MIT (FC-MIT) [35] as illustrated in Fig. 1.11(a). Further BC-MIT, can be induced by temperature and pressure as shown in Fig. 1.11(b). Additional parameter can be chemical pressure, which can be introduced by ionic substitution with different ionic radii than the host. However, FC-MIT can also be introduced by substitution e.g. Ti substitution [35]. There are handful of reports on BFO in which MIT has been induced by temperature [2] and pressure [24]. But the contradictory fact is that when MIT induced by pressure, it has been shows Mott-like and due to new reason of transition from high spin to low spin [24]. However, when it is induced by temperature, the transition occurs due to second order structural phase transition [2], while in principle, MIT is first order phase transition. Additionally in one report, it is argued that charge transfer – MIT occurs in BFO [36]. So there is inconsistency in reports and these results do not seem to be consistent with the existing Physics.
Figure 1.11: Illustration for (a) metal insulator transition (MIT) and its mechanism and (b) Band width control MIT and BFO [2], [24]
1.5 GENERAL FEATURES OF METAL INSULATOR TRANSITION

In this section, we will describe a few terms associated with MIT [35].

1.5.1 MOTT INSULATOR AND METAL INSULATOR TRANSITION

As per band model, Mott insulator should be conductor; where d - electrons are present in upper band; but (as Mott argued) strong electron –electron interaction, the band splits into upper empty and lower filled band. Hence, these strongly correlated electron system are insulators and known as Mott insulators.

With the controlled variation of parameters, Mott insulators can become metal and the corresponding transition is known as metal insulator transition. There are two class of Mott insulator: 1. Mott-Hubbard insulator and 2. Charge transfer insulator. The latter is due to the involvement of p-orbital band.

1.5.2 HUBBARD MODEL

It is the simplified theoretical model for MIT established for s –orbit. However, it enables to understand the dynamics of transition, approximately. The Hamiltonian is given as:

$$\mathcal{H} = -t \sum_{\langle i,j \rangle, \sigma} (c_{i\sigma}^\dagger c_{j\sigma} + c_{j\sigma}^\dagger c_{i\sigma}) + U \sum_{j} \hat{n}_{j\uparrow} \hat{n}_{j\downarrow} - \mu \sum_{i\alpha} n_{i\sigma} \quad ...(1.2)$$

Where, t is transfer integral, $c_{i\sigma}^\dagger (c_{i\sigma})$ is creator (annihilator) operator at site i with spin $\sigma$, U is onsite Coulombian repulsion and $n_{i\alpha} = c_{i\alpha}^\dagger c_{i\sigma}$ is number operator for single electron band system[35].

1.5.3 SUBSTITUTION (CHEMICAL PRESSURE) AND BANDWIDTH CONTROL

The electron correlation strength (ECS) can be controlled by altering the lattice parameter or substitution, provided the original lattice structure does not alter. The d and therefore The ECS can be achieved by either controlling the transfer interaction (t_{pd}) or One electron bandwidth (W) providing the coulomb interaction remains unaltered. Now, W can be controlled by applying the pressure as attempt in case of BFO by Ref. [24]. The other way to controlling the W, is chemical substitution. For this, A –site substitution by elements of different ionic radii, is especially effective in case of perovskite (ABO$_3$) materials. The lattice distortion governed by tolerance factor (Goldsmith, t_{GS}). As t_{GS} decrease from its ideal value of 1, B-O-B bond bent as illustrated in Fig. 1.13 for Fe at B
site. This bending alters the W as the effective d- electron transfer interaction between B – sites is governed by super transfer process via O 2p state [35].

