Chapter 1

Introduction

1.1 Historical review

The global population's steady growth has led to a significant surge in global energy consumption. Charge-based to spin-based technologies are the main focus of current research on materials for storing and processing information. In the 21st century, information and communication technology (ICT) pose crucial challenges for everyone globally. Multi-functional materials that respond to various external stimuli, such as magnetic fields, electric fields, pressure, etc., are needed to address the rising demand for the next generation of spintronic devices. Magnetism and ferroelectricity are, in fact, fundamental components of contemporary spintronics technology[2].

Spintronics is an exciting new technology that aims to address key issues with traditional electrical components. The quest for materials with strongly correlated electrical and magnetic properties has received special attention. In reality, this technology has the potential to unify the fundamental features of existing semiconductor microelectronics and magnetic storage devices into a single chip. Traditionally, electronic systems solely harnessed the charge of electrons as their fundamental degree of freedom, processing information through binary bits of 0 and 1. The ongoing advancements in conventional electronics have largely relied on reducing the size of components such as transistors and capacitors in integrated circuits. However, spintronics exploits both the charge and spin of electrons to transport and store information, representing 0 bits as spin up and 1 bit as spin down. This integration of magnetic properties based on spin (storage hard drive) and semiconductor properties based on charge (integrated circuits) is achieved within a single chip, enabling these functionalities within a single device[3].

This revolutionary technology has several benefits over conventional electronics. Traditional electronics have volatile random-access memory (RAM), This implies they lose data when the power (electricity) is switched off. In spintronics, the spin of an electron is not energy-dependent (i.e., permanent magnetism, non-volatile), guaranteeing that information is maintained even when power is switched off. Furthermore, capacitors in traditional electronics must be recharged regularly owing to charge leakage, which consumes additional energy. Spintronics devices, on the other hand, require less power since changing the spin states from 0 to 1 takes less energy. As previously stated, the intriguing idea of changing magnetism via electric rather than magnetic forces provided the original technological drive for multiferroics research. In our daily life, we are surrounded by electronic devices. In ordinary electronic devices, we need an electric component for processing information and calculations, for which silicon is mainly used. We also need a magnetic component for storing data. To control magnetism, we traditionally need a magnetic field, for which we need a circular coil of wire and run an electric current through it, consuming a lot of energy and power, and resulting in bulky and less efficient systems. A paradigm shift is needed to improve existing technology and support proposed new technology. For this, we need a material that possesses both properties in the same material[4,5].

Multiferroic materials have received a lot of focus in recent years, mainly due to their various applications in the technology field, where they can be utilized for data storage, spintronics, and microelectronic devices. Multiferroic materials exhibit multiple fundamental ferroic properties in the same state[5].

1.2 Primary Ferroics

Ferroic is the general name given to the study of ferromagnetic, ferroelectric, and ferroelastic materials individually. Based on their symmetry characteristics for time and space inversion, four families of ferroic materials have been found and characterized[6].

