CHAPTER 1
INTRODUCTION

1.1 INTRODUCTION

Study of ferroelectric materials started over a century ago when large piezoelectric constants were observed in Rochelle salt [1-2]. Over the following few decades, hysteresis was reported in the dielectric function, polarization, and strain of this material and theories emerged to account for its anomalous dielectric, piezoelectric, elastic, and phase transition behaviors [2]. In the 1930s potassium dehydrogenate phosphate (KH$_2$PO$_4$) was discovered to be ferroelectric [3] and a theory of the ferroelectric phase transition was developed [4]. Later on, ferroelectricity was observed in BaTiO$_3$ and related perovskite-structure oxides in the 1940 [5], which have stimulated research in both synthesis and characterization of ferroelectric materials. Over the last one or more decades there has been a great emphasis in the understanding of fundamental physics of ferroelectrics [6], which has contributed in optimizing the properties of materials for specific device applications.

The advances in science and technology demand new materials to cater its expanding requirements in device fabrication. Magneto-electric multiferroic materials, which possess both magnetic and ferroelectric ordering, are found to have variety of applications in magneto-electric sensors driven magnetic data storage and recording devices [7-9]. In recent years, there has been significant increase in research on multiferroic systems due to its good magneto-electric coupling exhibited by thin films and bulk form of some of the transition metal oxides [8-9]. Ferroelectric polarization and magnetization are being used in transducers and actuators (because of their piezoelectricity), capacitors (because of their high dielectric permittivity), memory applications (because their hysteresis properties result in two stable states of opposite polarization), MRAMs (magnetic random access memories) and FeRAMs (ferroelectric random access memories) respectively. Coexistence of polarization and magnetization simultaneously at room temperature in a multiferroic material allows the realization of four-state logic devices in electronics [9].
1.2 FERROICS TO MULTIFERROICS

1.2.1 DIELECTRIC MATERIALS

Dielectric materials are like an insulator and exhibit or may be made to exhibit an electric dipole structure; that is, there is a separation of positive and negative electrically charged entities on a molecular or atomic level. As a result of dipole interactions with electric fields, dielectric materials are used in capacitors [10]. Dielectric constant is independent of the electric field strength for fields below a certain critical value. From the basics of electrostatics and Gauss’s law, one can determine the dielectric constant of a material considering the geometry of a parallel plate capacitor as,

$$\vec{D} = \vec{E} + 4\pi \vec{P} = \varepsilon \vec{E}$$ \hspace{1cm} (1.0)

Where \( \vec{D} \) is displacement vector. For an isotropic linear dielectric, the polarization vector \( \vec{P} \) is proportional and parallel to the applied field vector \( \vec{E} \). \( \varepsilon \) is the static dielectric constant of the medium. From eq. (1.0)

$$\varepsilon = 1 + 4\pi \chi$$ \hspace{1cm} (1.1)

where \( \chi \) (= \( P/E \)) is known as the electrical susceptibility. For isotropic dielectrics \( \varepsilon \) and \( \chi \) are scalar quantities, which are dependent on the molecular properties of the dielectric. The dielectric constant is determined by the polarizability of the lattice. The polarizability, \( \alpha \), of an atom (or molecule) is defined by

$$\vec{p} = \alpha \vec{F}$$ \hspace{1cm} (1.2)

where \( \vec{p} \) is the electric dipole moment and \( \vec{F} \) is the local or effective field acting on the given atom. The polarization \( P \) is defined as the net dipole moment per unit volume and is given by

$$P = \sum N_i p_i = \sum N_i \alpha_i E$$ \hspace{1cm} (1.3)

where \( N_i \) is the number of dipoles per unit volume.

where \( E \) is the applied field, and \( E_{\text{int}} \) is the internal field acting on the ion \( i \) due to the other ions. It is usually expressed as a power series in odd powers of the polarization.
1.2.2 POLARIZATION IN DIELECTRIC MATERIALS

The total polarizability may usually be separated into three parts: electronic, ionic, and dipolar. **Electronic polarization** is a phenomenon of the relative displacement of negative and positive charges of atoms or molecules under the application of external electric field. Electronic polarization can also be described as charge redistribution in a material caused by an external electric field. The charge redistribution and the energy loss involved in the redistribution process require some amount of energy [10]. The polarization process is presented at the expense of the potential energy released because the total potential energy of the system in an electric field is smaller after the electric polarization than before it. **Ionic polarization** occurs only in materials that are ionic. An applied electric field acts to displace cations in one direction and anions in the opposite direction, which gives rise to a net dipole moment. The magnitude of the dipole moment for each ion pair is equal to the product of the relative displacement and the charge on each ion.

The third type, **orientation polarization**, is found only in substances that possess permanent dipole moments. Polarization results from a rotation of the permanent moments into the direction of the applied field. This alignment tendency is counteracted by the thermal vibrations of the atoms, such that the polarization decreases with increasing temperature.

In heterogeneous materials there is usually also an interracial polarization arising from the accumulation of charges at structural interfaces. This is of little fundamental interest, but it is of considerable practical interest because commercial insulating materials are usually heterogeneous.

1.2.3 FERROELECTRICITY

Ferroics, in general, indicates ferromagnetic, ferroelectric, and ferroelastic materials [11-12]. Ferroic crystals have three characteristics: (i) a spontaneous order parameter i.e. electric polarization, magnetization or elastic deformation; (ii) the occurrence of multiple domain states over the length scale, where the order parameter is essentially uniform and whose boundaries move under an external field and (iii) hysteresis caused by field-induced domain motion during order parameter reversal. The properties of ferroic materials are often superior to conventional materials because of their spontaneous order parameters and large nonlinear coefficients. Due to inherent structural nonlinearity, such ferroic properties render sensors more sensitivity and actuators more powerful. Ferroelectric materials are dielectrics which possess a switchable spontaneous, electric polarization $P_S$ in the absence of an external
electric field. The direction of the polarization can be switched by an oppositely aligned external electric field larger than the coercive field $E_C$. The non-linear behavior of polarization $P$ as a function of electric field is characterized by a hysteresis loop [13-14].

Polarization becomes saturated at sufficiently large fields, and a remnant polarization ($P_r$), exists in the zero electric field. Ferroelectricity is an ordering phenomenon which disappears at a critical temperature called the Curie temperature ($T_C$), above which the material is paraelectric. The dielectric constant $\varepsilon_r$, or electrical susceptibility $\chi = \varepsilon - 1$, is large in ferroelectric materials, and diverges at the Curie temperature, when the polarization is most susceptible to applied electric fields. The dielectric constant is a measure of the polarizability of the material; $P = \varepsilon_0 \chi E$, where $\varepsilon_0$ is the permittivity of free space.

The symmetry of the crystallographic point groups imposes restrictions on the possibility of ferroelectricity in a crystal. There are 32 crystallographic point groups out of which 21 are non-centrosymmetric. Twenty of these 21 point groups exhibit ferroelectricity. The materials, which exhibit ferroelectricity also exhibit piezoelectricity where, mechanical stress can induce polarization, and an electric field can induce strain. Piezoelectricity is a strong, linear coupling between electric polarization and mechanical stress, opposed to the weak, quadratic electrostriction effect found in all dielectric materials. Ten of the twenty non-centrosymmetric point groups possess one unique polar axis and hence exhibit pyroelectricity where polarization changes with change in temperature. All pyroelectric materials are also piezoelectric, but piezoelectric materials without one unique polar axis are not pyroelectric. All ferroelectric materials are pyroelectric, but all pyroelectrics are not ferroelectric. The distinguishing feature is whether the spontaneous polarization can be switched by an external field or not, a feature which must be tested experimentally as it cannot be predicted a priori from symmetry considerations.