![Figure 1.12: Bending of Fe-O-Fe angle](image)

In BFO, the strong ligand field approximation is applicable; therefore, p-d transfer Interaction ($t_{pd}$) is proportional to tolerance factor ($t_{GS}$) and in terms of bond angle, it can be given as:

$$t_{pd} \propto \cos (\pi - \theta_{Fe-O})$$  

Therefore band width, $W \approx \cos^2(\theta_{Fe-O})$  

1.6 **POLARONIC HOPPING MODELS**

In disorder semiconductor/insulator system, thermally assisted carrier tunnelling between localized states due to fluctuating potentials namely polaronic hopping, is major migration at lower temperature. In hopping process, two conduction mechanisms are involved (i) linear Arrhenius relation ruled nearest neighbour hopping (NNH) and (ii) non-linear Mott relations ruled variable range hopping (VRH). VRH can be further divided in to two categories, namely long range polaronic hopping (LRH) and short range polaronic hopping (SRH) as illustrated in Fig.1.14 [37]. In order to understand proper hopping mechanism, following relations have been used to calculate the various activation energies;
Equation (1.5) is used to analyse activation energy ($E_a$) in case of thermally activated hopping. Equation (1.6) is used to calculate activation energy in case of NNH ($E_{NNH}$). Equation (1.7) is general Mott relation for VRH. In these equations, $T$ is the absolute temperature. $\rho_0$, $\rho_{0,NNH}$ and $\rho_{0,VRH}$ are pre-factor constants. Later, two pre-factors are temperature dependent and their relation with temperature is given by three different hopping models as follows [38]–[40]:

**For NNH,**

$$\rho_{0,NNH} = \rho_0 T$$  \hspace{1cm} (Holstein)  \hspace{1cm} .....(1.8)

**For VRH,**

$$\rho_{0,VRH} = \rho_{0,ES} T; p = \frac{1}{2}$$  \hspace{1cm} (Efros-Shklovskii)  \hspace{1cm} .....(1.9)

$$\rho_{0,M} T^{1/2}; p = \frac{1}{4}$$  \hspace{1cm} (Mott-3D)  \hspace{1cm} .....(1.10)

Where, $T_0$ is the characteristic temperature, $k_B$ is the Boltzmann constant and $p$ is scaling factor used in VRH. The value of $T_0$ can be estimated from modified resistivity (or conductivity)-temperature plot. The modification depends on model applied for the system. In the present work, two hopping conduction model has been used (1) Mott’s -3D and (2) Efros-Shklovskii model.
**Mott’s - 3D model:**

One of the basic assumptions used in Mott’s VRH model [40] is density of state remains constant and the coulomb energy gap ($\Delta_{CG}$) is not considered, consequently the hopping energy ($\Delta_{hop,M}$) should be greater than $\Delta_{CG}$. In this model, $p$ is equal to $1/(d+1)$; $d = 3$ for 3D. Thus, $p = \frac{1}{4}$ for Mott’s 3D hopping conduction,

$$\rho = \rho_{0,M} T^{1/2} \exp \left( \frac{T_{0,M}}{T} \right)^{1/4}$$  

$$T_{0,M} = \frac{\beta}{k_B N(\varepsilon_f) \xi^3}; \beta = 18.5 \pm 0.2 (scaling) Or, \frac{24}{\pi} (analytical)$$  

Where, $N(\varepsilon_f)$ is the density of localized states at the Fermi level and $\xi$ is localization length.

**Efros-Shklovskii (ES) model:**

In ES model [38], [41], the basic assumption is that density of state is not constant and it consider the coulomb energy gap ($\Delta_{CG}$), consequently the hopping energy ($\Delta_{hop,ES}$) should be less than $\Delta_{CG}$. In this model, $p = 1/2$ for Mott’s 3D hopping conduction,

$$\rho = \rho_{0,ES} T \exp \left( \frac{T_{0,ES}}{T} \right)^{1/2}$$  

$$T_{0,ES} = \frac{2.8a^2}{4\pi \varepsilon_0 \varepsilon_s k_B \xi} \equiv c/\xi$$

**Percolation and localization length:**

The percolation threshold for an array of $N$ donors can be given as

$$\zeta_c = \ln(\rho/\rho_{0,VRH})$$  

$$\zeta_c = \left( \frac{T_{0,ES}}{T} \right)^{1/2}$$  

$$\zeta_c \geq \zeta_{ij} = 2r_{ij}/\xi + \varepsilon_{ij}/k_B T$$

Where $\zeta_{ij}$ is percolation value, for a given system, $\varepsilon_{ij}$ is activation energy calculated from bulk measurement, $r_{ij}$ is the shortest distance between octahedral sites and $k_B$ is the Boltzmann constant. There using above relations, temperature corresponding to threshold percolation length can be given as,

$$2r_{ij}/\xi + \varepsilon_{ij}/k_B T = (c/\xi T)^{1/2} \text{ or, } \varepsilon_{ij}/k_B T - (c/\xi T)^{1/2} + 2r_{ij}/\xi = 0$$

