

Chapter 1 Introduction

1.1 Historical review

James Clerk Maxwell in the 19th-century, first time combined the magnetism and electricity into a common discipline through his famous Maxwell's equations. However, in solids, the scenario is little different, and these orderings are considered to be completely disjoint because of their different sources of origin. The electron spins are responsible for the magnetism, whereas the electric charge of electrons and ions govern the electrical properties. However, there are many cases where these degrees of freedom are highly co-related, e.g., in the case of Spintronics devices. The electron's spin can control the transport properties of the solid and vice-versa, which led to the evidence of coupling between magnetic and electrical ordering in the materials [1].

Further, the cross-coupling between these two ferroic orderings, i.e., the application of the external magnetic field used to control or switch polarization and vice-versa described as a magneto-electric (ME) coupling in the materials. Smolenskii and Bokov first experimentally affirmed the presence of magnetic and ferroelectric ordering in single phase material, i.e., Nickel iodine boracites ($\text{Ni}_3\text{B}_7\text{O}_{13}\text{I}$) with Neel temperature $T_N \sim 60\text{K}$ and Curie temperature $T_c \sim 400\text{K}$. However, large unit cell, needle shape like crystal growth and low working temperature has restricted $\text{Ni}_3\text{B}_7\text{O}_{13}\text{I}$ for device applications [2-4]. Later, H. Schmid used the term 'Multiferroic' to describe these co-existences of primary ferroic orderings in the materials [2]. Subsequently, many research works were carried out on these materials in the past few years in order to know not only about their exotic physics behind their physical properties but also to know about their potential applications. However, due to their complex crystal structure, weak ME coupling, a small value of magnetization and polarization and low Curie temperature make it unfeasible for

direct application. These shortcomings led scientists to discover a variety of perovskite material (ABO_3 type).

In case of perovskite materials, ferroelectricity is generally caused by the presence of an empty d-shell (d^0) on the A-site, while partially filled d or f shells (d^n) of transition-metals or rare-earth ions on B-site is a prerequisite for ferromagnetic ordering. For example, In first discovered mixed perovskite $Pb(W_{2/3}Fe_{1/3})O_3$ and $Pb(Nb_{1/2}Fe_{1/2})O_3$ which simultaneously shows ferroelectricity and magnetization are caused by diamagnetic ions (W, Nb) and (Fe, Fe) ions respectively [3]. However, these materials are entirely incompatible for commercial applications just because of their low value of T_N and T_C . Subsequently, a lot of research work is going on magneto-electric (ME) multiferroics to improve multiferroic properties and control magneto-dielectric (MD) coupling in the material in different forms: bulk, nano, and thin-film multilayer. In 2003, Ramesh and N.A. Spaldin postulated a very large ferroelectricity in Bismuth ferrite (BFO) thin films at room temperature [4].

1.2 Primary Ferroics

A functional material is usually called ferroic when its physical properties can be affected or changed by changing its surrounding conditions such as temperature, pressure, stress, electric and magnetic field [5]. The term ferroic is driven from the Latin word “ferm” means ‘iron’ refers the oldest famous ferroic material [6]. Typically known materials, which shows primary orders such as ferroelectric, ferromagnetic or ferroelastic are known as primary ferroic materials. They display a significant change in the properties in the vicinity of the critical temperature with some symmetry breaking and show a well-defined hysteresis loop which is proportional to the

respective external fields [7]. The ferroic materials are often more superior than the conventional materials because of their large non-linear coefficient and spontaneous order parameters. Due to this reason, they have the potential for a large number of technical applications in the area of sensor, actuators, communication, medicine and memory devices.

1.2.1 Ferromagnetic materials

Ferromagnetism is the oldest known ferroic property observed around 600 BC in magnetite or loadstone by its ability to attract iron. Ferromagnetic materials exhibited a spontaneous magnetization due to parallel alignment of uncompensated spins with each other known as domain, with a significant positive magnetic susceptibility. In ferromagnetic materials, the spin magnetic moment contribution is more than that of orbital magnetic moment. Further, ferromagnetic materials show a phase transition from the ferromagnetic phase to paramagnetic phase as the temperature is increased above its Curie temperature (T_C) by parallel alignment of domains with some symmetry breaking [8].

In Physics, different types of magnetic orderings are also reported such paramagnetic, ferromagnetic, antiferromagnetic, and ferrimagnetic as shown in Figure 1.1. All orderings are observed in a paramagnetic state below characteristic Neel temperature (T_N). In paramagnetic substances, magnetic dipoles are in random orientation in the absence of a magnetic field. Paramagnetic materials such as titanium, aluminum, oxygen are weakly magnetized in the presence of strong magnetic field due to induced magnetic field in the materials. Once the external field is removed the magnetic dipoles cannot retain their induced direction and the magnetic properties decrease due to the thermal energy (agitation). In the anti-ferromagnetic phase, the magnetic moment is usually related to the spins of atoms or molecules pointing in one

direction with a regular pattern having neighboring spins pointing in the opposite direction. Usually, antiferromagnetic ordering appears only below a particular temperature and disappears at a critical temperature known as Neel temperature (T_N), above which it behaves like a paramagnetic material. For example, manganese oxide exhibits anti-parallel alignment of spins below $T_N \sim 122\text{K}$. The super exchange interaction between spins acts to the anti-parallel alignment of neighboring spins [9].

Ferro-magnets exhibit a type of magnetism similar to anti-ferromagnet and display the parallel alignment of neighboring spins. However, in the ferrimagnetic materials, some of the moments are unequal, resulting in a non-zero net magnetization.

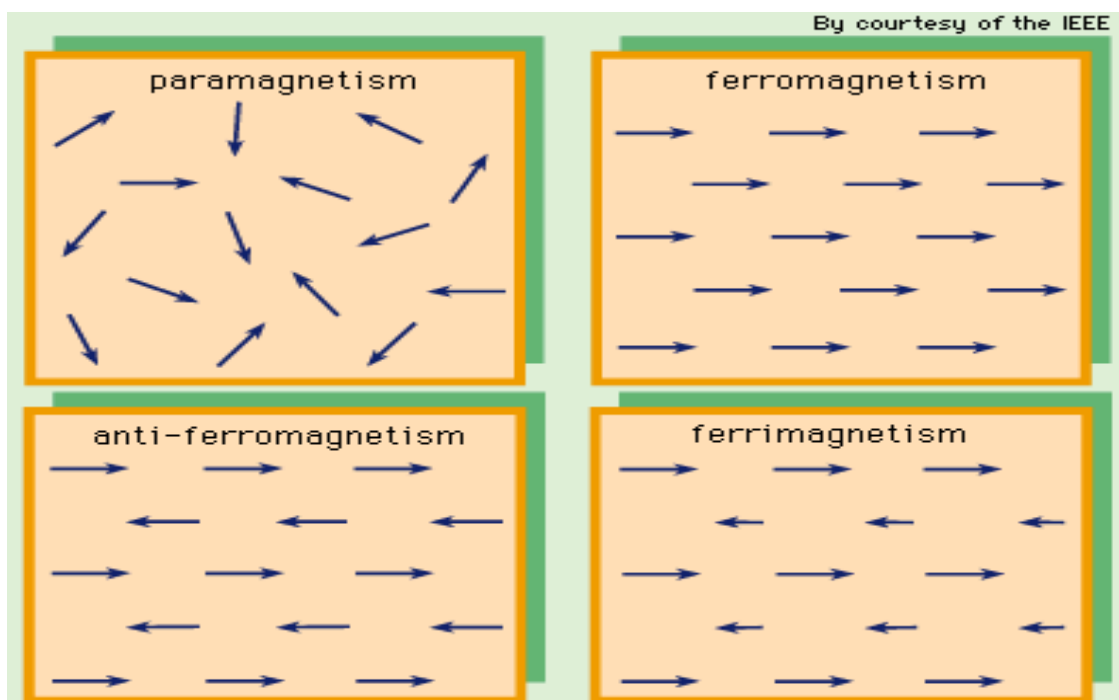


Figure 1.1 Schematic illustration of the orientation of magnetic moments in materials [source <http://electrons.wikidot.com/magnetism-iron-oxide-magnetite>]

1.2.2 Ferroelectric materials

Ferroelectric materials are dielectric materials which possess net electric polarization even when the external electric field is removed. They have two or more stable orientations of the spontaneous polarization in the absence of an electric field, which can be reoriented by the application of the external electric field. The first ferroelectric material Rochelle salt ($\text{NaKC}_2\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$) was discovered by J. Valasek in 1920 [10]. He suggested that in ferroelectric materials, electric dipoles are aligned parallel to each other known as domain structure which is the reason behind (corresponds to) the hysteresis loop behavior of the materials. Moreover, a ferroic material undergoes a phase transition from a non-ferroic (higher symmetry) to ferroic (lower symmetry) state when it is cooled below the critical temperature known as Curie temperature (T_C) of the material. For example, PbTiO_3 undergoes a phase transition between paraelectric (cubic) and ferroelectric (tetragonal) at $T_C \sim 753\text{K}$ [11].