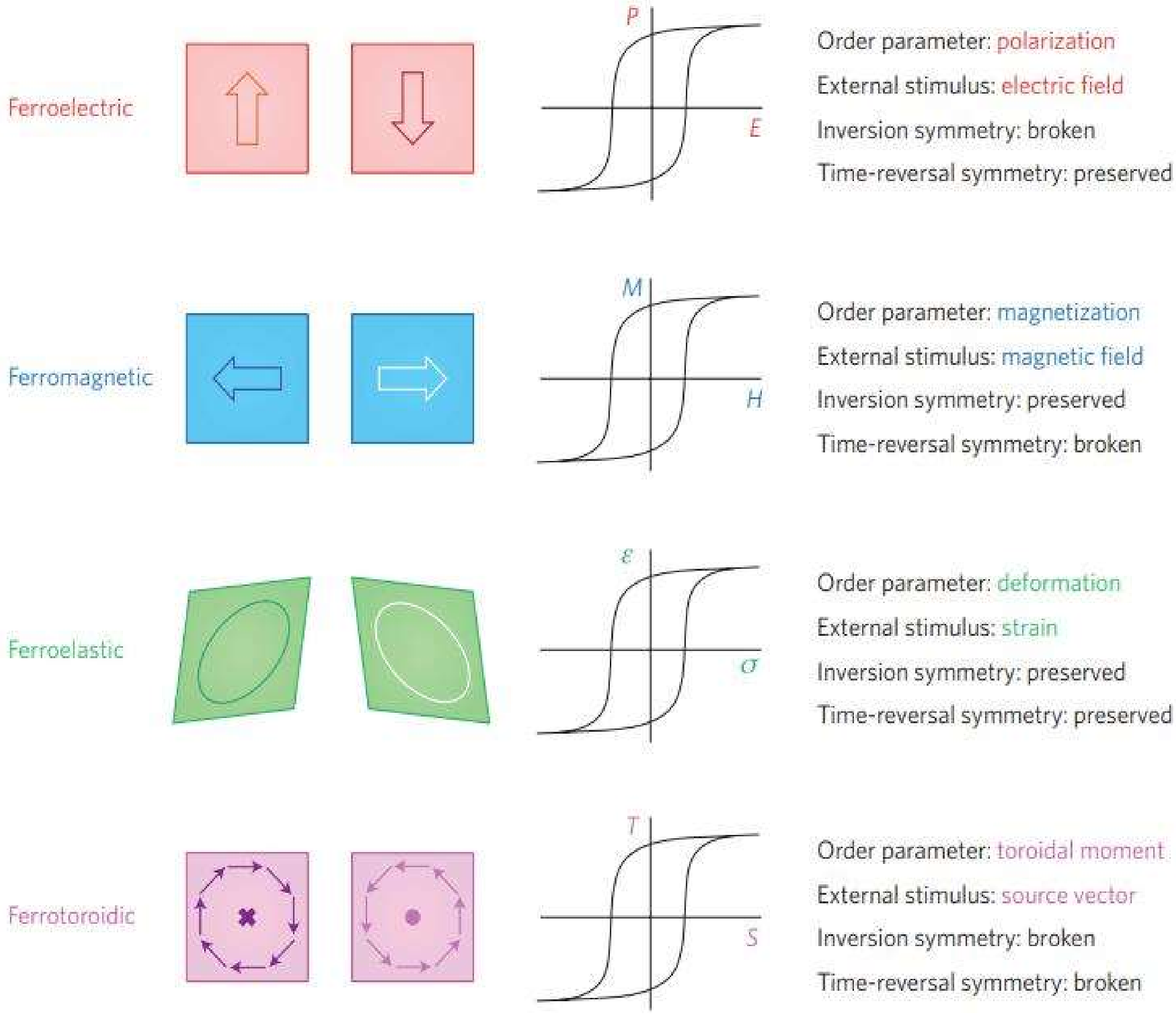


Figure 1.1: *Diagram showing the ferroic orders, conjugated fields, and associated symmetry operations.*

The well-known primary ferroic orders are (1) ferroelectricity (FE), which violates space-inversion symmetry; (2) ferromagnetism (FM), which violates time-reversal symmetry; and (3) ferroelasticity (FA), which violates neither space-inversion symmetry nor time-reversal symmetry, and they can be switched by the conjugate electric (E), magnetic (H), and stress (σ) fields, respectively. Along with these three standard ferroic orders, (4) ferrotoroidicity (FT), which breaks both time-reversal and space-inversion symmetry, needs to be switchable by combined magnetic and electric fields. These spontaneous order features, namely magnetization (M), polarization (P), and strain (ε), below a certain temperature known as the Curie point, are reorientable by an external switching force[7]. A domain is a crystal area that corresponds to the alignment of the order parameter along a single axis[8]. Before applying a switching force (E, H, σ), the domains are randomly oriented, resulting in no net order parameter in the sample. The domains align with the fields when the field is applied and raised, resulting in a net order parameter. At larger fields (Hs, s, Ps), the order parameter saturates, and even when the field is reduced to zero, a finite value of the order parameter which is called the remanent order parameter (Hr, r, Pr) persists. As a result, the M-H/-/P-E response demonstrates hysteresis[7].