Solving this equation, one can estimate critical temperature for a given system.
1.7 APPLICATIONS AND LIMITATIONS

BFO being ferroelectric materials with high value of polarization is obvious candidate for random access memory (RAM) and hence, FERAM devices [23]. In Sm substituted BFO, significant value of $d_{33}$ has been observed [23] and hence piezoelectricity which can be used for actuators application. Further, recently photo catalytic process is observed in BFO [25], thus it can also be used in energy harvesting. Being a multiferroic material, it has a potential to be used in spintronics based devices as well.

In addition to all this, it is found that BFO can generate terahertz radiations [42]. It is special because terahertz radiation works in those regimes where major concern of BFO i.e., leakage current is not a problem [12]. Thus, BFO is a material with huge potential for various applications. But, there are a few basic challenges that hinders its potential into realism [4], [12], viz.,

- Synthesis of single phase BFO is still difficult.
- Volatile nature of Bismuth drastically affects the stoichiometry in the system.
- Difference between $T_C$ and $T_N$ is too large (~460 K).
- High leakage current
- RT electric field induced decomposition into Fe$_3$O$_4$ etc.

1.8 SCOPE OF WORK IN BISMUTH FERRITE

As discussed earlier, BFO is an important and interesting material not only due to its ferroic properties, but also because of its ambiguous multifunctional properties, which many times shake the present state of fundamental science [12]. Apart from the coexistence of ferroelectricity and magnetism in multiferroics oxides; there are new findings such as ferroelectricity induced by spiral spin order, magnetic exchange striction, or charge order [4], [12] etc. Based on these ideas, new oxides have been predicted to be multiferroics, some of which await direct experimental verification. Presently, Physics of multiferroics is itself in its infant days [4], [12] but problem in BFO is still a step ahead. For instances, structure in bulk (rhombohedral) and thin film (monoclinic) are different. Apart from this, there are many questions raised by Scott and Catalan such as why many dielectric anomalies/transitions termed as ghost, metal- insulator transition (MIT) etc. occur in these materials? Secondly, the nature of transport/spin glass behaviour, magneto-electric (ME) coupling and electrical conduction behaviour is not clear so far [12].
In spite of the fact that BFO is most studied multiferroic materials number of publication is not large enough as compared to graphene and Fig.1.12 shows its increase in publication is just parallel to overall ferrites. It is just 6-8% of overall publications on ferrite (data is taken from Science Direct for period of 1996-2015). It is also an important point to mention that most of its publications are based on multifunctional ferroic properties. There are a very few papers in which physics of this materials is inspected. The other areas of research e.g., compositional tailoring, strain-engineering and domain engineering are almost untouched for this material. Although lots of publications on modified BFO are present but predictive compositional tailoring in BFO is still missing. Almost every efforts has been made to enhance sample quality, hence reduction in leakage current, enhancement of ferroelectric or magnetic properties on the basis of random selection of substitution. Thus, BFO is a worthy material to study not only for its multifunctional ferroic properties but also for its Physics of magnetism and FE, charge and spin transport, phase/ghost transitions etc. and materials engineering.

1.8.1 PROBLEM STATEMENT

1.8.1.1 DIELECTRIC ANOMALIES AND ITS ORIGIN

The basic problems rose by Catalan and Scott [12], are still unanswered. Out of those many problems, we focussed our self on dielectric anomalies appeared in BFO samples. In BFO, many dielectric anomalies have been observed as explained earlier. It is
claimed that, 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). Origin of many of anomalies is not known, especially Polomska transition, hence termed as ghost transition. It is related to spin wave propagation and therefore conduction behaviour should be affected.