1.2.3 Ferroelastic materials

Ferroelastic materials possess a spontaneous strain which can be controlled hysterically by the application of externally applied stress. They show similar behavior to that of ferroelectricity and ferromagnetism, and its Ferroelastic domains can also be switched by electrical and mechanical force [12].

1.3 Multiferroics materials

As discussed earlier, the term multiferroic was first coined by H. Schmid in 1994 [2]. According to him, multiferroic is the coexistence of more than one ferroic or anti-ferroic properties (like ferromagnetic, ferroelectric, ferroelastic etc.) in a single-phase sample [1, 2, 15]. Among these

multiferroics, the materials possessing ferroelectric (anti-ferroelectric) and ferromagnetic (anti-ferromagnetic) properties are called magnetoelectric (ME) compounds as shown in Figure 1.2 [13].

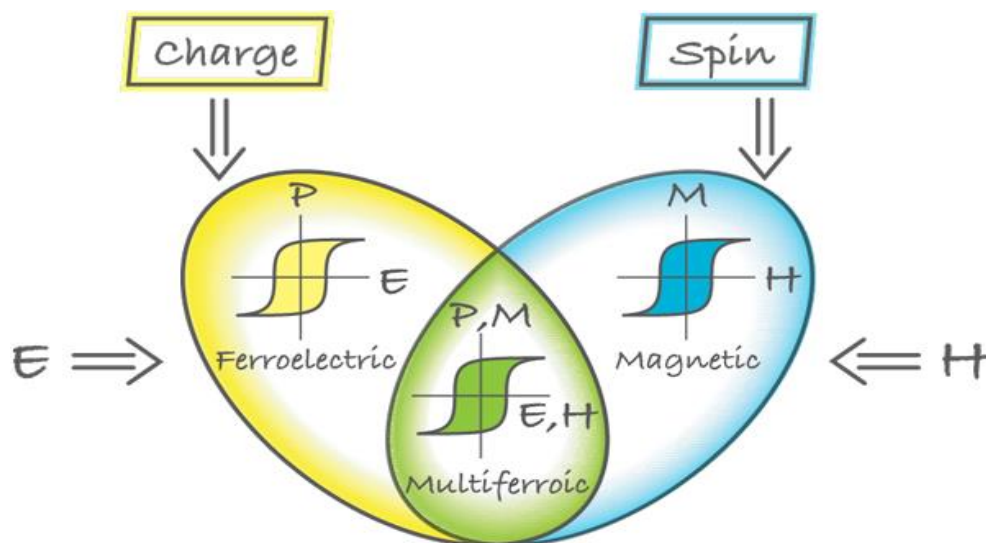


Figure 1.2 Schematic illustrations of multiferroics defined from the combination of ferroelectric and magnetic properties[1].

In this figure, the magnetization of ferromagnetic materials can be referred as a blue circle on the right, and yellow circle on left displays ferroelectricity (Polarization) loop of ferroelectric materials and the intersection between these circles describes the ME multiferroic compound. In ME compounds, intrinsic polarization can be induced by the application of external magnetic field and application of an external electric field can induce magnetization. This mutual controllability between the electric and magnetic ordering is known as magneto-electric (ME) coupling. Astrov et al. first experimentally affirmed the presence of linear ME coupling in antiferromagnetic Cr_2O_3 . The coupling between these properties in a ME compound makes them essential for industrial applications such as in Spintronics devices, magnetoelectric sensor, and

data storage devices. Also they have attracted huge attention due to their enhanced physical properties and the underlying physics behind them.

1.4 Symmetry consideration

In a multiferroic system, the presence of more than one primary ferroic properties is closely related to the combination of breaking symmetry conditions. The primary ferroic properties (i.e., ferroelectricity, ferromagnetic and ferroelasticity) are described by their behavior under spatial inversion (**SI**) and time reversal (**TR**) symmetries. The breaking of **SI** symmetry requires the change in electric dipole moment in the material while **TR** symmetry breaking can be switched inducing magnetic ordering. In ME multiferroics, ferroelectric and magnetic phases co-exist, so it requires the simultaneous breaking of both **SI** and **TR** symmetry conditions. In general, many of the hampering mechanism needed to lower the symmetry resulting in the various type of multiferroics materials which are briefly described below [14].

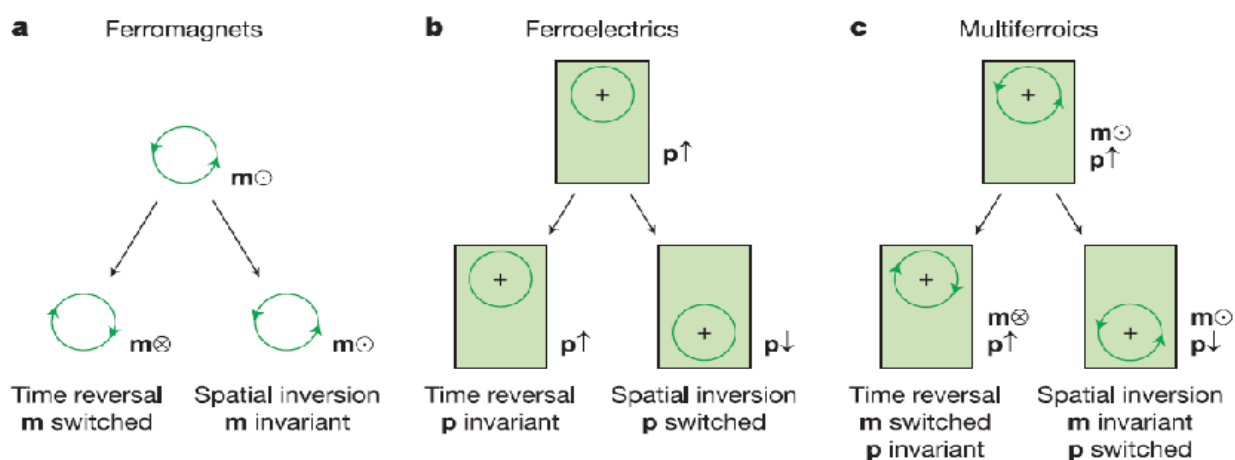


Figure 1.3 Classification of “ferroic” orders according to symmetry [9].

1.5 Classification of multiferroics materials

Multiferroic materials are classified on the basis of various mechanism causing magnetism and ferroelectricity in the system. Broadly, they are divided into two categories with further subdivisions.

1.5.1 Type-I Multiferroics

These types of multiferroics have different sources of magnetism and ferroelectricity and often appear at different temperatures [2, 18]. They are also known as “Old” multiferroics and show weak ME coupling because of the independent sources of ordering state. They display large spontaneous polarization, which usually happen due to the distorted structure. However, the critical temperature of transition from ferro to para is above the room temperature. Examples of type-I multiferroics are BiFeO_3 ($T_C \sim 1100\text{K}$, $T_N \sim 643\text{K}$, $P \sim 90\mu\text{C}/\text{cm}^2$) and BiMnO_3 ($T_C \sim 770\text{K}$, $T_N \sim 105\text{K}$, $P \sim 3.8\mu\text{C}/\text{cm}^2$). Type-I multiferroics exhibit linear ME coupling as well as their dielectric susceptibility shows an anomaly nears magnetic phase transition.

Based on the mechanism of ferroelectricity origin, Type-I multiferroic is classified into several sub classes:

1. **Multiferroic Perovskite (d^0 vs. d^n)**
2. **Ferroelectricity due to lone pairs**
3. **Ferroelectricity due to charge ordering**
4. **Geometric Ferroelectricity**

1.5.1.1 Multiferroic Perovskite (d^0 vs. d^n)

There are many perovskite ferroelectrics and perovskite magnetic materials known individually, but the combination of them cannot show both ferroelectric and magnetic properties in perovskite structure. This is because of the microscopic origin of ferroelectricity, which needs displacement of transition metal ions having empty d shell such as Ti^{+4} , Ta^{+5} , W^{+6} and contrary to this the presence of partially filled d shells of transition metals cause magnetism in the perovskite. This problem is well known as “ d^0 vs. d^n problem”. For example, in mixed perovskite the magnetism is caused due to the presence of real d^n ions (red circles) whereas, ferroelectricity is due to off-center shift of d^0 ions (green) from the center of O_6 octahedra (yellow plaquettes) causing polarization, accompanied with magnetic moments (red arrows) [1, 19].