1.3 Types of Magnetic Materials

Magnetic materials are divided into five different categories based on their magnetic behavior, which is determined by analyzing their magnetic susceptibility. Magnetic materials are classified into diamagnetic, paramagnetic, ferromagnetic, antiferromagnetic, and ferrimagnetic.

1.3.1 Diamagnetic Materials

Diamagnetic materials have zero magnetic moments in the absence of a magnetic field, these materials possess a small or zero magnetic susceptibility. Diamagnetic susceptibility is a temperature-independent property. When these materials are exposed to the magnetic field, they are opposite the external magnetic field. They generate a magnetic field that opposes the external magnetic field, resulting in a weak repulsion force. All of the electrons in diamagnetic materials are coupled, and there is no net magnetic moment. Gold, copper, silver, and most other non-magnetic materials are examples of diamagnetic materials. Diamagnetic materials are not attracted to a magnet, and they do not retain magnetism once the external magnetic field is removed.

1.3.2 Ferromagnetism Materials

Ferromagnetism arises from the alignment of the spins of electrons in the material. The spins of neighboring electrons are aligned in one direction, resulting in a net magnetic moment. At high temperatures, Thermal energy cause magnetic moments to point in random directions, resulting in zero net magnetization. However, as the temperature decreases below a critical temperature called the Curie temperature (T_C), the magnetic moments become aligned, and the material becomes magnetized[9]. When a magnetic field is applied to the material, the spins align with the field, causing the material to become magnetized. When subjected to a magnetic field, these materials exhibit a high magnetic attraction. They are distinguished by a huge magnetic moment, which leads them to be strongly attracted to magnetic fields. These materials are found in a variety of applications, such as generators, electric engines, magnetic storage devices, transformers, and MRI scanners. Even after the external magnetic field is removed, ferromagnetic materials can maintain magnetization. This characteristic is known as hysteresis, and it is essential for the functioning of magnetic storage devices and other uses that require a permanent magnet. Iron, nickel, cobalt, and some of their alloys are examples of these materials. Diamagnetic materials are weakly repelled, while paramagnetic materials are weakly attracted to applied magnetic fields.