Ferroelectrics can be classified as proper or improper, depending on the origin of the polarization. In displacive ferroelectrics, the spontaneous polarization arises from displacements of cations with respect to the anion sublattice, creating electric dipoles which are aligned in one direction, breaking the inversion symmetry. In contrast with conventional displacive ferroelectrics also known as proper ferroelectrics, polarization in improper ferroelectrics is not the primary order parameter. In improper ferroelectrics, polarization results as a secondary effect from a lattice distortion, e.g. in magnetic spiral spin induced ferroelectrics. Polarization can also arise from ordering of the orientation of anion groups, charge ordering [15-17] orbital ordering [18-20], cooperative tilting of polyhedra (geometric
ferroelectrics) [21], or layered ordering in asymmetric superlattices [22]. Long range
coulombic forces are responsible for the alignment of electric dipoles in one direction in
displacive ferroelectrics, while short range coulombic forces (e.g. ionic bonds) favour centro-
symmetry; ferroelectricity thus requires long-range forces to dominate over short range
forces. Partial covalent bonding is the common mechanism for stabilising ferroelectric dipoles
by off centering of cations relative to the anion sublattice.

Perovskite oxides are the most important ferroelectric materials from both a scientific
and a technological perspective. The generic formula of perovskite oxides is ABO$_3$, where the
sum of the valence of the A and B site must be +VI to encounter –VI charge on oxygen to
maintain charge neutrality in stoichiometric materials. This yields three principal types of
perovskites based on cation valence distribution; I-V, II-IV and III-III perovskites. The larger
A cation resides in a 12-coordinated dodecahedron, while the smaller B cation is octahedrally
coordinated.

Materials with antiparallel dipoles are known as antiferroelectrics, and thus exhibit no
spontaneous polarization as the moments from the two oppositely oriented sublattices cancel
each other. The number of simple ferro and anti-ferroelectric perovskites is restricted by the
prerequisite of a narrow B-O π*-bond to stabilise off-centering of B cations to create dipoles,
anti-parallel as well as parallel [23]. Hence, (anti)ferroelectric perovskites have B cations
from the early part of the transition metal block of the periodic table of elements, typically
Ti$^{4+}$, Nb$^{5+}$, Mo$^{6+}$, W$^{6+}$. Partial covalent bonding between a 6s$^2$ lone pair on the A-site and O
2p can stabilise ferroelectricity at room temperature, even if the B cation has non-zero d-
electrons [24-25].

1.2.3.1 FERROELECTRICITY BY PERMANENT DIPOLES

The spontaneous polarization is a consequence of the positioning within the unit cell.
The ions are located at the corners of the unit cell. The dipole moment results from the
relative displacements of ions from their symmetrical positions. The ions are located near, but
slightly below, the centers of each of the six faces, whereas the ion is displaced upward from
the unit cell center. Thus, a permanent ionic dipole moment is associated with each unit cell.
However, when barium titanate is heated above its ferroelectric Curie temperature [120°C
(250°F)] [26], the unit cell becomes cubic, and all ions assume symmetric positions within the
cubic unit cell; the material now has a cubic perovskite structure, and the ferroelectric
behavior ceases. Spontaneous polarization of this group of materials results as a consequence
of interactions between adjacent permanent dipoles wherein they mutually align at dipole
moment in the same direction. For example, with barium titanate, the relative displacements of $O^2-$ and $Ti^{4+}$ ions are in the same direction for all the unit cells within some volume region of the specimen. Other materials, which display ferroelectricity are Rochelle salt potassium dihydrogen phosphate potassium niobate and lead zirconate–titanate. Ferroelectrics have extremely high dielectric constants at relatively low applied field frequencies; for example room temperature dielectric constant of barium titanate may be as high as 5000 [27-28]. Consequently, capacitors made from these materials can be significantly smaller than capacitors made from other dielectric materials.

1.2.3.2 FERROELECTRICITY BY LONE-PAIR ELECTRONS

In general, those ions with two valence electrons can participate in chemical bonds using (sp)-hybridized states such as $sp^2$ or $sp^3$. This tendency may not always be true and, for some materials, these two electrons may not eventually participate in such bonding. They are called the ‘lone-pair’ electrons [28-29]. The ions $Bi^{3+}$ and $Pb^{2+}$ have two valence electrons in an s-orbit, which belong to the lone pairs. The lone-pair state is unstable and will invoke a mixing between the $(ns)^2$ ground state and a low-lying $(ns)^1(np)^1$ excited state, which eventually leads these ions to break the inversion symmetry [30-33]. This ‘stereochemical activity of the lone pair’ helps to stabilize the off-centre distortion and in turn, the ferroelectricity. In typical ferroelectrics like PbTiO$_3$ based materials, the lone-pair mechanism and the ligand-field hybridization take place simultaneously [31]. The ions with lone-pair electrons, such as $Bi^{3+}$ and $Pb^{2+}$, always locate at A-sites in an ABO$_3$ perovskite structure. This allows magnetic transition metal (TM) ions to locate at B-sites so that the incompatibility for TM ions to induce both magnetism and ferroelectricity is partially circumvented. The typical examples are $BiFeO_3$ and $BiMnO_3$, where the B-site ions contribute to the magnetism and A-site ions contribute to polarization via a lone-pair mechanism, eventually leads to the ferroelectricity. In both $BiMnO_3$ and $BiFeO_3$, $Bi^{3+}$ ions with two electrons in 6 s orbital (lone-pair) shift away from the centrosymmetric positions with respect to the surrounding oxygen ions, favouring the ferroelectricity. The magnetism is, of course, from $Fe^{3+}$ or $Mn^{3+}$ ions. $BiMnO_3$ is unique, in which both magnetization and polarization are reasonably large. In fact, it is one of the very exceptional multiferroics offering both ferroelectric and ferromagnetic orders. $BiMnO_3$ has a monoclinic perovskite structure with space group C2 symmetry [34-35] and shows a ferroelectric transition at $T_{ferroelectric} \sim 800K$. The 6s ‘lone pairs’ around Bi ions are approximately spherical in shape and forming rings of localization. This spherically distributed lone pair forms a domain of
localized charges that is reducible and tends to be unstable. In addition, the localization tendency of the lone pairs to form a lobe pattern can be strong enough to drive a structural distortion [34-35]. The traditional lone-pair geometry, the visible regions in the surface correspond to the lobe-like Bi lone pairs allowed by the distorted geometry of the monoclinic structure. Further calculations reveal that the localized lone pair in the distorted structure is not only composed of the expected Bi 6s and 6p states, but also some contribution from the 2p states on the oxygen ligands [36-37]. These predictions suggest that the lone pairs of the Bi ions in BiMnO$_3$ are stereochemically active and are the primary driving force for the highly distorted monoclinic structure and, thus, ferroelectricity in bismuth maganite i.e. BiMnO$_3$.

1.2.4 MAGNETIC MATERIALS

The magnetic moment of a free atom has three principal sources: (i) the spin with which electrons are endowed, (ii) their orbital angular momentum about the nucleus and (iii) the change in the orbital moment induced by an applied magnetic field [38]. The first two effects give paramagnetic contributions to the magnetization, and the third gives a diamagnetic contribution. In the ground 1s state of the hydrogen atom, the orbital moment is zero, and the magnetic moment is that of the electron spin along with a small induced diamagnetic moment. In the 1s$^2$ state of helium the spin and orbital moments are both zero, and there is only an induced moment. Atoms with all filled electron shells have zero spin and zero orbital moment: finite moments are associated with unfilled shells.