1.5.1.2 Ferroelectricity due to lone pairs

In perovskite-based multiferroics like $BiFeO_3$ and $BaTiO_3$, the ferroelectricity distortion is caused due to the ordering of lone pairs concerning oxygen octahedral cage. For example, in $BiFeO_3$, Bi^{+3} ions have two valence electrons in $6s^2$ outer shells, these electrons do not participate in chemical bonding and are called dangling electrons. These electrons break the local inversion symmetry. Moreover, these dangling electrons of Bi^{+3} ions (orange) may hybridize with p-orbital of surrounding oxygen which results in structural distortion (green arrow) and hence induces ferroelectricity [15].

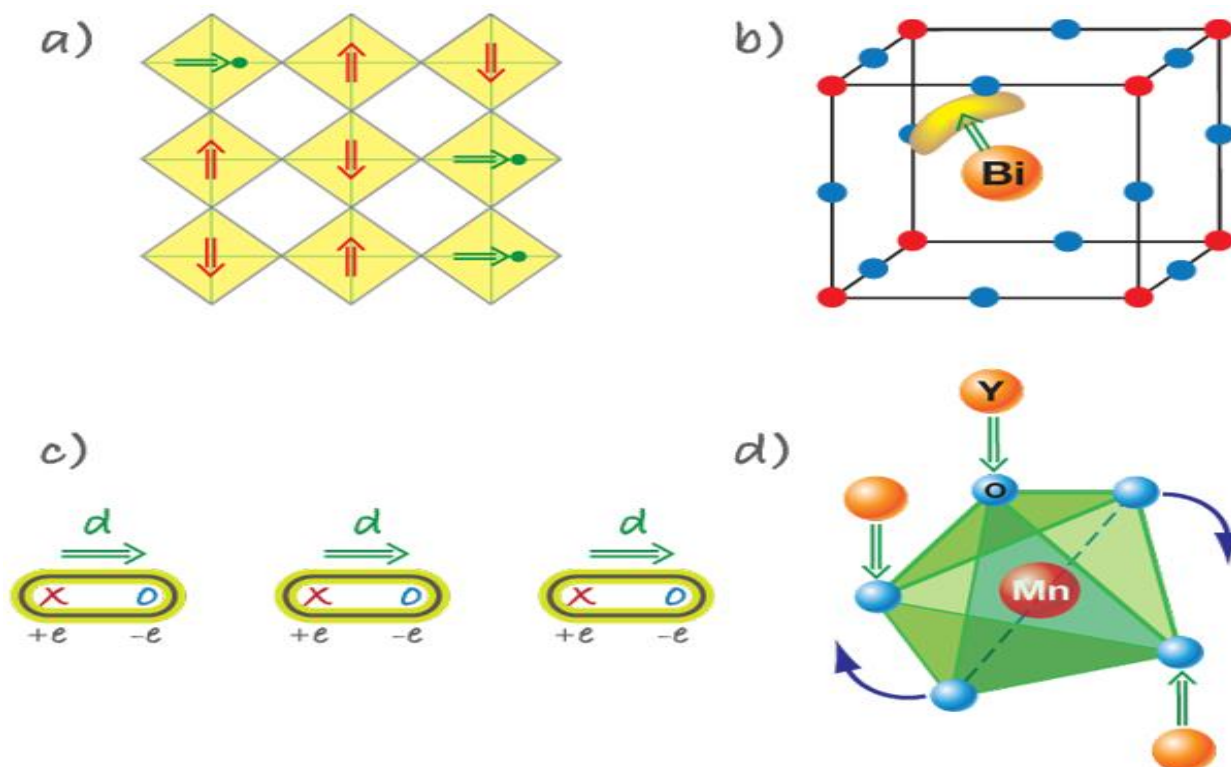


Figure 1.4 Origin and microscopic mechanism of ferroelectricity in type-I multiferroics (a) In mixed perovskite, a d^0 ion (green circles) cause for ferroelectricity and magnetic d^n ions (red circles) responsible for magnetism. (b) Ferroelectricity due to lone pairs (c) Charged-ordered ferroelectricity in multiferroics and (d) Geometrically frustrated ferroelectricity [1].

1.5.1.3 Ferroelectricity due to charge ordering

Charge ordering is another mechanism that can lead to ferroelectricity. It is primarily seen in transition metal compounds and ions containing mixed valences. In these systems, charge ordering changes the bond lengths and this can lead to ferroelectric polarization. For example, multiferroics LuFe_2O_4 shows charge ordering ferroelectricity below 330K [16].

1.5.1.4 Geometric Ferroelectricity

The multiferroics, whose ferroelectric state depends on the structural distortion falls under this category. Ferroelectricity in frustrated multiferroic RMnO_3 ($R=\text{Y}, \text{Ho}$ etc.) is driven by structural instability. For example, ferroelectricity in YMnO_3 is caused by tilting a rigid MnO_5 block unit.

Because of this tilting, Y and oxygen ions come closer to each other and form a dipole (green arrows), producing a polarization in a particular direction [17].

1.5.2 Type-II Multiferroics

Type-II multiferroics are linked to the novel multiferroics in which ferroelectricity can be induced by the application of an external magnetic field. They are called “new” multiferroics and exhibit strong ME coupling due to the magnetically driven ferroelectricity. Moreover, they show weak polarization because of the centrosymmetry structure which can be strongly influenced by an external magnetic field. On the basis of their multiferroic behavior, these are classified into two types: -

1. Spiral Type-II.
2. Collinear Spin ordering.

1.5.2.1 Spiral Type-II Multiferroics.

In these systems, the ferroelectricity is induced in magnetic phases with spiral magnetic structure by breaking the inversion symmetry. The orthorhombic multiferroic materials such as RMnO_3 (R = rare-earth elements) and RMn_2O_5 exhibit a variety of magnetic ordering with different size of R [2, 22]. For example, in sinusoidal antiferromagnetic multiferroics TbMnO_3 , there is no experimental evidence of electric polarization obtained in between 40 to 30K, but it displays very small polarization induced below 30K due to change in magnetic structure from sinusoidal to helical [18].

Katsura, Nagaosa, and Balatsky (KNB) in 2005 first successfully developed a model in order to explain the ME effect in non-collinear magnets. From the KNB theory, a non-collinear spin pair drives a ferroelectric polarization \mathbf{P} ; this is given by,

$$\mathbf{P} \sim r_{ij} \mathbf{x} (\mathbf{S}_i \mathbf{x} \mathbf{S}_j)$$

Where, r_{ij} is a unit vector pointing from lattice site i to j and \mathbf{S}_i and \mathbf{S}_j are neighboring spins.

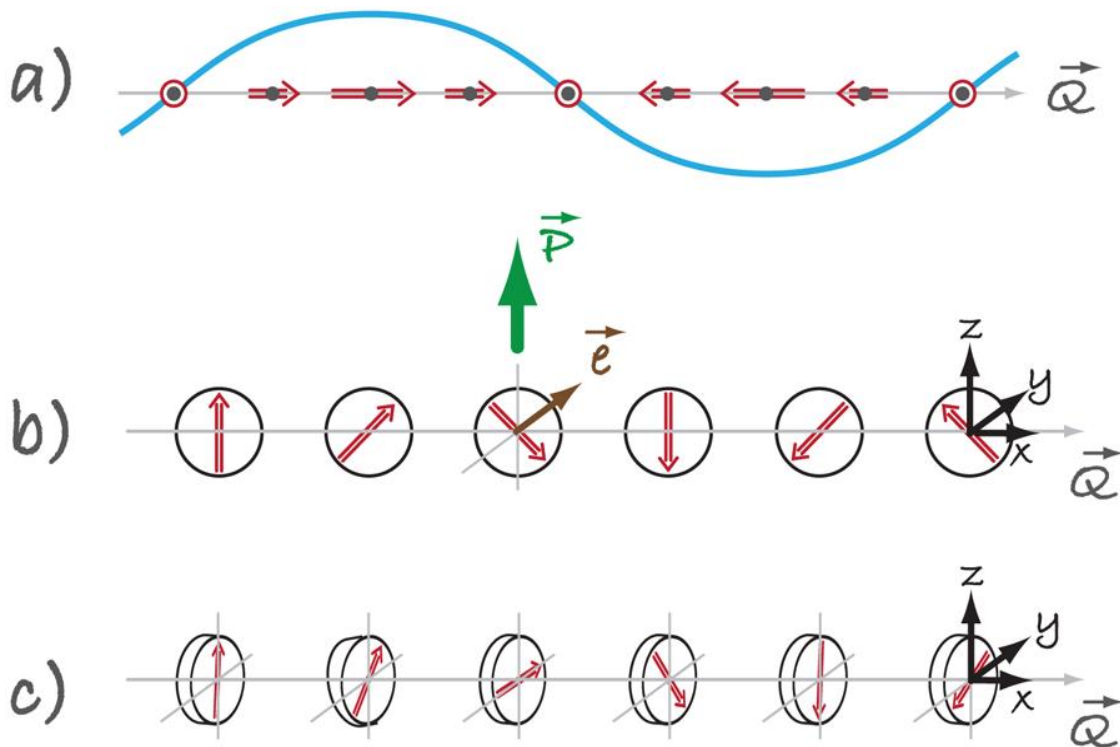


Figure 1.5 Different types of spin structures relevant for type-II multiferroics. (a) Sinusoidal spin wave, in which spins have to point along one direction but vary in magnitude. This structure is centrosymmetric, and consequently, the value of ferroelectricity is zero. (b) The cycloidal spiral with the wave vector $\mathbf{Q} = Q_x$ and spins rotating in the (x,z) -plane. It is in this case where one finds non-zero polarization, $P_z \neq 0$. (c) In a so-called proper screw; the spins rotate in a plane perpendicular to \mathbf{Q} . Here, the inversion symmetry is broken, but most often it does not produce polarization although in some instances it might [1].