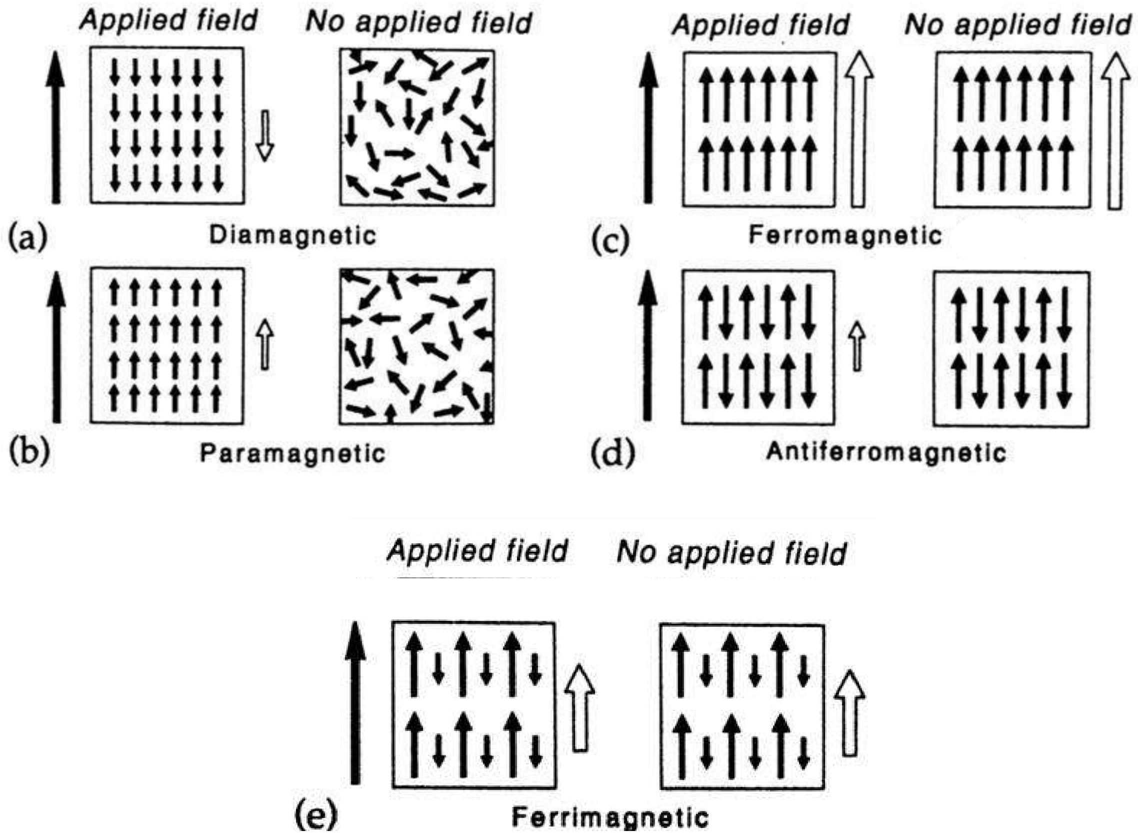


Figure 1.2: *Several types of magnetic order: (a) Diamagnetic, (b) Paramagnetic, (c) Ferromagnetic, (d) Antiferromagnetic, and (e) Ferrimagnetic.*

1.3.3 Paramagnetic Materials

Paramagnetic materials are materials that are weakly attracted to a magnetic field. This attraction occurs because the material contains unpaired electrons that have magnetic moments. When a magnetic field is applied, these magnetic moments align with the external field, causing a net magnetic moment in the material. However, this alignment is weak, and the material's magnetic characteristics are lost when the external field is removed. Platinum, aluminum, titanium, and gadolinium are some examples of paramagnetic materials. These materials have unpaired electrons in their atomic or molecular orbitals, which give them a weak magnetic moment. generally, the magnetic properties of paramagnetic materials are much weaker than those of ferromagnetic or ferrimagnetic materials, which are strongly attracted to magnetic fields and retain their magnetic properties even when the external field is removed.

1.3.4 Antiferromagnetic Materials

Antiferromagnetic materials are a type of magnetic material where the magnetic moments of adjacent atoms or ions in the material are oriented in opposite directions, resulting in a net magnetic moment of zero. This is in contrast to ferromagnetic materials where the magnetic moments are all oriented in the same direction, resulting in a net magnetic moment. Antiferromagnetic materials are often found in materials with a crystal lattice structure, such as iron, manganese, and chromium. The exchange interaction between the magnetic moments of neighboring atoms causes antiferromagnetic ordering, which favors antiparallel alignment. One of the distinguishing features of antiferromagnetic materials is their high magnetic anisotropy, which makes them useful in applications such as magnetic sensors, magnetic memory devices, and spintronics. Antiferromagnetic materials can also exhibit a range of interesting phenomena, such as spin-charge coupling and spin Hall effect, which have potential applications in quantum computing and information processing. Overall, antiferromagnetic materials have significant potential for various technological applications and are an active area of research in the field of condensed matter physics.