**Diamagnetism** is a very weak form of magnetism that is non permanent and persists only while an external field is being applied. It is induced by a change in the orbital motion of electrons due to an applied magnetic field. The magnitude of the induced magnetic moment is extremely small, and in a direction opposite to that of the applied field. Thus, the relative permeability is less than unity, and the magnetic susceptibility is negative.

For some solid materials, each atom possesses a permanent dipole moment by virtue of incomplete cancellation of electron spin and/or orbital magnetic moments. In the absence of an external magnetic field, the orientations of these atomic magnetic moments are random, such that a piece of material possesses no net macroscopic magnetization. These atomic dipoles are free to rotate, and **paramagnetism** results when they preferentially align, by rotation, with an external field. These magnetic dipoles are acted on individually with no mutual interaction between adjacent dipoles. The dipoles align with the external field, they enhance it, giving rise to a relative permeability that is greater than unity, which is small but positive magnetic susceptibility. Both diamagnetic and paramagnetic materials are considered
to be nonmagnetic because they exhibit magnetization only in the presence of an external field.

### 1.2.4.1 Ferromagnetism

Certain metallic materials possess a permanent magnetic moment in the absence of an external field, and show very large and permanent magnetizations. Ferromagnetic (FM) materials exhibit parallel alignment of magnetic moments to one another resulting in net spontaneous magnetization even in the zero magnetic field. Permanent magnetic moments in ferromagnetic materials result from atomic magnetic moments due to electron spin—uncancelled electron spins as a consequence of the electron structure. There is also an orbital magnetic moment contribution that is small in comparison to the spin moment.

Furthermore, in a ferromagnetic material, coupling interactions cause net spin magnetic moments of adjacent atoms to align with one another, even in the absence of an external field. The origin of these coupling forces is not completely understood, but it is thought to arise from the electronic structure of the metal. This mutual spin alignment exists over relatively large volume regions of the crystal called domains. If the magnetic moment is large enough, an applied dc magnetic field can force a nearest neighbour to align in the same direction provided the interaction is larger than the thermal energy (k_B T) of the atom in the lattice. The Curie temperature (T_C) is the temperature at which the interaction energy is greater than the thermal energy. Ferromagnetic materials exhibit paramagnetism above the Curie temperature as thermal energy interaction energy and randomise the moments leading to very small magnetic moments [29]. Magnetic susceptibility of ferromagnetic materials are always positive and as high as 10^6. Molecular field in FM materials are strong enough to magnetize the substance without magnetic field. The Curie-Weiss law and Langevin’s theory, T_C can be obtained in terms of molecular field constant (γ) as:

\[
T_C = \frac{\gamma N m^2}{3 k_B}
\]  

(1.4)

Large value of γ at high T_C revealing that FM materials with interacting magnetic moments require a large thermal energy to disrupt their magnetic ordering and to induce phase transition to paramagnetic phase. T_C can be represented in terms of quantum mechanical Brillouin function with Langevin’s theory, along with appropriate choice of J, as

\[
T_C = \frac{\gamma N g^2 J(J+1)}{3 k_B}
\]  

(1.5)
However, Curie-Weiss law and Langevin’s theory are inadequate to explain the fractional magnetic moment exhibited by some FM materials. Fractional magnetic moments were described later on the basis of band theory. The mechanism of inducing magnetism is identified with an exchange energy that gives rise to Hund’s rule for spin allocation in atoms [30]. The exchange energy is reduced with same electron spin. The exchange interaction in transition metals can be considered as the shift in energy of the 3d band for electrons with one spin direction. If the Fermi energy lies within the 3d band, then the band displacement will lead to more electrons of the lower energy spin direction, resulting in spontaneous magnetic moment in the ground state and external magnetic field is not required to induce magnetization. The bulk material exhibits magnetization below $T_C$. This is due to the existence of domains, where all the atomic moments align in the same direction so that within each domain the magnetization is saturated. However, the magnetization vectors of different domains are not parallel to each other, so the net magnetization is less than the value for the complete alignment of all the moments [32].

The magnetic moments of the sample increases with increasing DC magnetic field. When $H$ is decreased from the saturation point, $M$ does not decrease to the same value as it possesses while increasing the field. When the field is lowered the domains, aligned with the increasing field do not return to the original orientation. When $H$ is returned to Zero, the materials still have a magnetization, referred as remnant magnetization ($M_r$). In order to remove remnant magnetization, a field has to be applied in the opposite direction to the internal field. This field is known as coercive field ($H_C$) [38]. A full cycle of magnetization ($M$) of a material in response to an applied magnetic field ($H$) is called a hysteresis loop. $M_S$, $M_r$ and $H_C$, all are the characteristic parameters of ferromagnetic material whose value depends on the condition by which they are synthesized.

1.2.4.2 ANTIFERROMAGNETISM

Antiferromagnetic substances have a small positive susceptibility at all temperatures, but their susceptibilities vary in a peculiar way with temperature. In AFM materials, the interaction between magnetic moments tends to align the moments antiparallel to each other. These materials can be considered as a system consisting of two interpenetrating but identical sublattices of magnetic ions, in which one set of magnetic ions is spontaneously magnetized below a critical temperature called Neel temperature ($T_N$). AFM materials are known to have mainly zero net magnetization. $\chi_{AF}$ is positive with very low value. Curie-Weiss law is more appropriate for AFM materials since most of them are ionic salts with localized magnetic
moments, but with a negative value for \( \theta \). Antiferromagnetic susceptibility is expressed as below:

\[
\chi_{\text{AF}} = \frac{C}{T - (-\theta)} = \frac{C}{T + \theta} \tag{1.6}
\]

The negative value of \( \theta \) shows antiparallel magnetic moments. Below \( T_N \), \( \chi_{\text{AFM}} \) is found to decrease with temperature. Magnetic anisotropy plays an important role in AFM materials which results magnetic moments perpendicular rather than parallel to the applied magnetic field. In the case of magnetic oxides, a superexchange interaction between magnetic cations mediated through \( \text{O}^{2-} \) anions, leads into the overall AFM alignment in which oxygen donates up-spin and down-spin electrons from its 2\text{p}-orbital to the 3d-orbital of magnetic ions, like Mn\textsuperscript{2+}, Co\textsuperscript{2+} ions. AFM materials are now explored for spin-valve applications.

1.2.4.3 FERRIMAGNETISM

Ferrimagnetic materials exhibit spontaneous magnetization at room temperature, just like ferromagnetics. They consist of magnetically saturated domains and exhibit magnetic saturation and hysteresis. Their spontaneous magnetization disappears above a certain critical temperature \( (T_c) \), also called the Curie temperature, and they become paramagnetic. They also show antiparallel alignments of localized moments like AFM materials. Magnetization in these materials occurs due to imbalance in oppositely aligned sublattices. Ferrimagnetic materials can also be better explained using Weiss molecular field theory, as most of these materials are ionic solids with largely localized electrons. Ferrimagnetic theory was developed by Neel, in continuation with the theory on AFM. However, in the case of ferrimagnetic materials, three interactions are considered as the A and B sublattices are not structurally identical. This consists of nearest neighbour A-B interactions that align the magnetic moments of the two sublattices antiparallel, and FM-next nearest neighbour A-A and B-B interactions. Here A and B represents the atoms/ions at the sites of different symmetry, like tetrahedral and octahedral sites in cubic spinel lattice.