Later, Mostovoy modified the KVB theory by using a phenomenological theory and showed that polarization \mathbf{P} in a cycloidal spiral system is defined as

$$\mathbf{P} \sim r_{ij} \mathbf{x} (\mathbf{S}_i \mathbf{x} \mathbf{S}_j) \mathbf{x} [\mathbf{Q} \mathbf{x} \mathbf{e}]$$

Here, Q = Wave vector describing the spirals.

e = Spin rotation axis.

This equation indicates that spin-orbit interaction gives rise to induced electric polarization and the direction of resultant induced ferroelectric order is perpendicular to the propagation vector and lies in the plane of the spin spiral [19]. This theory explains the origin of ME coupling in multiferroics $TbMnO_3$, $BaNiFe_4$, $W_3V_2O_8$ and $MnWO_4$.

1.5.2.2 Collinear spin ordering:

In this type of multiferroics, ferroelectricity originates from magneto-striction and also works for collinear magnetic structure without requiring the presence of spin-orbit coupling. One of the standard example is Ca_3CoMnO_6 .

Ca_3CoMnO_6 is a typical collinear multiferroic consisting of a one-dimensional chain of alternative transition metal (Co^{+2} and Mn^{+4}) with different valancies along the chain, as shown in the Figure (1.6). In Ca_3CoMnO_6 , ferroelectricity is induced by exchange striction arising from transition metal Co^{+2} and Mn^{+4} due to unequal vacancies [20]. Generally, exchange-striction in transition metal oxides depends on not only the distance between the metal's ions but also on the bond angle between metal-oxygen-metal. This effect was also observed in identical magnetic ions because in transition metal oxides the exchange occurs via intermediate oxygen. In strongly frustrated magnetites $RMnO_3$ (R = rare-earth elements) exchange striction drives due to shifting of oxygen ions, similar to the Mn-Mn bonds, thus resulting in polarization along the shifting direction.

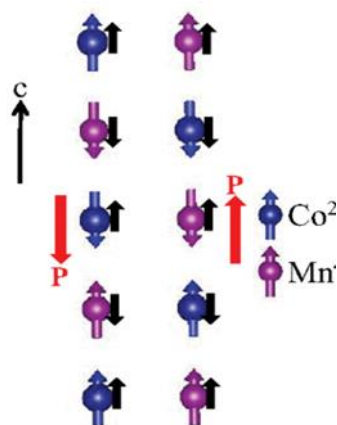


Figure 1.6 Co/Mn Ising chain with two states of spin ordering in $\text{Ca}_3\text{CoMnO}_6$. Ions are displaced from ideal positions (broken circles) leading to an electric polarization [21].

1.6 Magnetolectric coupling

The magnetolectric (ME) coupling describe the phenomenon of dependency of two fields on each other i.e., induction of a magnetic state of a material by application of the external electric field and vice-versa[22]. Generally, insulating materials such as composite multiferroics oxides display this ME phenomenon. These materials are categorized into two main groups: Single phase multiferroics and composites materials. In single phase multiferroics, electric and magnetic order co-occurs in the same phase. They can show a very week ME effect, approximately 10^{-5} . The change in magnetization is affected by the electric field at low temperature.

The second group is composite materials which are formed by combining two different phases at the atomic level. In this ME composite system, two different phases and the ME coupling are present across the interface due to strain mediated ME effect [23]. For example, in ferromagnetic-ferroelectric composite system magnetic field incites strain in magnetic

component because of the magnetostrictive effect which is transferred mechanically to the ferroelectric component and can be described as follows:

$$\text{Direct ME effect} = \frac{\text{Magnetic}}{\text{Mechanical}} \times \frac{\text{Mechanical}}{\text{Magnetic}}$$

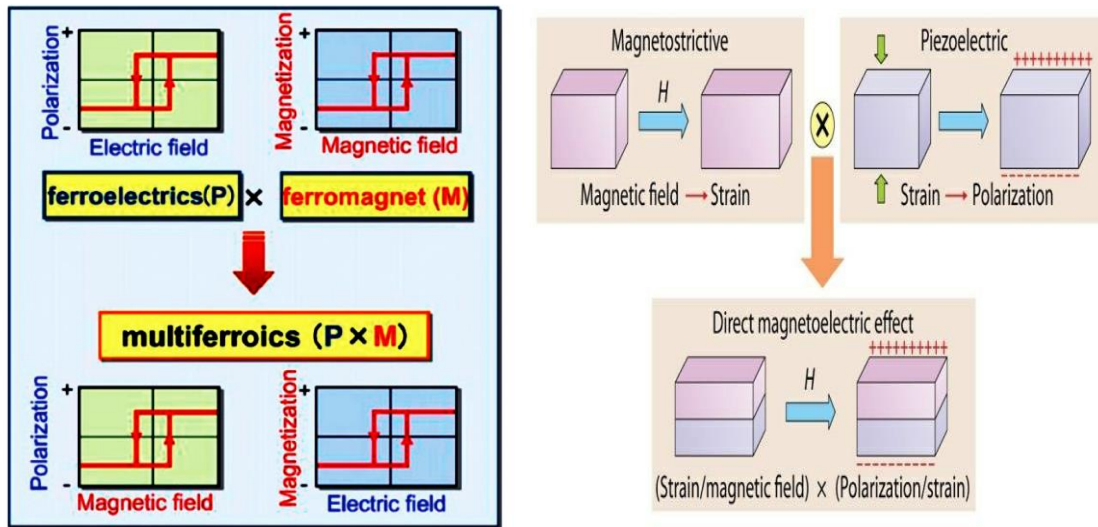


Figure 1.7 (a) Magnetoelectric coupling. (b) Direct magnetoelectric effect[24].

The development of ME coupling in a single-phase crystal customarily described in Landau theory, where we can express the system's free energy in terms of an electric and magnetic field applied on the system:

$$F(E,H) = F_0 - P_i^S E_i - M_i^S H_i - \frac{1}{2} \mu_{ij} H_i H_j - \frac{1}{2} \epsilon_{ij} E_i E_j - \alpha_{ij} E_i H_j - \frac{1}{2} \beta_{ijk} E_i H_j H_k - \frac{1}{2} \gamma_{ijk} H_i E_j E_k - \dots$$

Where, P_i^S and M_i^S represent the static polarization and magnetization of the materials respectively, whereas μ_{ij} and ϵ_{ij} are the magnetic and electric susceptibilities [6, 25]. The sixth term on the right-hand side describes the magnetoelectric coupling which depends on the

polarization and magnetization. The term α_{ij} represents the linear ME coupling coefficient. Fortunately, most of the materials show linear ME coupling which quantifies the dependence of magnetization on the electric field or dependence of polarization on the magnetic field. The other higher terms contain coefficients β_{ijk} and γ_{ijk} which describe-order coupling terms in the materials.

The polarization and magnetization can be established from the free energy F by differentiating it w. r. to the electric and magnetic field respectively.

$$P_i = \alpha_{ij}H_j + \frac{\beta_{ijk}}{2}H_jH_k + \dots$$

and

$$\mu_0 M_i = \alpha_{ij} + \frac{\gamma_{ijk}}{2}E_jE_k + \dots$$

Unfortunately, the ME effect in single phase materials is typically too small to apply them practically as the term α_{ij} is limited by the relation

$$\alpha^2 \leq \epsilon_0 \mu_0 \epsilon_{ii} \mu_{jj}$$

1.7 Perovskite materials

Perovskite materials exhibit the same crystal structure as Calcium titanium oxides (CaTiO_3) or ABX_3 type structure. These materials have attracted massive attention because of their unusual properties, majorly arising due to their complex structure. During the course of time these properties are thoroughly studied by the researchers and developers for both practical applications and theoretical modeling. A natural perovskite is a type of mineral that was first

found in the Ural Mountains and named after Russian mineralogist Lev Aleksevich von Perovski. The general formula of perovskite type structure is ABX_3 , where A and B are two cations having different atomic radii and X is an anion, mostly a fluorine atom or oxygen as shown in the Figure 1.8 [26]. The oxidation state of the A cation varies from +1 to +3 and the B cation from +3 to +6. Generally, 'B' cations have 6-fold co-ordination surrounded by six anions. Where, cation 'A' is cubo octahedrally coordinated within the BO_6 polyhedral framework. It is found that metallic elements which are stable in the perovskite structure have the tolerance factor (t) in the range of 0.75 to 1.