1.8.1.2 CONDUCTION BEHAVIOUR

BFO is typical example of strongly correlated electronic system [24]. It is mentioned earlier, there is controversy regarding its conduction behaviour and MIT. Thus conduction mechanism is needed to understand. Further, modification in behaviour due to substitution can enlighten the study in the depth.

1.8.1.3 MAGNETISM AND MAGNETOELECTRIC COUPLING

Canting and spin cycloid, as mentioned in section 1.4.1.2, is observed due to coupling between ferroelectricity and magnetism. But, spin cycloid, in principle does not allow linear ME coupling. However, cycloid removal is feasible either by application of high magnetic field, by suitable substitution or by epitaxial strain. In such cases one can observe the linear ME coupling [12]. Thus substitution effect can alter the ME coupling behaviour.

1.8.2 OBJECTIVE

Thus, in view of the above, apart from studying multifunctional property (ferroelectric, magnetic etc) for substituted bismuth ferrite, we will focus our studies on:

1. Dielectric anomalies and its origin
2. Conduction behaviour (MI transition and its Mott-like behavior)
3. ME coupling at room temperature.

Before the selection of substituents, it appears necessary to know, how the substitution and which substituent will be effective for MIT. For this, we have to understand the features of MIT and, also conduction behaviour models. Thus, in the following sections, a brief description of MIT and polaronic conduction models is presented.

1.9 SELECTION OF SUBSTITUENTS

Fig. 1.15 shows modern periodic table, Bi is heavy element of 15th column and 6th row, with atomic number 83. In BFO, Bi is at A-site and has been replaced either by
alkaline earth elements (2\textsuperscript{nd} column) or by lanthanides (3\textsuperscript{rd} column, 6\textsuperscript{th} row). Fe is metal, with atomic number 26, has been positioned in 8\textsuperscript{th} column and 4\textsuperscript{th} row, in this Table. In BFO, Fe is at B-site and has been replaced by transition metals. In the present work, we have selected encircled elements for primary study in order to see the substitution effect in BFO. A few results of these samples are shown in Appendix A.

![Periodic Table Image]

**Figure 1.15**: Selection of Substituents and their position in modern periodic table

Rare earths are f -block elements, its substitution at A-site may alter magnetic properties of sample in addition to reduction in leakage current. From fundamental point of view, rare earths typically Lanthanides substitution at A-site may modify the one electron bandwidth (W). For this purpose, we have substituted 8 lanthanides Ce, Nd, Sm, Eu, Gd, Dy and Ho along with La to BFO matrix to synthesize the Bi\(_1-x\)Re\(_x\)FeO\(_3\) where Re is above mentioned lanthanides and x= 0.08 (abbreviated as BLFO, BCFO, BNFO, BSFO, BEFO, BGFO, BDFO and BHFO). As tolerance factor is a parameter, which reflect the p-d interaction, therefore a graph between tolerance factor and different substitution to BFO with x = 0.08 has been plotted and shown in Fig. 1.16. It found that it smallest for Sm and Ho, thus more distortion and hence, possibility of decreasing the one electron bandwidth increase. This fact is also supported from plot of band width, W (using eqn. 1.4) shown in
Fig. 1.17; where Sm and Ho along with La and Gd lie on the upper side. Additionally, as per literature [23], Sm substituted BFO show high value of $d_{33}$. Hence, Sm substituted BFO has been selected for a detailed study further.

![Figure 1.16: Variation in Goldsmith tolerance factor for different substitution with $x = 0.08$](image1.png)

On the other hand for B-site substitution, Ti substituted BFO shows core shell microstructure due to its nano-structural variation (see Appendix B); simultaneously in this sample, secondary phase formation is minimum. In addition to this magnetic ferroic
behaviour is similar to Nb and W substituted. Ti substituted BFO is reported for reduced leakage current [43]–[46].

Therefore, in the thesis, after optimization of processing conditions for bismuth ferrite, the electric behaviour of BFO has been studied. It has been followed by the synthesis and characterisation of Ti substituted BFO, Sm substituted BFO and Sm-Ti co-substituted BFO. In the last, keeping the objective of thesis in the mind, a comparative and comprehensive analysis is presented, which is followed by the conclusion of the thesis.