1.3 MULTIFERROISM

“Multiferroic” materials are those materials, which show simultaneously two or more than two ferroic properties i.e. ferroelectricity, ferromagnetism and ferroelasticity. Existence of more than two order parameter promised new applications [39]. The phase control in different types of couplings present in the materials. The electric field \( E \), magnetic field \( H \), and stress \( \zeta \) control the electric polarization \( P \), magnetization \( M \), and strain \( \varepsilon \), respectively.
In primary ferroics, the electric fields $E$ controls the polarization $P$, the magnetic field $H$ controls the magnetization $M$ and stress $\sigma$ controls the strain $\varepsilon$. Magneto-electric coupling occurs between the magnetic field $H$ and the polarization $P$ or between the electric field $E$ and the magnetization $M$. Piezoelectric coupling is represented by the arrows between stress $\sigma$ and polarization $P$ or between electric field $E$ and strain $\varepsilon$.

![Figure 1.1](image1.png)

**Figure 1.1:** Relationship between ferroelectricity, magnetism and ferroelasticity [40-42].

![Figure 1.2](image2.png)

**Figure 1.2:** A schematic Venn-diagram showing the relations between multiferroic and magneto-electric materials [43].

In the late 90’s, Nicola Hill (now Spaldin) started to investigate why there are so few magnetic (ferro or antiferro) ferroelectric perovskites [40-42]. Polarization requires
displacement of cations from their centro-symmetric positions with respect to the oxygen sublattice. Polarization in BaTiO$_3$ and KNbO$_3$ are due to partial covalent bonding between empty d orbitals of the B cations and O 2p orbitals.

On the other hand, magnetism requires unpaired $d$ orbitals electrons of the B cations, which is partial covalent bonded between B cations and oxygen. Unpaired electrons in $f$ orbitals of rare earth A cations can induced magnetic moment, but only at too low temperatures. Lone pairs of Pb$^{2+}$ and Bi$^{3+}$ have shown partial covalent bonding with O 2p orbitals. The role of the $6s^2$ lone pair was extensively studied for BiMnO$_3$ [42]. Charge ordering in BiMnO$_3$ (electronic ferroelectricity) [44-46] and “geometric ferroelectricity”, as in YMnO$_3$ [46] are other microscopic mechanisms that can stabilise ferroelectric dipoles in magnetic materials.

1.3.1 MAGNETO-ELECTRIC EFFECT

The magneto-electric effects are described the coupling between electric and magnetic fields in materials i.e. magnetization (M) induced by an electric field (E) or polarization (P) induced by a magnetic field (H). In 1888, Rontgen observed that a moving dielectric body placed in an electric field becomes magnetized [47]. In 1894, when considering crystal symmetry, Curie predicted the possibility of an intrinsic magneto-electric effect in some crystals [48-49]. The first successful observation of the magneto-electric effect was realized in Cr$_2$O$_3$ [50]. Up to now, more than 100 compounds that exhibit the magneto-electric effect have been discovered [51-56]. In recent years, the term magneto-electric-multiferroics has become more popular, this term contains not only ferro-electromagnets but also all the materials in which any two of the following ferroic orders co-exist.

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

$$F(E,H) = F_0 - P^S_i E_i - M^S_i H_i - \frac{1}{2} \varepsilon_0 \varepsilon_i E_i E_j - \frac{1}{2} \mu_0 \mu_{ij} H_i H_j - \alpha_{ij} E_i H_j - \frac{1}{2} \beta_{ijk} E_i H_j H_k - \frac{1}{2} \gamma_{ijk} H_i E_j E_k$$ (1.7)

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, $P_i^S$ and $M_i^S$ are the components of spontaneous polarization, $P^S$ and magnetization, $M^S$, $\varepsilon_0$ and $\mu_0$ are the dielectric permittivity and magnetic susceptibility of
vacuum, $\varepsilon_{ij}$ and $\mu_{ij}$ are the second-order tensors of dielectric and magnetic parameters, $\beta_{ijk}$ and $\gamma_{ijk}$ are the third-order tensor coefficients and most importantly, $a_{ij}$ is the components of tensor $\alpha$ which is designated as the linear magneto-electric effect and corresponds to the induction of polarization by a magnetic field or a magnetization by an electric field.

Unfortunately, the magneto-electric effect in single-phase compounds is usually too small. The breakthrough in terms of the giant magneto-electric effect was achieved in composite materials; for example, in the simplest case the multilayer structures composed of a ferromagnetic piezomagnetic layer and a ferroelectric piezoelectric layer [57-59]. In the composites, the magneto-electric effect is generated as a product property of the magnetostrictive and piezoelectric effects, which is a macroscopic mechanical transfer process. A linear magneto-electric polarization is induced by a weak a.c. magnetic field imposed onto a d.c. bias magnetic field. These composites are used for practical applications in a number of devices such as microwave components, magnetic field sensors and magnetic memories. For example, it was reported recently that the magneto-electric composites can be used as probes in scanning probe microscopy to develop a near-field room temperature scanning magnetic probe microscope [59].

1.3.2 INCONGRUITY BETWEEN FERROELECTRICITY AND MAGNETISM

Ferroelectricity and magnetism are two opposite phenomena. Ferroelectricity required empty d shell and magnetism needed partially filled d shell [60-62]. The time symmetry can be invariant for ferroelectricity.

![Figure 1.3](image_url)  
**Figure 1.3:** Incompatibility between ferroelectricity and magnetism.
For different type of symmetry, they possess different polarization state. Magnetism and spin order must have time-reversal symmetry. Multiferroics are rare in nature due restricted symmetry. There are no common characteristics between magnetism and ferroelectricity. Spontaneous polarization can be switched by an electric field in ferroelectric (FE) materials. FE materials usually undergo series of phase transitions at high-temperature. Ionically bonded perovskite oxides are not ferroelectric due to short range coloumb repulsions between electron clouds of ions. Ferroelectricity in BaTiO$_3$ is due to ligand field hybridization of Ti ions with oxygen ions. The empty d shell of Ti$^{4+}$ creates strong covalent with the surrounding oxygen anions on repulsion which shift Ti$^{4+}$ from the center of TiO$_6$ octahedra [63].

1.3.3 INTEGRATION MECHANISM BETWEEN FERROELECTRICITY AND MAGNETISM

As we know that FE materials are required B-site ions with an empty d-orbital. FM materials are needed B-site ions with partially filled d orbitals [64-66]. These two types of compounds are known to have similar phenomenology, but opposite mechanism due to isostructural characteristics, there exists always a possibility to integrate their polar orders. According to Maxwell equations, electric and magnetic field are coupled to each other. A moving charge produces a magnetic field. Due to the formal relation between electric and magnetic polarizations both respond to external field and show anomalies at the critical temperature. In FE materials, the covalent bond between TM and oxygen shows the hopping of electron which is like spin exchange interaction between magnetic ions. Spin exchange induces long-range spin order and macroscopic magnetization in materials [67]. A-sites cations are responsible for ferroelectricity like Bi$^{3+}$ and Pb$^{2+}$ whereas B-sites ions are known to contribute magnetism. The ferroelectricity is induced by A-sites cations and magnetism due to B-sites anions. This breaks down the possibility of exclusion of either of the two process like ferroelectricity and magnetism in the same materials [68].