Tolerance factor (t) which is defined as

$$t = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)}$$

Where, r_A , r_B and r_X are the ionic radii of A, B and X ions, respectively [26–28].

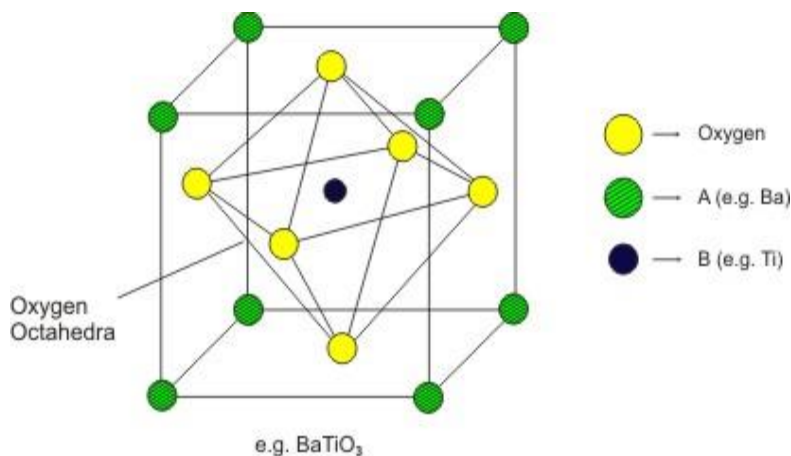


Figure 1.8 ABX_3 perovskite structure. (Source: https://nptel.ac.in/courses/113104005/lecture4/4_2.htm)

Depending upon the atoms/molecules used in the structure, the resulting perovskite can have many different properties and many practical applications including:

- Superconductivity
- Colossal Magneto-resistance
- Oxidation/reduction catalysis
- Spin-dependent transport
- Optoelectronic properties

1.8 Bismuth Ferrite (BiFeO_3)

BiFeO_3 (also abbreviated as BFO) is one of the most promising and well-known multiferroic substances since early 1960s. The formation of single phase polycrystalline BFO is an arduous task, because the synthesis of single phase BFO leads to the formation of secondary phases $\text{Bi}_2\text{Fe}_4\text{O}_9$, $\text{Bi}_{25}\text{FeO}_{39}$ and $\text{Bi}_{46}\text{Fe}_2\text{O}_{72}$ due to volatile nature of bismuth oxide. Acbenbacti and his colleagues first successfully prepared single phase BFO by using diluted HNO_3 to remove undesirable phases [29]. Kubel and Schmid in 1990 determined the atomic position of single phase BFO by using the X-ray diffraction technique. Ramesh and his group in 2003 found the significant enhancement in remanent polarization (more than 15 times larger than that in bulk) in the thin layer of BFO [4]. In the last few decades, BFO is the most promising multiferroic material among all discovered multiferroics. It possesses a distorted rhombohedral perovskite structure belongs to the space group $R3c$ and have both ferroelectric transition temperature ($T_C = 1100$ K) and antiferromagnetic ($T_N = 650$ K) above room temperature [30, 31]. The co-existence of electric and magnetic orderings in multiferroic materials provides the potential application in data-storage systems, multiple-state memories, high energy density capacitors and in the field of Spintronics.

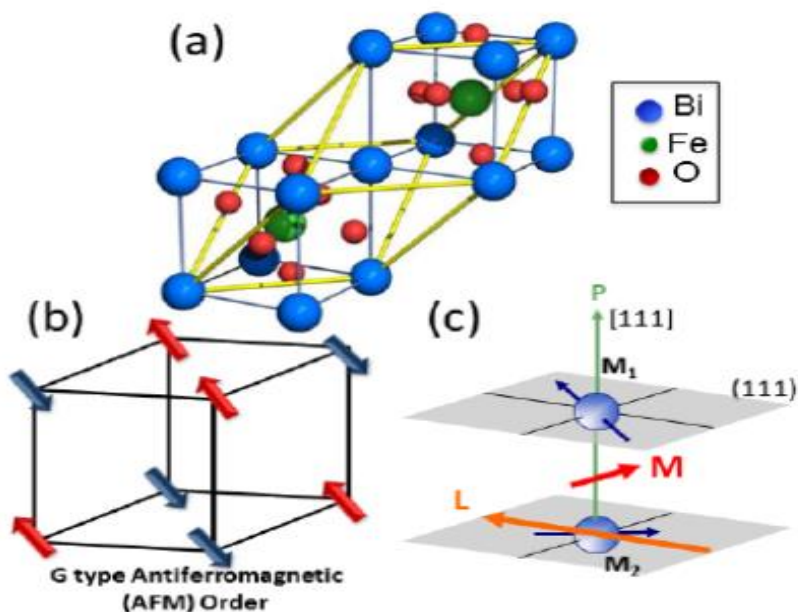


Figure 1.9 Schematic diagram of crystal structure of BFO unit cell. The unit cell can be pictured as a pseudo-cubic structure which is outlined in blue. Two pseudo-cubic structures are needed to describe the rhombohedral unit cell. (b) Schematic diagram of the magnetic lattice of BiFeO_3 showing G-type antiferromagnetic cell where the nearest neighbor spins are antiparallel. The Fe spin resides in pseudo-cubic. (c) Schematic diagram of the arrangement of the macroscopic order parameter (P, L, and M) of the thin film [24].

BFO is the type-I multiferroic compound as it has a different source for ferroelectric and magnetic ordering. The ferroelectricity is due to the presence of lone pair of electrons in the 6s orbital of Bi atom, while partially filled d-orbitals of Fe atom is responsible for magnetic ordering in BFO [32, 33]. BFO shows sizeable spontaneous polarization of order $10\text{-}100\mu\text{C}/\text{cm}^2$ because of polar displacement of cations and anions relative to each other, pointing along one of the eight pseudo-cubic [111] axes [34]. This displacement of Bi, Fe, and O concerning each other may be visualized as the freezing of the zone center ($q \rightarrow 000$) Γ_4 - mode of the cubic paraelectric state, bringing down the symmetry from $\text{Pm}\bar{3}\text{m}$ to R3m .

However, the high leakage current, low resistivity, structural variability and the instability of a single phase formation have restricted the applications of BFO. The reason for all these problems to prevail is supremely because of two shortcomings: (1) The presence of Fe^{+3} ions and (2) Oxygen vacancies. Finding answers to these problems, BFO was subjected to many research works by partial substitution at A(Bi)- and B(Fe)- site of BiFeO_3 . Several groups have tried to enhance the ferroelectric, ferromagnetic and optical properties of BFO using doping mechanism. During the course of time, it was revealed that the suitable dopant substitutions like lanthanides e.g. La, Dy, Sm helps in improving the multiferroic nature of BFO [35–37]. For example, substitution of La at Bi site can increase the dielectric constant in BFO and decrease the antiferromagnetic Neel temperature (T_N) value from 643 to 603 K at 1MHz. Chauhan et al. observed that there was a structural phase transition when 15% of Fe is replaced by an Mn atom (of BFO sample) lead to significant enhancement in magnetization [10]. One of the most challenging problems in the emerging field of multiferroics is to enhance and control ME coupling at room temperature. Thus, many efforts have been reported in recent years in order to achieve large ME coupling near room temperature. This can be achieved by suppressing the cycloid spin structure (~62nm) or by fabrication of nanoparticles (less than 62nm) or by suitable chemical substitution of rare-earth elements (La^{+3} , Gd^{+3} , Nd^{+3} , Dy^{+3} , Sm^{+3}) and non-magnetic ions (Zr^{+4} , Ti^{+4}) respectively at A- and B- site of BFO. Synthesis of a solid solution of BFO with other stable ABO_3 - type perovskite such as BaTiO_3 , PbTiO_3 , and rare earth manganites RMnO_3 (R= Gd, Y, Dy), are desired to have improved magnetoelectric (ME) properties near room temperature.

Furthermore, several attempts have been made to synthesis other composite systems with BFO apart from mixing any of the systems mentioned above. Different combinations of bulk, Nano and thin-film multilayer have resulted in improvement of ME properties. Recently, Li Yan et al. have calculated the direct ME exchange interaction on epitaxial self-assembled BFO-CFO nano-composite thin films on 001 SRO/STO [38].