1.3.5 Ferroelectric Materials

Valasek observed ferroelectricity in Rochelle salt in 1920. The phrase "Ferro", meaning "iron", was Even though most ferroelectric materials do not contain iron, this term is used to denote this type of feature in the system. Ferroelectric materials have spontaneous electric polarization that can be reversed by applying an external electric field. As they are capable of two or more stable polarization states, Ferroelectric materials have numerous applications, including sensors, capacitors, and memory devices. The spontaneous polarization in ferroelectric substances results from the shifting of both positively and negatively charged ions throughout the crystal structure of the material. The material becomes polarized as a result of the displacements of the net dipole moment. Ferroelectric materials maintain their polarization even after the applied electric field stops, in contrast to regular dielectric materials which lose it. Lead zirconate titanate (PZT), barium titanate ($BaTiO_3$), lithium tantalate ($LiTaO_3$), and potassium niobate ($KNbO_3$) are a few examples of ferroelectric materials. Due to their special qualities, these materials can be used for a variety of purposes, including piezoelectric sensors and non-volatile memory.

Proper ferroelectric materials are those where the breaking of crystal symmetry, i.e., the primary order parameter, occurs at the transition temperature in the region of polarization.

Improper ferroelectric materials are those where polarization is not due to the breaking of crystal symmetry, but instead due to secondary order parameters, such as magnetic ordering (e.g., $TbMnO_3$). Improper ferroelectrics exhibit more complex domain structures, which frequently display a richer diversity of behavior.

Pyroelectrics are materials that display spontaneous polarization due to changes in temperature, specifically below an ordering temperature. Pyroelectric ferroelectrics are a subclass of pyroelectric materials. Any material that falls under the category of polar crystal symmetry displays piezoelectricity. However, it is important to note that while all pyroelectric crystals are piezoelectric, not all piezoelectric crystals are pyroelectric.

1.4 Coupling of Order Parameters

1.4.1 Magnetoelectric Coupling defines the effect of an electric (magnetic) field on a material's magnetization (polarization), less power is needed to change a magnetic state via voltage (i.e., an electric field) than to change it directly through applying current (magnetic field). Importantly, multiferroic materials exhibit the magnetoelectric effect caused by the interaction of the ferroelectric and magnetic order parameters, which is still under investigation.

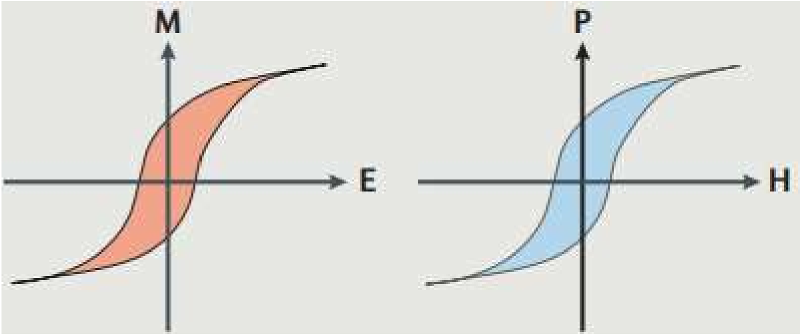
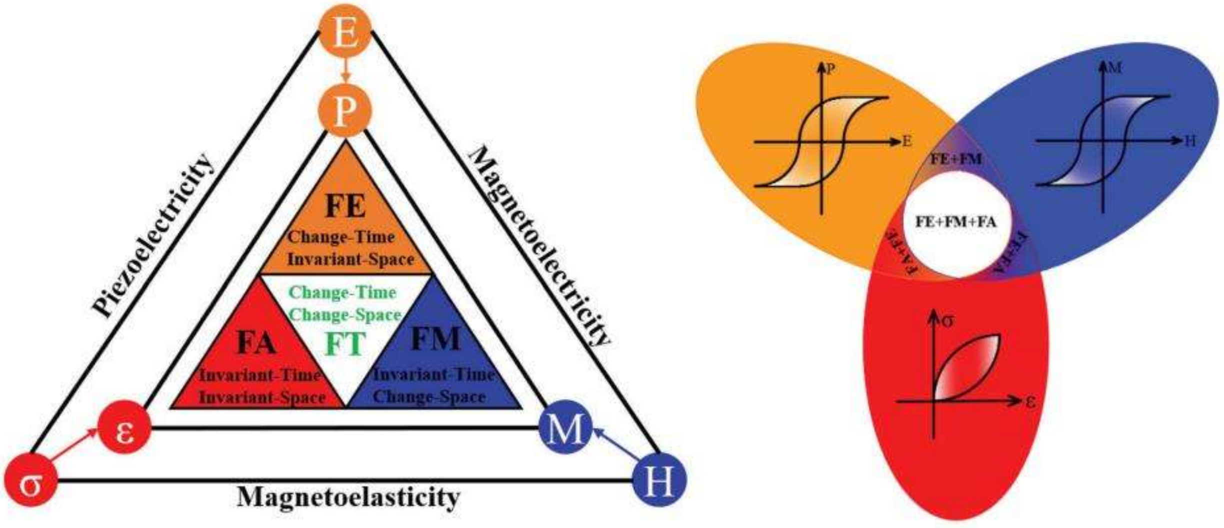