1.4 MULTIFERROIC MATERIALS

1.4.1 BISMUTH PEROVSKITES STRUCTURE WITHOUT Fe; BiMO$_3$

The perovskites based on Bi at A-sites can be expressed as BiMO$_3$, where M = Al, Ga, In, Sc, Cr etc. or modified elements at M sites. The following table contains information about BiMO$_3$ in details with various elements [69-72].
Table 1.1: Selected properties of BiMO$_3$ compounds

<table>
<thead>
<tr>
<th>M</th>
<th>Space Group</th>
<th>Ferroelectricity</th>
<th>Magnetism</th>
<th>Synthesis Condition</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>R3c</td>
<td>$T_c &gt; 520^\circ$C $P_s$~9µC/cm$^2$</td>
<td>$d^9$</td>
<td>1000°C 6 GPa</td>
<td>73-74</td>
</tr>
<tr>
<td>Ga</td>
<td>Pcca</td>
<td>Centrosym.</td>
<td>$d^9$</td>
<td>1200°C 6 GPa</td>
<td>75</td>
</tr>
<tr>
<td>In</td>
<td>Pna2$_1$</td>
<td>$T_c &gt; 600^\circ$C $P_s$~189µC/cm$^2$</td>
<td>$d^9$</td>
<td>1000°C 6 GPa</td>
<td>76</td>
</tr>
<tr>
<td>Sc</td>
<td>C2/c</td>
<td>Centrosym.</td>
<td>$d^9$</td>
<td>1140°C 6 GPa</td>
<td>77</td>
</tr>
<tr>
<td>Cr</td>
<td>C2/c</td>
<td>Centrosym.</td>
<td>$T_N ~ 109K$ AFM G-type</td>
<td>1380°C 6 GPa</td>
<td>78</td>
</tr>
<tr>
<td>Mn</td>
<td>C2/c</td>
<td>Centrosym.</td>
<td>$T_c ~ 100K$ FM</td>
<td>500-1110°C 4-6 GPa</td>
<td>79-91</td>
</tr>
<tr>
<td>Co</td>
<td>P4mm</td>
<td>$T_c &gt; 247^\circ$C $P_s$~1759µC/cm$^2$</td>
<td>$T_N ~ 197K$ AFM C-type</td>
<td>970°C 6 GPa</td>
<td>92-94</td>
</tr>
<tr>
<td>Ni</td>
<td>P$^+$</td>
<td>Centrosym.</td>
<td>$T_N ~ 27K$ AFM</td>
<td>1000°C 6 GPa</td>
<td>95-96</td>
</tr>
<tr>
<td>Cr$<em>{0.5}$Fe$</em>{0.5}$</td>
<td>R3c</td>
<td>$T_c$ unkown $P_s$~639µC/cm$^2$</td>
<td>$T_N ~ 130K$ AFM</td>
<td>1000°C 6 GPa</td>
<td>97</td>
</tr>
<tr>
<td>Ni$<em>{0.5}$Mn$</em>{0.5}$</td>
<td>C2</td>
<td>$T_c$ unkown $P_s$~209µC/cm$^2$</td>
<td>$T_N ~ 140K$ FM</td>
<td>800°C 6 GPa</td>
<td>98</td>
</tr>
<tr>
<td>Mn$<em>{2/3}$Ni$</em>{1/3}$</td>
<td>Pn2$_1$m</td>
<td>$T_c$ unkown $P_s$~609µC/cm$^2$</td>
<td>Short range order</td>
<td>800°C Ambient P</td>
<td>99</td>
</tr>
<tr>
<td>Ti$<em>{3/8}$Fe$</em>{2/8}$Ni$_{3/8}$</td>
<td>R3c</td>
<td>$T_c$~730°C $P_s$~0.59µC/cm$^2$</td>
<td></td>
<td>Multiple Firing. Ambient P</td>
<td>100</td>
</tr>
<tr>
<td>Ti$<em>{3/8}$Fe$</em>{2/8}$Mg$_{3/8}$</td>
<td>R3c</td>
<td>$T_c$~730°C $P_s$~0.59µC/cm$^2$</td>
<td></td>
<td>Multiple Firing. Ambient P</td>
<td>100</td>
</tr>
</tbody>
</table>

1.4.2 III-III FERRITE PEROVSKITES WITHOUT Bi; AFeO$_3$, A = Y, La, Pr...Yb, Lu

The III-III ferrites are known as orthoferrites which have orthorhombic structure with space group Pbnm. The orthoferrites have also G-type antiferromagnetic nature with $T_N$ in the range of 350-467$^\circ$C [23]. Rare earth Ln cations with unpaired f electrons have magnetic exchange between 4f orbitals with Fe 3d orbitals, which is responsible for small polarization in LnFeO$_3$ materials. Moreover, the $T_N$ of Ln based ferrites is very low [101-102].
1.5 BiFeO$_3$ MULTIFERROIC

BiFeO$_3$ (BFO) has shown the multiferroic properties like ferroelectricity and magnetism above room temperature, which have rhombohedrally distorted perovskite structure with $a = b = c = 5.633$ Å, $\alpha = \beta = \gamma = 59.4^\circ$ and space group R3c at room temperature. The ferroelectric curie temperature is $T_C \sim 1103$ K and the antiferromagnetic Néel point is $T_N \sim 643$ K. BFO has canted spin structure, which is responsible for weak ferromagnetism in these systems at room temperature [59-60]. The high $T_C$ refers to a large polarization. Polycrystalline BFO is known to have small value of polarization. High leakage current, defects and non-stoichiometry are responsible for small polarization. Ferroelectricity and magnetism in BFO can be significantly enhanced by substitution of rare-earth ions [67–70].

BiFeO$_3$ is known to have a complicated magnetic spin alignment, which has been confirmed by Neutron diffraction experiment. Neutron diffraction has shown spatially modulated spin structure over a wavelength of $\lambda = 62$ nm [60]. The spiral spin wave vector is along $[10\overline{1}]$ directions and the polarization is oriented in $[111]$ directions. The magnetism in these samples may be vanished if the sample size is as small as cycloid wavelength (~62 nm). The suppression of cycloid spin order is induced to enhance magnetism in nanoscale BiFeO$_3$ and thin film samples [74]. There are only a few multiferroics which exhibit the curie temperature at significantly high temperature and magnetic transition temperature at relatively low temperature. These materials are the centre of attraction in recent years. These are given in the following table with their characteristic temperature and chemical formula. Among there BiFeO$_3$ is the only material which has drawn the attention of researchers worldwide in last few years due to its multifunctional properties.

<table>
<thead>
<tr>
<th>Materials</th>
<th>$T_C$</th>
<th>$T_N$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TbMnO$_3$</td>
<td>27 K</td>
<td>41 K</td>
</tr>
<tr>
<td>GdMnO$_3$</td>
<td>23 K</td>
<td>43 K</td>
</tr>
<tr>
<td>DyMnO$_3$</td>
<td>18 K</td>
<td>39 K</td>
</tr>
<tr>
<td>BiFeO$_3$</td>
<td>1083 K</td>
<td>653 K</td>
</tr>
<tr>
<td>BiMnO$_3$</td>
<td>750 K</td>
<td>FM $T_C = 105$ K</td>
</tr>
<tr>
<td>YMnO$_3$</td>
<td>900 K</td>
<td>70 K</td>
</tr>
</tbody>
</table>
From the above table, it is clear that only bismuth ferrite exhibits magnetic and ferroelectric characteristics above room temperature hence, it is a potential candidate for electronic industry.