1.9 Introduction to RMnO₃: Phase diagram and physical properties

Rare-earth (RE) manganites containing the general formula RMnO₃ (R: La, Pr, Nd, Y, Sm, Eu, Gd, Dy, Tb, etc.) have been in key attention due to their strong ME coupling, colossal magnetoresistance (CMR), charge ordering and recently magnetically induced ferroelectricity [13, 18, 22, 39, 40]. RE manganites are classified into various structures crystallographically, depending on the basis of ionic radii of rare earth elements. Thermodynamically, relatively larger ionic radii (R: La, Pr, Nd, Sm, Gd, Dy, Tb) stabilizes in orthorhombic structure with space group Pnma/Pbnm and compounds with smaller ionic radii (R: Ho, Er, Tm, Yb, La, Sc, In) belongs to hexagonal structure of space group P6₃cm.

In the orthorhombic crystal structure, both Mn and RE form an octahedron occupy the coordination numbers 6 and 12 respectively, while in a hexagonal structure, Mn and RE have the coordination numbers 5 and 7 respectively [13, 18, 22, 39, 40]. For the RE magnets, the tolerance factor can be used to determine the hexagonal boundary manganites and orthorhombic manganites as shown in the Figure 1.10. Notably, the smaller the value of Goldschmidt factor, the more is structural distortion between P6₃cm and Pnma phases near the boundary [41].

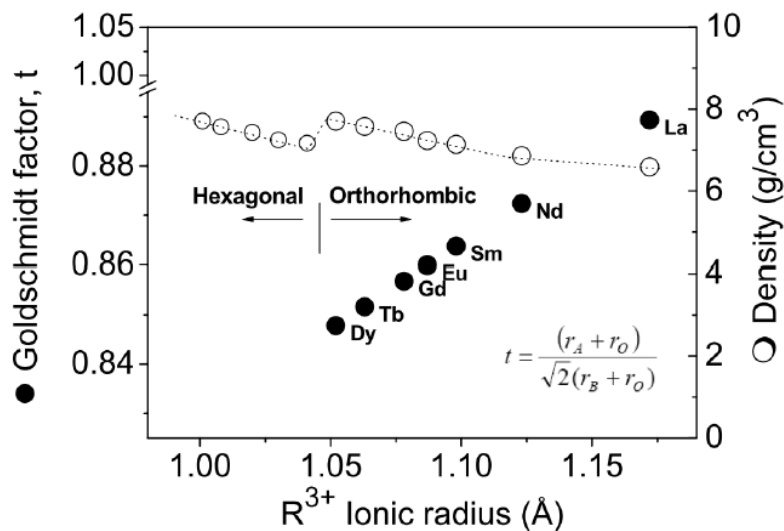


Figure 1.10 Evolution of the tolerance factor and density of the RMnO_3 phase as a function of ionic radius [41].

Among the all discovered RE manganites perovskite, terbium manganite (TbMnO_3) is the most studied multiferroic system, because of its robust ME coupling between AFM and ferroelectric ordering. It possesses orthorhombic distorted perovskite structure (Space group: Pbnm) with lattices parameters $a = 5.296\text{\AA}$, $b = 5.837\text{\AA}$ and $c = 7.404\text{\AA}$ at room temperature, and is antiferromagnetic in nature containing three electrons in t_{2g} orbitals and e_g doubly degenerated orbitals. At low temperature, it displays many magnetic transitions.

The spins of Mn^{+3} moments ordered antiferromagnetically from collinear sinusoidal to a non-collinear spin structure at $\sim 27\text{K}$. Underneath this lock in temperature $T_{\text{lock}} \sim 27\text{K}$ spontaneous polarizations of $0.06\mu\text{C}/\text{cm}^2$ have been observed along c-direction. Presence of ferroelectricity underneath $\sim 27\text{K}$ temperature is identified with the change from sinusoidal to helical spin ordering [42]. Furthermore, the second magnetic ordering appears below $\sim 7\text{K}$ for a magnetic field higher than 2T. It is associated with **TR** symmetry breaking below 27K, and the appearance

of spontaneous polarization has also been observed because of broken spiral reversal symmetry [43, 44]. It demonstrates the spiral magnetic structure induced the ferroelectricity in the TbMnO_3 . It is commonly acknowledged that ferroelectric polarization is originated by the cycloidal spin ordering [45].

1.10 Exchange bias phenomenology

The Conventional Exchange bias (CEB) is a phenomenon where there is a hysteresis loop shift along the magnetic field axis. It was observed when the materials cool down through its Neel temperature (T_N) in presence of a magnetic field. The exchange interaction takes place at the interface between the hard magnetic material and the soft magnetic material [45, 46]. At first, Meiklejohn and Bean found this exchange anisotropy phenomenon in Co/CoO (10-100Å) nanoparticles. During the last two decades, the EB effect is receiving exceptional attention due to its significant applications in Spintronics, giant magnetoresistance (GMR), high-density data storage memory devices (MRAM) and many more [47].

The spontaneous exchange bias (SEB) on the other hand has gained much more attention because unidirectional anisotropy develops spontaneously in a field, even if the material is not cooling down through T_N . Apart from interacting interfaces between FM and AFM materials, the effect has so far been observed in different types of heterostructures, such as ferromagnetic–antiferromagnetic, ferromagnetic–spin-glass–antiferromagnetic, ferromagnetic–ferrimagnetic, ferromagnetic–dilute antiferromagnetic, etc. in different geometries like bilayers, core-shell nanostructures, granular composites and super lattices [46, 48]. Overall the CEB is found more commonly in the literature, whereas the SEB has been reported for a smaller number of materials

such as $\text{BiFeO}_3\text{-Bi}_2\text{Fe}_4\text{O}_9$ nano-composite, Mn_2PtGa Heusler alloys, and polycrystalline $\text{Co}_{0.75}\text{Cu}_{0.25}\text{Cr}_2\text{O}_4$ samples [46, 49].

1.10.1 Phenomenological model of EB

The Figure below (1.11) shows the magnetic spin arrangement of ferromagnetic-antiferromagnetic heterostructures which leads to the exchange-bias (EB) phenomena. When the heterostructures system is cooled in the presence of a magnetic field above (or through) the Neel temperature (T_N) of antiferromagnetic materials but below the ordering temperature (T_C) of the ferromagnetic materials ($T_N < T < T_C$), the EB originates in the AFM-FM system, and it is because of the interface coupling at the boundary of two system.

An antiferromagnetic layer is in direct contact to a ferromagnetic one. When the sample is cooled under the applied magnetic field in a temperature range $T_N < T < T_C$, AFM spins aligned randomly in a paramagnetic state, whereas the FM spins line up along the axis of field direction. The magnetic hysteresis loop of samples showed typical ferromagnetic behavior centered on zero field axis (shown in Figure (1.11.1)) and found not to be affected by the adjacent AF layer. When the temperature is below the antiferromagnetic critical temperature (T_N), due to the exchange interaction across the interface, AF spins of first monolayer couple with FM spins along the field direction. The next monolayer of the AF layer can still be aligned antiparallel to the previous layer following AF order, and thus the magnetic hysteresis leads to a typical ferromagnetic hysteresis (see Figure (1.11.2)).