Figure 1.3: The best multiferroic magnetoelectric material depicts.

The combination of both magnetic and ferroelectric ordering in a single crystal symmetry is an uncommon occurrence, as magnetic ordering requires the presence of a localized unpaired electron "d^n" orbital, whereas ferroelectric ordering requires a local off-centered distortion and an empty "d^0" orbital. There are only a few naturally occurring multiferroic materials, and the majority of them exhibit magnetic ordering considerably below ambient temperature and/or are antiferromagnetic[10].

1.4.2 Piezoelectricity is defined as a change in the strain as a function of applied electric field or polarization as a function of applied stress. This phenomenon mainly occurs in all non-centrosymmetric materials.



(a) **(b)**

Figure 1.4: *Different ferroic orders (a) FE breaking the symmetry of space-inversion; FM breaking the symmetry of time-reversal; FA breaking neither the symmetry of space-inversion nor the symmetry of time-reversal; and FT breaking both the symmetry of space-inversion and the symmetry of time-reversal. (b) Shown ferroic orders cross-coupling with each other.*

1.4.3 Piezo-magnetism defined a change in magnetization as a function of applied stress or a change in the strain as a linear function of the applied magnetic field.

1.4.4 Electrostriction is defined as the change in the strain as a quadratic function of an applied electric field.

1.4.5 Magnetoelasticity has defined a change in the strain as a quadratic function of an applied magnetic field.

1.5 Multiferroics Materials

Multiferroicity refers to the presence of more than one ferroic order, namely ferro/antiferroelectric, ferro/antiferromagnetic, and ferroelastic, in the same material[10]. Current research focuses mostly on multiferroic materials that exhibit both magnetism and ferroelectricity. Magnetoelectric material is another name for this sort of multiferroic material. These materials have piqued the interest of physicists and materials scientists because they are predicted to be utilized in the development of multistate memory systems due to the magnetoelectric coupling effect.