1.5.1 PHASE DIAGRAM OF BiFeO₃

BiFeO₃ can be prepared using Bi₂O₃ and Fe₂O₃ in appropriate amounts in equimolar proportion at high temperature. These raw materials decompose at high temperature to produce BiFeO₃ according to the following equation

\[ \text{Bi}_2\text{O}_3 + \text{Fe}_2\text{O}_3 \rightarrow 2\text{BiFeO}_3 \]  

(1.8)

Bismuth ferrite is found to have parasitic phases, which nucleate in the form of impurities at grain boundaries [50]. BiFeO₃ is metastable in air [49, 51-52]. Oxygen vacancies and impurities are important for thin films, because they play key role to enhance the remnant magnetization [19, 21]. In addition to the impurities and defects, BiFeO₃ also yield magnetite phase (Fe₃O₄) as a byproduct [53], as seen in the following reaction

\[ 6\text{BiFeO}_3 \rightarrow 2\text{Fe}_3\text{O}_4 + 3\text{Bi}_2\text{O}_3 + \text{O} \]  

(1.9)

Figure 1.4: Compositional phase diagram of BiFeO₃ [49].

The presence Fe₃O₄ and Fe₂O₃ phases are identified by micro-Raman studies because Raman spectra for Fe₃O₄ are different as compared to Fe₂O₃ [52]. However, the Bi₂O₃ cannot be detected because of glass-forming compound or evaporation during thermal decomposition. It
is known that Bi$_2$O$_3$ melts above 800°C [49]. For thin films of BiFeO$_3$, this decomposition mechanism gives the possibility for the appearance of remnant magnetization, which may be due to localized traces of magnetite in BFO sample.

Bi$_2$O$_3$ – Fe$_2$O$_3$ phase diagram is shown in Fig. 1.4, which shows complexity of BFO formation. From the phase diagram, it can be seen that pure phase formation of BFO is very crucial at temperature ~ 825 °C and only equimolar concentration of Bi and Fe ensures pure BFO phase formation. The above treatise highlights what are difficulties in BiFeO$_3$ for synthesis and practical applications. These are the problems which are being encountered with BiFeO$_3$ to use as a technologically relevant material.

1.5.2 PROPERTIES OF BiFeO$_3$

The properties of BiFeO$_3$ are summarised in Table 1.3.

### Table 1.3: Structural and physical properties of BiFeO$_3$.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Values</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal System$^a$</td>
<td>Trigonal</td>
<td>104</td>
</tr>
<tr>
<td></td>
<td>$a_{\text{hex}} = 5.5787$ Å, $c_{\text{hex}} = 13.8688$ Å</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$a_{\text{rh}} = 5.6343$ Å, $a_{\text{rh}} = 59.348^\circ$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$a_{\text{pc}} = 3.965$ Å, $a_{\text{pc}} = 89.35^\circ$</td>
<td></td>
</tr>
<tr>
<td>Space group</td>
<td>R3c, 161</td>
<td>104</td>
</tr>
<tr>
<td>Tolerance Factor$^b$</td>
<td>$t = 0.890$</td>
<td>104-106</td>
</tr>
<tr>
<td>Density</td>
<td>8.40 g/cm$^3$</td>
<td></td>
</tr>
<tr>
<td>Ferroelectricity</td>
<td>$T_c = 820$-$830^\circ$C</td>
<td>105-106</td>
</tr>
<tr>
<td>Polarization$^c$</td>
<td>90-100 µC/cm$^2$</td>
<td>107-111</td>
</tr>
<tr>
<td>Dielectric constant</td>
<td>$\varepsilon_r = 30$</td>
<td>112-113</td>
</tr>
<tr>
<td>Antiferromagnetism</td>
<td>Canted G-type, $T_N = 370^\circ$C</td>
<td>105</td>
</tr>
<tr>
<td>Piezoelectricity</td>
<td>$D_{33} = 15$-$60$ pm/V</td>
<td>110-111</td>
</tr>
</tbody>
</table>

$^a$ Trigonal crystals can be represented as rhombohedral, hexagonal or pseudocubic unit cell axes and lattice parameters.

$^b$ Assuming six-coordinated high spin Fe$^{3+}$ and eight-coordinated Bi$^{3+}$ with ionic radii from Shannon.

$^c$ Inferred from measurements on thin films, single crystals, bulk ceramics and Berry phase calculations.

1.5.2.1 CRYSTAL STRUCTURE

BiFeO$_3$ is rhombohedrally distorted perovskite oxide material. The perovskite structure can be described by corner-sharing of BO$_6$ octahedra with 12-coordinate. The relative sizes of dopent is important for the geometric [114-115] and thermodynamic stability [116] of the perovskite structure, and Goldschmidt criterion has been used to describe perovskite structure which is based on the tolerance factor ‘$t$’ according to the following
equation:

\[ t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)} \]  

(1.10)

where \( r_A, r_B \) and \( r_O \) are the ionic radii of the A and B cation and \( O^{2-} \) anion respectively. For ‘t’ close to unity means cubic perovskite structure is stable. For \( 1.0 < t < 1.065 \), it is tetragonal perovskite with space group P4mm [23]. When the cations are too large and tolerance factor is more than one, it forms hexagonal structures. Tolerance factors larger than one are commonly found in I-V and II-IV perovskites.

When the cations are too small to fit into dodecahedral voids due to the size mismatch, which induces tilting of an octahedra to reduce the size of the dodecahedron. Tolerance factors less than unity is commonly found in II-IV and III-III perovskites. The crystal structure changes from cubic to rhombohedral and then orthorhombic with decreasing tolerance factor [23, 117-118]

The geometrical stability of perovskite structure is described by the polyhedral volume ratio \( V_A/V_B \), which computes the size mismatch [119-122]. For cubic structure \( t = 1 \) and volume ratio is \( V_A/V_B = 5.0 \). When \( V_A/V_B \) ratio decreases from 5.0 in to \( \overline{R\overline{3}}c \) (rhombohedral), \( R\overline{3}c \) (rhombohedral) and Pbnm (orthorhombic) in decreasing order [123].

Rhombohedral perovskites are mostly found with four space groups. The space group \( R\overline{3}m \) symmetry occurs in the materials when displacements of the A and B cation occur along [111] pseudocubic axis. This rhombohedral symmetry has been found to take place when elongation of the primitive unit cell is along [111] axis.

![Figure 1.5: (a) Rotation of oxygen octahedra (b) Displacement of oxygen [124].](image)

The space group \( \overline{R\overline{3}}c \) has been found due to anti-ferrodistortive rotation of the \( BO_6 \)
octahedra. The R3c space group in BiFeO₃ is attributed to the polar distortion of R3m and anti-ferrodistortion in R̅3c. Elongation along pseudocubic [111] axis and rombohedral angle less than 60° is responsible for breaking of inversion symmetry which results \( V_A/V_B < 5.0 \).

**Figure 1.6:** (a) Relation between pseudo cubic, rhombohedral and hexagonal unit cell of BiFeO₃ with space group R3c. (b) Hexagonal unit cell of BiFeO₃ (c) Rotation of FeO₆ octahedra rotate antiparallel.