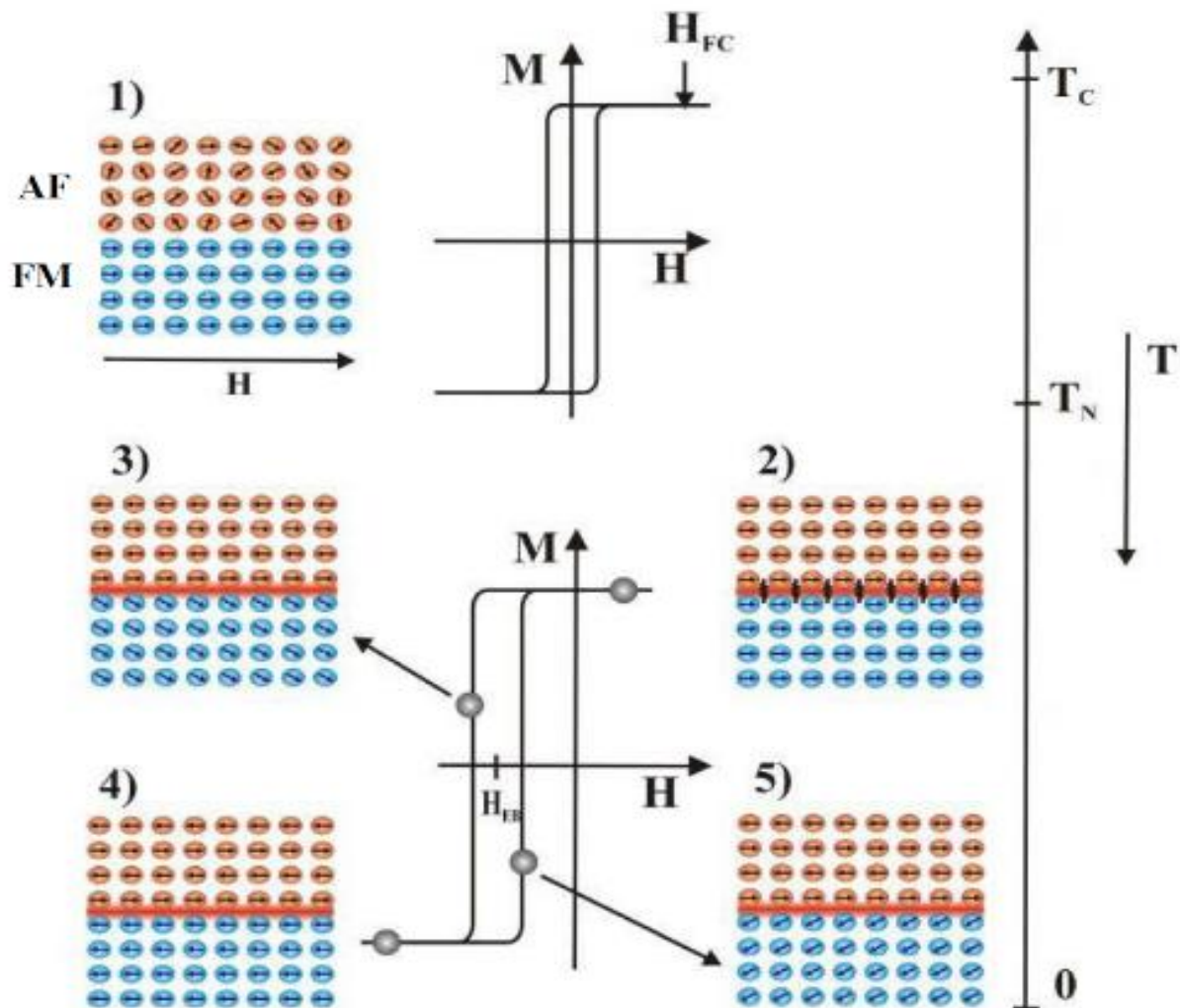


Figure 1.11 Phenomenological picture of exchange bias for an AF-FM bilayer [50].

It is important to note that due to the uncompensated spins at the AFM/FM interface leads to a small finite magnetization at this monolayer. It is accepted that both the antiferromagnetic and the ferromagnet are in a single domain state and both will stay in this state during the magnetization reversal process. When the field is reversed, the FM spin starts to point along the field direction while AFM spins remain untouched due to significant AFM anisotropy at the interface (see Figure (1.11.3)). This proceeds out to reversed field sweeping to the extent where

the FM spins have to point along the field and antiparallel to the antiferromagnetic spin at the boundary between AFM and FM. Therefore, the FM spin has one single configuration, i.e., anisotropy becomes unidirectional as shown in Figure 1.11.4. In transit one more from negative saturation to positive field direction, the FM spins easily begin to switch at smaller external force, due to interaction with the AFM spins. Therefore, the magnetization curve is moved to the negative direction of the field (see Figure 1.11.5). This shifting of the hysteresis loop from the center is known as exchange bias, which is negative here and relates to the orientation of FM spins under an application of an external magnetic field [50].

1.10.2 Training effect

It is the most essential property of the EB system which is explained as a gradual reduction in EB phenomena when continuous hysteresis loop measurement is repeated for several times at a fixed temperature [51, 52]. This effect involves a reduction in the coercive field (H_C) and EB field (H_{EB}) with sequential hysteresis loop measurement at fixed temperature $H_{EB} (1^{st} \text{loop}) > H_{EB} (2^{nd} \text{loop}) > \dots > H_{EB} (n^{th} \text{loop})$. This effect is manifested in antiferromagnetic/ferromagnet heterostructures due to the spin reconfiguration of antiferromagnetic domains at the pinning layer when cycling heterostructures through consecutive hysteresis measurements. It was first experimentally observed in heterostructures of ferromagnetic and antiferromagnetic thin film [1]. We can express the reduction of H_{EB} corresponding to the number of field cycle (n) using the following empirical formula.

$$H_{EB}(n) - H_{EB}^{\infty} \propto \frac{1}{n^{1/2}} \quad (1.1)$$

Where, n is the number of the loops and, H_{EB}^{∞} is the value of H_{EB} at $n=\infty$ [46]. Generally, there are two types of training effects reported in the EB system. First, reduction of H_{EB} in between first and second loop ($n < 2$) [53] and second, the reduction over a higher number of loops $n \geq 2$. Equation (1.1) which is driven from the series expansion approach, is found to follow the second type of training effect i.e., $n \geq 2$ [54]. This breakdown of the empirical equation at $n=1$ is due to spin flop transition of AF spins after which they are trapped in a metastable configuration for subsequent loop after the second hysteresis loop. Recently, Binek et al. modified the interpretation of training effect in FM/AFM heterostructures and proposed a recursive equation that describe the evolution of the H_{EB} vs. n for all n , as given below

$$\mu_0 (H_{EB}(n+1) - H_{EB}(n)) = -\gamma(\mu_0 (H_{EB}(n) - H_{EB}^{\infty}))^3. \quad (1.2)$$

Here, γ is a sample-dependent constant and H_{EB}^{∞} is the EB field in the limit of infinite loops [55, 56].

1.11 Literature review

The current interest in the most popular multiferroic BFO was invigorated by Ramesh and his colleagues (2003). They successfully grew a single phase BFO thin film (50-100nm) onto SrTiO₃ (100) single crystal by a pulsed laser deposition method. The film show unexpectedly large remnant polarization (50 to 60 $\mu\text{C}/\text{cm}^2$) almost 15 times higher than that of the bulk and also display significant ferroelectricity of 1.0 Bohr magneton (μB) per unit cell [4]. Later, there were several research groups in France during 2006-07 also grew single-phase thin film affirmed the higher value of polarization in the first observed in thin films, indicating that it is intrinsic. This report of science paper has demonstrated enormously stimulating and has motivated both new

principal physics, and potential applications, leading to an extremely rapid development of the emergent field of multiferroics.

1.11.1 Chemical substitution in BiFeO₃

In the past few years, research works have been performed to improve the multiferroic properties of BFO by appropriate substitutions of rare-earth (RE) and diamagnetic cations. Generally, A-site is changed in BFO looking for phase stabilization of perovskite by suppressing their impurities phase and improved their multifunctional properties. For example, Lee et al. modified BFO crystal structure from rhombohedral (R3c) to orthorhombic (Pbnm) by doping La and Sm in BFO at morphotropic phase boundary at $x=0.3$ and 0.14 respectively [57]. Zhang et al. and Das et al. observed the improved dielectric and magnetic properties for La substitution for Bi in BFO and decreased in the antiferromagnetic T_N value from 643 to 603 K at 1MHz [58]. Khonekel et al. observed the impact of the diamagnetic ions such as Ca^{+2} , Sr^{+2} , Pb^{+2} , and Ba^{+2} on the crystal structure of the BFO and improved the multiferroic properties of BFO. They also observed structural modification from R3c to Pnma and enhanced ferroelectricity and magnetism in Gd^{+3} , Dy^{+3} , Sm^{+3} , and Nd^{+3} substituted BFO [59]. Zhang et al. observed the effect of diamagnetic ions Pb^{+2} on BFO stabilize the crystal structure and improved the ME coupling of BFO [60].

In the last decade, there are numerous attempts that have been reported by suitable chemical substitution of metal and non-metal dopants at B-site of BFO to enhance the ME properties. Kiselev et al. studied the magnetic behavior of BFO by neutron diffraction and observed spin in neighboring positions are antiparallel with every other (G-type antiferromagnetic magnetic

order), resulting in an exceedingly weak magnetization [60]. Chauhan et al. reported that 15% replacement of Fe ion by Mn ions led to the structural phase transition in BFO sample and also showed the relation of change in magnetic properties with changing Mn concentration [61]. Wei et al. studied crossover from the antiferromagnetic to ferromagnetic ordering in non-magnetic Zr-doped BFO [62].

Moreover, co-doping is an effective way to improve the multiferroic properties of BFO for various applications significantly. For example, Huang et al. have observed 10% co-substitution of Ca and Mn in BFO thin films modified the crystal structure and improved ferroelectricity property [63]. Li et al. enhanced the ferromagnetism of BFO by transition metal (La and Mn) doping ($\text{Bi}_{0.9}\text{La}_{0.1}\text{Fe}_{0.95}\text{Mn}_{0.05}\text{O}_3$) [64]. Chakrabarti et al. reported improved magnetic and ferroelectric properties of Eu-Co co-substituted BFO nanoparticles [65]. Yu et al. prepared La and V co-substituted BFO through the rapid sintering technique and improved electrical properties [66].