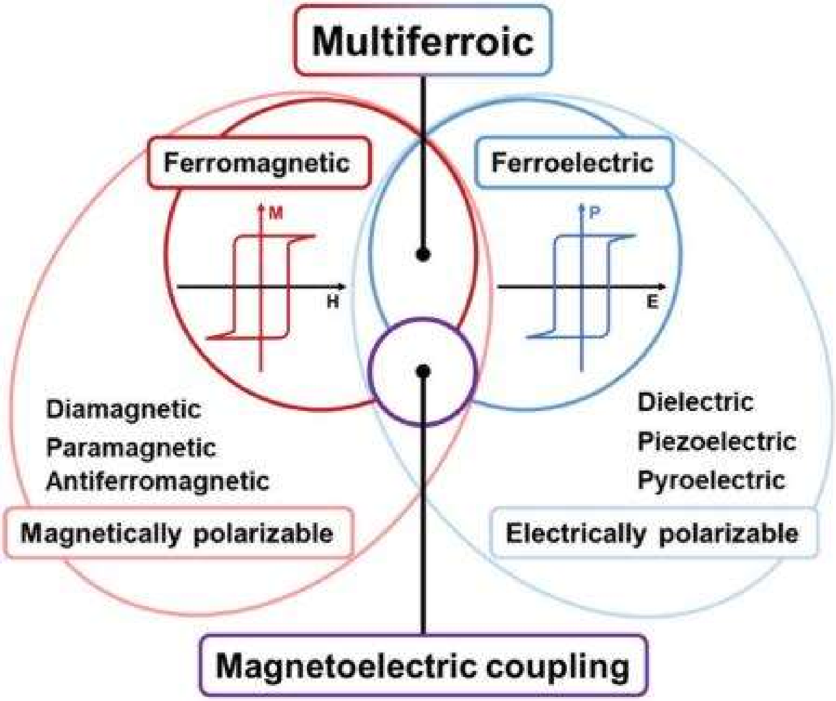


Figure 1.5: *Demonstration of magnetoelectric multiferroics using a Venn diagram.*

In recent years, researchers have focused on multiferroics to better understand the fundamental process of magnetoelectric coupling in single-phase and composite materials. Single-phase compounds (such as $BiFeO_3$, $BiMnO_3$, $YMnO_3$, etc.) are rare due to the contradiction between the conventional mechanisms of ferroelectricity (cation-off centering – requires empty d orbitals of transition element) and ferromagnetism (requires partially filled d-orbitals of transition element). When two distinct atoms are present in the system, ferroelectricity and magnetism coexist in single-phase compounds, with one atom responsible for creating electrical dipole moments and the other carrying the magnetic moment. Bismuth ferrite ($BiFeO_3$) is a well-known single-phase compound in which Bi^{3+} ions produce ferroelectric ordering and Fe^{3+} ions induce magnetic ordering. Figure 1.5 depicts the possible linkage of several order parameters[11].

1.6 Classification of Multiferroics Materials

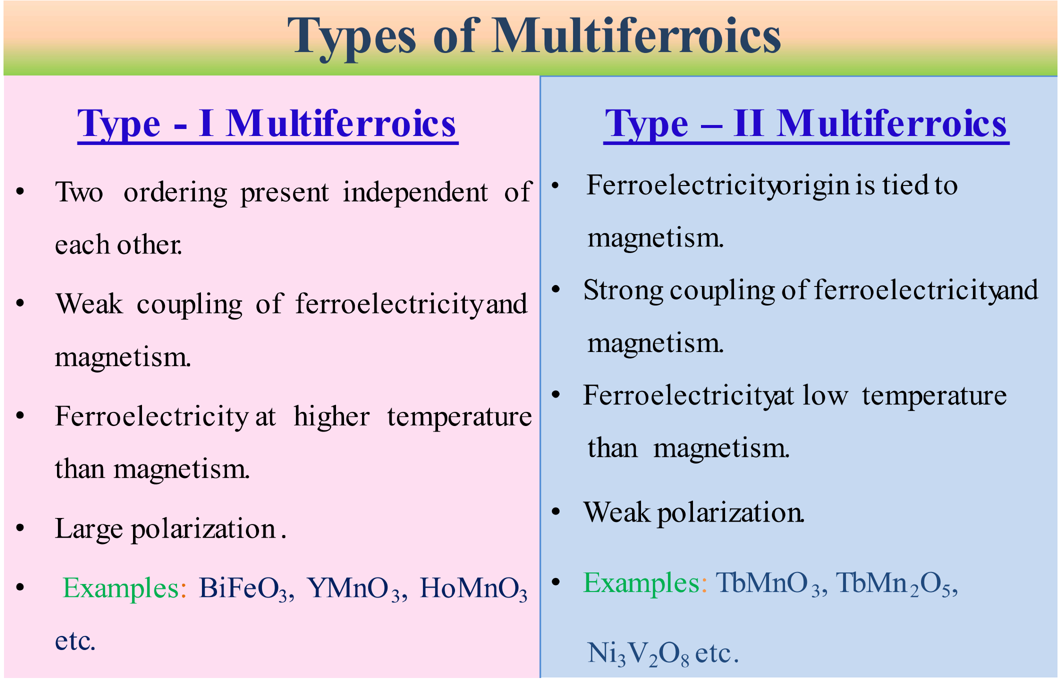
Khomskii (2009) divided multiferroic materials into two categories, namely type-I, and type-II. In a type-I multiferroic, the sources of the two order parameters, i.e., Ferroelectricity (FE) and magnetism are not the same thing, and the coupling between the two is often weak. The ferroelectric order parameter breaks spatial inversion symmetry, while the magnetic order parameter breaks time-reversal symmetry, coexisting within these type-I multiferroics at different temperatures with weak coupling. The ferroelectric transition temperature (T_{FE}) is significantly higher than the magnetic ordering transition temperature (T_C) in these materials. The presence of large polarization (usually resulting from the distorted structure) and high T_{FE} make type-I multiferroics more popular. Examples of type-I multiferroic materials are $BiFeO_3$ (T_{FE} ~1100K, T_C=643K, P~90μC/cm2) and $YMnO_3$ (T_{FE} ~914K, T_C=76K, P~6μC/cm2). On the other hand, in type-II multiferroic materials, magnetism is initiated by ferroelectricity[12,13].