The R3c space group can be defined with rhombohedral (rh), hexagonal (h) or pseudocubic (pc) axes. Rhombohedral and hexagonal lattice parameters are related by:

\[
a_{\text{rh}} = \frac{a_{\text{h}}}{2 \sin \left( \frac{\alpha_{\text{rh}}}{2} \right)} \quad \text{and} \quad \alpha_{\text{rh}} = 2 \arcsin \left( \frac{3a_{\text{h}}}{2 \sqrt{3a_{\text{h}}^2 + c_{\text{h}}^2}} \right) \quad (1.11)
\]

The pseudocubic angle \( \alpha_{\text{pc}} \) is related to the rhombohedral angle by:

\[
\alpha_{\text{pc}} = 90 + \arcsin \left( \frac{1 - 2 \cos \alpha_{\text{rh}}}{3 - 2 \cos \alpha_{\text{rh}}} \right) \quad (1.12)
\]

The hexagonal unit cell with R3c symmetry contains 7 formula units. The polar displacements and spontaneous polarization is along c-axis. The rhombohedral angle is 59.35° produces a large distortion in unit cell. The rhombohedral angle is described by

\[
\alpha_{\text{rh}} = 2 \arcsin \left[ \frac{3a}{2 \sqrt{3a^2 + 6c^2}} \right].
\]

Atomic positions Bi, Fe and O in R3c space group of BiFeO₃ are given in Table 1.4 [125].
Table 1.4: Atomic position BiFeO$_3$ in R3c space group

<table>
<thead>
<tr>
<th>Atomic/position</th>
<th>X</th>
<th>y</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi$^{3+}$</td>
<td>0</td>
<td>0</td>
<td>¼ + s = 0.30</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>0</td>
<td>0</td>
<td>t = 0.02</td>
</tr>
<tr>
<td>O$^{2-}$</td>
<td>1/6-2e-2d = 0.23</td>
<td>1/3-4d = 0.34</td>
<td>1/12</td>
</tr>
</tbody>
</table>

1.5.2.2 MAGNETIC STRUCTURE

BiFeO$_3$ is antiferromagnetic with G-type ordering [126]; each Fe$^{3+}$ ion with spin up is surrounded by six nearest neighbours with spin down. The plane of magnetization is (001)$_{\text{hex}}$ perpendicular to the polar [111]$_{\text{hex}}$ axis [127]. Tilting of the FeO$_6$ octahedra reduces the Fe-O-Fe angle from 180° to 154-155°. The antiparallel magnetic sublattices are canted due to Dzyaloshinskii-Moriya interaction [124, 128-129]. Canting of the sublattices creates a weak ferromagnetic moment. So, BiFeO$_3$ possesses both ferroelectric and weak ferromagnetic polarization [130-131]. The weak ferromagnetic moment is cancelled due to spin cycloid or spiral modulation of the spin structure with a periodicity of wave length ~ 62 nm [132].

![Figure 1.7](image)

Figure 1.7: (a) G-type antiferromagnetic ordering [110], (b) Weak ferromagnetic moment caused by the Dzyaloshinskii-Moriya interaction [124], (c) Cycloidal modulation of the spin structure [112].

1.5.2.3 MAGNETO-ELECTRIC COPULING

The cycloidal modulation avoids weak ferromagnetic polarization, which is also exploitation of magneto-electric effect. The cycloidal spin is suppressed above large magnetic fields and BFO become magneto-electric material. The coupling between ferroelectricity and
magnetism in BFO is attributed to the cycloidal spin structure [133-134]. BiFeO$_3$ is a ferroelectric material with weak ferromagnetism, which is induced by Dzyaloshinskii-Moriya interaction [135]. Theoretical study on BiFeO$_3$ suggested that magnetic moment can be reversed by antiferrodistortive rotation of the FeO$_6$ octahedra [136]. The overlapping of ferroelectric and antiferromagnetic domains in BFO has induced strong coupling between ferroelectric and magnetic order in BFO, which first shows electric voltage control of magnetic order at room temperature [135]. The origin of magneto-electric coupling is not yet fully clear, which is expected to attract considerable attention in near future [133].

1.5.2.4 PHASE TRANSITIONS VS. DEFECTS

It has been observed from the literature that dielectric anomalies of BFO based compounds have been found to occur at different temperatures which varies from report one to report 2. So the anomalies in BFO have been reported at various temperatures like 130, 200, 280, 370, 460, 600, 670, 740 and 845°C. Some of these anomalies could be attributed to parasitic phases and defects. Anomaly at 370°C is caused by magneto-electric coupling due to characteristic temperature of pure BFO i.e. antiferromagnetic Neel temperature ($T_{\text{Neel}}$), and anomaly at 845°C is attributed to $\alpha$ to $\beta$ phase transition [137]. Anomaly near 185°C is observed in dielectric and thermal expansion. This anomaly is called “ghost” transition, which is reported by Polomska. The transition at 185°C is not generally observed in dielectric behavior and also phonon behavior. BFO magnetic transition is orthoferrites. Still, there are lots of issues in BFO which are not addressed properly so far.

1.5.2.5 RESISTIVITY OF BiFeO$_3$

The dc resistivity value of bulk BFO is higher than $10^{10}$ Ohm cm. With increasing temperature, the resistivity of sample decreases like as wide bandgap semiconductor.
Arrhenius plots show a change in resistivity slope [137-139]. The activation energy of charge carriers is found decreasing from 1.3 to 0.6 eV as material is heated above antiferromagnetic temperature. This shows that magnetic ordering affects the conductivity bandgap. At very high temperature resistivity anomalies are correlated with α (rhombohedral) to β (orthorhombic) transition, β (orthorhombic) to γ (cubic) transition. The resistivity decreases at α to β phase [137].

1.5.2.6 BANDGAP AND METAL INSULATOR TRANSITION

The direct optical bandgap of BFO has been reported to be in the range 2.3 to 2.8 eV at room temperature. But in some reports, it is suggested that the bandgap is roughly in the range of 0.4-1.0 eV, which is an indirect band gap and also smaller than the direct one. BFO behaves as a direct-bandgap semiconductor at room temperature [137]. The optical bandgap decreases with increasing temperature and goes to zero immediately at γ phase, which is showing a temperature driven Metal-Insulator (MI) transition in BFO. MI transitions have really been observed in BFO at room temperature with 50 GPa pressure, as well as temperature at 1204 K with 1 atm pressure. MI transition has not been reported in any perovskite ferrite other than BFO [137].

The evidence of MI transition near 1204 K is first confirmed by optical bandgap goes to zero at that temperature; second, that the reflectivity increases rapidly; third, that the magnetism disappears; fourth, that the temperature derivate of resistivity changes. As the temperature increases, bandgap decreases to 1.6 eV by 500°C. At 1204 K the structure becomes cubic and the conduction band minima overlap the valence band maxima. So, BFO is semimetal [140-141].

1.6 APPLICATIONS OF BiFeO₃

The value of voltage (electric polarization) to an external magnetic field can be measured by using of multiferroic materials or vice versa, i.e. magnetic polarization detected by electric polarization or electric field [142-144]. The modulation of amplitude and phase are possible by passing the signals through a fine line waveguide. Magneto-electric materials give the opportunity of modifying the magnetic polarization by electric polarization or voltage. The voltage applying across the slab produces a shift in the absorption line of multiferroic material, which resulting the modulation of the amplitude and phase of a propagating wave with the electric field. But unfortunately, almost all the existing multiferroic are antiferromagnetic and show a small magnetic moment [145-146]. So it is a big challenge to
detect the little change of external electric field by magnetization.

**Figure 1.9:** (a) Multiferroic materials as a magnetic field proving. The upper and lower are FM and middle layer is multiferroic. (b) The read-head device using the probe in (a) [142].

BiFeO$_3$ is a potential candidate for spintronic and magneto-electric applications. The bits can be written by applying an electric field. In spintronics devices the writing is done by the ferroelectric polarization, and reading by magnetic field. Reading antiferromagnetic states is not directly possible [142]. A voltage controls ferroelectric state of BiFeO$_3$, and specified the strong coupling between ferroelectric and antiferromagnetic plane. Ferroelectric polarization can be switched by antiferromagnetic planes.