Furthermore, in recent years numerous attempts have been reported in order to synthesize a solid solution of BFO with other stable ABO_3 -type perovskite such as BaTiO_3 , PbTiO_3 , and rare earth manganites RMnO_3 ($\text{R} = \text{Gd}, \text{Y}, \text{Dy}$) to improve the multiferroics and ME properties of BFO for desired potential applications in high energy density capacitors, multiple-state memories, data-storage systems, and in the field of Spintronics [67, 68]. Singh et al. reported the existence of the direct magneto-electric coupling in 0.9BiFeO_3 - 0.1BaTiO_3 solid solution utilizing magnetic, dielectric and calorimetric studies [69]. Yan et al. observed the enhanced dielectric and magnetic properties due to the suppression of the cycloid spin structure ($\sim 62\text{nm}$) in polycrystalline BiFeO_3 - $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ thin film [70]. Wu et al. found a morphotropic phase transition in

BiFeO₃-PbTiO₃ thin film exhibiting two different structural transition (i) cubic → tetragonal(T2) + tetragonal(T1) → tetragonal(T1) and (ii) cubic → tetragonal(T2) + tetragonal(T1) + rhombohedral (R3c) tetragonal(T1) + rhombohedral (R3c). Huo et al. reported enhanced multiferroics properties in solid solution of (1-x)BiFeO₃-xNa_{0.5}K_{0.5}NbO₃ (0.06 ≤ x ≤ 0.3) [71]. Recently, S.N. Tripathy et al. studied structural phase transition and improved ME coupling in the solid solution of BFO with different rare-earth manganites, i.e., BiFeO₃-RMnO₃ (R= Gd, Y, Dy) [67, 71].

1.11.2 Magnetolectric (ME) coupling

One of the most challenging problems in the emerging field of multiferroics is to enhance and control ME coupling between electric and magnetic order parameter in BFO at room temperature. Thus, many efforts have been reported in recent years in order to achieve large ME coupling near room temperature by suppressing the cycloid spin structure (~62nm) which is achieved by fabrication of nanoparticles less than 62nm. Suitable chemical substitution of rare-earth elements (La⁺³, Gd⁺³, Nd⁺³, Dy⁺³, Sm⁺³) and non-magnetic ions (Zr⁺⁴, Ti⁺⁴) at A- and B-site of BFO respectively [57, 62, 72] and synthesis of the solid solution of BFO with other stable ABO₃- type perovskite such as BaTiO₃, PbTiO₃, and rare earth manganites RMnO₃ (R= Gd, Y, Dy) observed for enhanced multiferroic and ME coupling of BFO [67, 68, 71, 73]. C. Ederer et al. studied the origin of magnetic properties and the existence of ME coupling in BFO using density functional theory within the local spin density approximation (LSDA) and LSDA+ U. They observed that BFO exhibits weak ferromagnetism of Dzyaloshinskii-Moriya (DM) type and the change in magnetization reversal induced by an electric field. M. Kumar et al. reported the evidence of ME coupling at room temperature, confirmed by an anomaly in dielectric

constant and loss tangent near room temperature in a solid solution of $\text{BiFe}_{0.75}\text{Ti}_{0.25}\text{O}_3$ [74]. M. Lorenz et al. quantitatively analyzed ME coupling for BaTiO_3 - BiFeO_3 composite thin film and obtained maximum magnetoelectric coefficient ($\alpha_{\text{ME}} = 0.075 \text{ V cm}^{-1}\text{Oe}^{-1}$) at a low magnetic field at room temperature using longitudinal AC method [75]. Bhattacharjee et al. observed direct evidence of magnetoelectric coupling in 0.73BiFeO_3 - 0.27PbTiO_3 solid solution. They also reported morphotropic phase boundary (MPB): $x=0.3$ tetragonal phase $P4\text{mm}$ and $x=0.27$ rhombohedral phase $R3\text{c}$ for $(1-x)\text{BiFeO}_3$ - $x\text{PbTiO}_3$ solid solution [24].

1.11.3 Bismuth ferrite (BFO)

In the last decade, BFO is the most promising multiferroic among all observed multiferroic materials, not only for industrial application such as Spintronics, data storage media, etc. but also for its profound Physics. M. S. Benardo et al. and his colleagues studied the reaction mechanism in the synthesis of multiferroic BiFeO_3 by solid state route. They observed the volatile nature of Bi ions leads the formation of secondary phases $\text{Bi}_{25}\text{FeO}_{39}$, $\text{Bi}_2\text{Fe}_4\text{O}_9$ along with BFO phase [76]. M.M. Kumar et al. eliminated the formation of secondary phase formation in the synthesis of single phase BFO by washing diluted nitric acid [77]. Kubel et al. reported a single phase of BFO got a distorted rhombohedral perovskite structure in the $R3\text{c}$ space group at room temperature [78]. Fisher and Tabares-Munoz observed single phase BFO shows ferroelectric Curie temperature ($T_{\text{c}} \sim 1103\text{K}$) and canted antiferromagnetic (G-type) Neel temperature ($T_{\text{N}} \sim 643\text{K}$) simultaneously. J. Peng et al. observed BFO exhibits type-I multiferroic compound, because the source of their ferroelectricity and magnetic order parameters have different sources. The Bi 6S lone pair electrons are responsible for ferroelectricity while magnetism comes from partially filled d-orbitals of Fe in BFO [20]. In 2003, K.Y. Yun et al. reported a giant polarization

of $166\mu\text{C}/\text{cm}^2$ with low leakage current density $\sim 10^{-4} \text{ A}/\text{cm}^2$ in BFO thin films deposited on Pt/TiO₂/SiO₂/Si substrates by using pulsed laser deposition technique [79].

1.11.4 Exchange bias

Conventional Exchange bias (CEB) is a phenomenon which displaces the hysteresis loop along the magnetic field axis. It is usually observed at the interface between hard and soft magnetic materials when cooled through the Neel temperature of hard magnetic materials [46, 79]. At first, Meiklejohn and Bean found this exchange anisotropy phenomenon in FM Co/AFM CoO (10-100Å) nanoparticles in 1956. After the discovery of EB in FM/AFM, it has also been discovered in various combinations between FM-spin glass, FM/FM, FM/Ferrimagnetic (Ferri) and Ferro/Ferri composite materials [80–82]. In recent times, BFO has attracted significant attention due to its interesting EB phenomena. S. Dong et al. studied the dynamic properties of spin cluster glass and a complex non-monotonic EB variation with temperature in single BFO nano crystal synthesized by a hydrothermal process [82]. K. Chakrabarti et al. reported significant EB effect in BFO/NiO nano crystal due to uncompensated surface spins across the interface. H. Bea et al. described the mechanism of exchange bias effect in CoFeB/BFO heterostructures in terms of Malzemoff's model. They found that the amplitude of the EB field inversely proportional to the size of the multiferroic domain [83].

1.12 Motivations

As discussed above, several major inherent issues associated with BFO are the following

- To synthesize pure single phase BFO, this is very difficult.
- To find high exchange bias near room temperature for device applications.

- To minimize the high leakage conductivity and dielectric loss.
- To enhance the weak ME coupling at room temperature.

Many research works have been done far and wide to address the previously mentioned issues. Different research groups have adopted different strategies to resolve these problems, some of which remain unsolved.

1.13 Outline of the thesis

The objective of the present work has been characterized based on the current issues, difficulties and current status in the field of BFO based multiferroics. A short outline is discussed below:

- (i) Chapter -1 gives an account of the basic theories behind the broad area of multiferroic materials and its related materials. We present a brief description of multiferroic phenomena based on a brief overview of the theoretical, conceptual and materials aspects. From the literature review, we have set our objective of the present investigation.
- (ii) In chapter-2, we have explained the different techniques employed in the synthesis of the samples, characterization and measurements.
- (iii) In Chapter-3, we have studied systemically the structural, magnetic and dielectric response of $\text{Bi}_{0.5}\text{La}_{0.5}\text{Fe}_{0.5}\text{Mn}_{0.5-x}\text{Ti}_x\text{O}_3$ (at $x=0$ and 0.05) multiferroics prepared by solid state method.
- (iv) Chapter-4 describes the X-ray diffraction, room temperature Raman analysis and dielectric measurement analysis of the non-magnetic Al substituted (Al on Fe-site) $\text{Bi}_{0.5}\text{La}_{0.5}\text{Mn}_{0.5}\text{Fe}_{0.5}\text{O}_3$ ceramic.