If the coupling is strong, flips the direction of the lower ferromagnetic (FM, blue) layer through exchange bias. In the FM-Metal-FM trilayer alignment can be controlled by ferroelectric state of the BiFeO$_3$ layer (green). Parallel FM layers provide a low resistance across the FM-Metal-FM trilayer, corresponding to a binary state “0”. Antiparallel alignment of the FM layers offers a high resistance, corresponding to binary state “1”. BiFeO$_3$ can also be used as a tunnelling barrier layer [148]. The ferroelectric states can controled by magnetic field [149-150]. The direction of the polarization can also be controled by tunnelling resistance [151-153].
Figure 1.10: BiFeO$_3$ using MERAM (green FE-AFM layer, FM electrode (blue)) [147].

BFO can also be used in four-state memories, where both the polarization and magnetization can modulate the tunnelling resistance [154]. BFO have highest switchable polarization among known perovskites. It is a most important candidate for substituting PbZr$_{1-x}$Ti$_x$O$_3$ (PZT). BFO is non toxic and lead free material, which adds additional benefits in health, safety and environmental purpose. It is possible that BFO fits into Si and SiO$_2$ based circuits. Leakage currents can be minimized and controlled by utilizing these materials. BiFeO$_3$ based FE memories have main concern on chemical compatibility [147]. Pure BiFeO$_3$ exhibit low piezoelectric coefficient, but pulsed laser deposition (PLD) grown films can show a piezoelectric coefficient $> 100$ pm/V at a morphotropic phase boundary. So, BFO can be a strong candidate for lead-free piezoelectric [155-156].

The optical bandgap of BiFeO$_3$ is in the range $\sim 2.2$-$2.8$ eV. BFO can be used as an optoelectronic devices, photoconductivity (sensors), photocatalysts and photovoltaic materials [157-158]. The semiconducting property of BiFeO$_3$ can be used in diodes [159-160]. The diode effect is also related to photovoltaic current. While BiFeO$_3$ is not likely to be used as a conventional solar cell, it may be used in future devices which are not only magnetic and ferroelectric, but also semiconductor and optical devices.
1.7 MOTIVATION OF THE PRESENT WORK

In last few years, multiferroic materials offer simultaneous presence of order parameters such as ferroelectricity, ferromagnetism and sometimes ferroelasticity in a single phase [9,161]. Further, the coupling among these parameters, especially between ferroelectric and ferromagnetic behavior, opens new opportunities for multiferroic materials in device applications such as four-state memory, spintronics and transducers [163-165]. So far, BiFeO$_3$ (BFO) is the only single phase material that shows multiferroic phenomenon at room temperature. It possesses rhombohedrally distorted perovskite structure with $R3c$ space group, high ferroelectric Curie temperature ($T_C \sim 830 \, ^\circ C$) and Neel temperature ($T_N \sim 370 \, ^\circ C$) with G-type antiferromagnetic (AF) behavior at room temperature. In BFO, ferroelectricity originates at A-site due to the stereochemically active 6$s^2$ lone pair of Bi$^{3+}$ ion while magnetic behavior appears at B-site in Fe$^{3+}$ ions [137]. Moreover, a large leakage current density caused by charge defects, nonstoichiometry and secondary phases makes it difficult to observe a well-saturated ferroelectric hysteresis loop. These, along with high dielectric loss hinder the use of BFO in devices. In order to improve electrical and magnetic properties, partial substitution of rare-earth ions (La$^{3+}$, Nd$^{3+}$, Sm$^{3+}$, Pr$^{3+/4+}$, Gd$^{3+}$, etc) at A-site for Bi$^{3+}$-ions or transition metal ion (Mn$^{3+}$, Ti$^{4+}$, Cr$^{3+}$, Co$^{2+}$, Sc$^{3+}$, etc) at B-site for Fe$^{3+}$-ions has been carried out [166-170]. Apparently, these substitutions have either improved the ferroelectric or the magnetic behavior.

Recently, increasing attention has been paid to the A and B-sites co-substituted BFO with the idea of further improving its properties [166-170]. Recent Studies on La$^{3+}$ and Ni$^{2+}$ co-substituted BFO films have shown leakage current density three orders of magnitude lower than pure BFO. Low leakage current density, observed in co-substituted film samples are found to have well-saturated ferroelectric hysteresis loop [171]. Enhanced dielectric, ferroelectric and anti-fatigue properties have also been reported in La$^{3+}$ and V$^{5+}$ co-substituted BFO (BLFV, $x = 0.0 - 0.10$) ceramics [172]. In addition to this, La doped polycrystalline BFO ceramic ($x = 0.10$) has shown a structural transition from rhombohedral to monoclinic with Nb$^{5+}$ ($x = 0.02$) substitution [174], not only ferroelectric properties, but magnetic properties have also been found to improve in B-sites doped ceramics. This development is arised due to several factors including structural transition with off-valent doping which has led to the collapse of the cycloid spin structure i.e. destruction of magnetic balance between the antiparallel sublattices of Fe$^{3+}$ ions. It has also affected grain size which has been found to decrease with off-valent ions (Nb$^{5+}$) substituted in BLFO (Bi$_{0.9}$La$_{0.1}$Fe$_{0.98}$Nb$_{0.02}$O$_3$) ceramics.
Kawae et al. (2010) have also reported their studies on Pr$^{3+}$ and Mn$^{4+}$ co-doped BFO thin films and found a significant reduction in current density of thin film samples in the high electric field regions [177]. Lan et al. (2011) investigated La$^{3+}$ and Zr$^{4+}$ co-substitution effect in BFO ceramics (BLFZ) and observed improved magnetic behavior as well as exchange bias effect [178]. They, however, did not notice any structural transition with 2 at% Zr co-substitution at Fe-site in BLF. This finding is in contrast to a monoclinic phase transition observed with Nb$^{5+}$ co-substitution in BLFO ceramics [175]. However, enhanced multiferroic properties in BLFZ ceramics were ascribed to grain size reduction and antiferromagnetic-ferromagnetic core-shell structure formation. Thus, it can be concluded that A-site substitution as well as A & B-sites simultaneously co-substituted BFO samples display better electrical and magnetic behavior and hence, these are more beneficial from the application point of view. Therefore, it is interesting to study the effect of substitution individually at A-sites and simultaneously at A & B-sites in BFO. From the literature survey, it appeared that BFO is highly important material from technological point of view. Further, these studies show that simultaneous co-substitution with equimolar concentration of dopants in BFO is still lacking. It is, therefore, require studying BFO rigorously using isovalent and off-valent substitutions at A and B sites individually and simultaneously.

In view of this, it will be worthwhile to study the effect of isovalent and offvalent dopands individually and simultaneously. We therefore, have synthesized pure BFO compound first for the purpose of self reliance and thereafter, isovalent substitutions at A-sites in BFO. For this, we have carried out research to study the effect of dopants (Pr$^{3+}$ and Y$^{3+}$) on structural, electrical, magnetic and optical properties of BFO ceramics. After studying the effect of A-site subsetuents, we have studied A and B-sites co-substituted BFO compounds. For this, we have considered Pr$^{3+}$ & Ti$^{4+}$ co-substitution simultaneously with equimolar concentration in BFO as one material system and Y$^{3+}$ & Ti$^{4+}$ in BFO as another materials system. Equimolar concentration of Ti$^{4+}$ with respect to Pr$^{3+}$ and Y$^{3+}$ has been taken into account to see the effect of Ti$^{4+}$ substitution in BPFO and BYFO lattices. Effect of these substitutions on structural, dielectric, ferroelectric and magnetic properties of BiFeO$_3$ has been studied.