1.6.1 Type-I Multiferroics

Type-I multiferroic the microscopic origin of ferroelectricity further classified as:

1.6.1.1 Ferroelectricity Due to Lone Pair of Electrons

Popular multiferroic materials, such as $BiFeO_3$, $BiMnO_3$, and $PbVO_3$, fall under the lone-pair class, where cations with highly polarizable $6s^2$ lone-pair (also called dangling bonds) electrons (Bi^{3+} and Pb^{2+}) play an important role in the formation of ferroelectricity (FE). The arrangement of lone pairs enhances both ferroelectric and magnetic characteristics. In these materials, the outermost $6s^2$ lone pair of electrons hybridizes with a vacant p orbital instead of forming a chemical bond, resulting in structural distortion and the region of ferroelectricity. The presence of transition metal ions (i.e., Fe^{3+} and $Mn^{3+)}$ is the source of magnetism, which contributes to the multiferroic behavior[14].



Types of Multiferroics

Type - I Multiferroics	Type – II Multiferroics
Two ordering present independent of each other.	Ferroelectricity origin is tied to magnetism.
Weak coupling of ferroelectricity and magnetism.	Strong coupling of ferroelectricity and magnetism.
Ferroelectricity at higher temperature than magnetism.	Ferroelectricity at low temperature than magnetism.
Large polarization.	Weak polarization.
Examples: $BiFeO_3$, $YMnO_3$, $HoMnO_3$ etc.	Examples: $TbMnO_3$, $TbMn_2O_5$, $Ni_3V_2O_8$ etc.

1.6.1.2 Ferroelectricity Due to Charge Ordering

Ferroelectricity due to charge ordering is a special group of multiferroic materials that are often found in transition metals with mixed valency. There are two common forms of charge order: site-centered charge order and bond-centered charge order, The centers of ions or bonds can be utilized to designate the charge order structure's mirror planes. To create ferroelectricity in charge-ordered multiferroics, these two forms of charge orders must be combined, i.e., the presence of inequivalent sites and bonds in the system at the same time. Examples of such systems include the frustrated charge-ordered systems $LuFe_2O_4$, manganite, and magnetite.

1.6.1.3 Multiferroic Perovskites

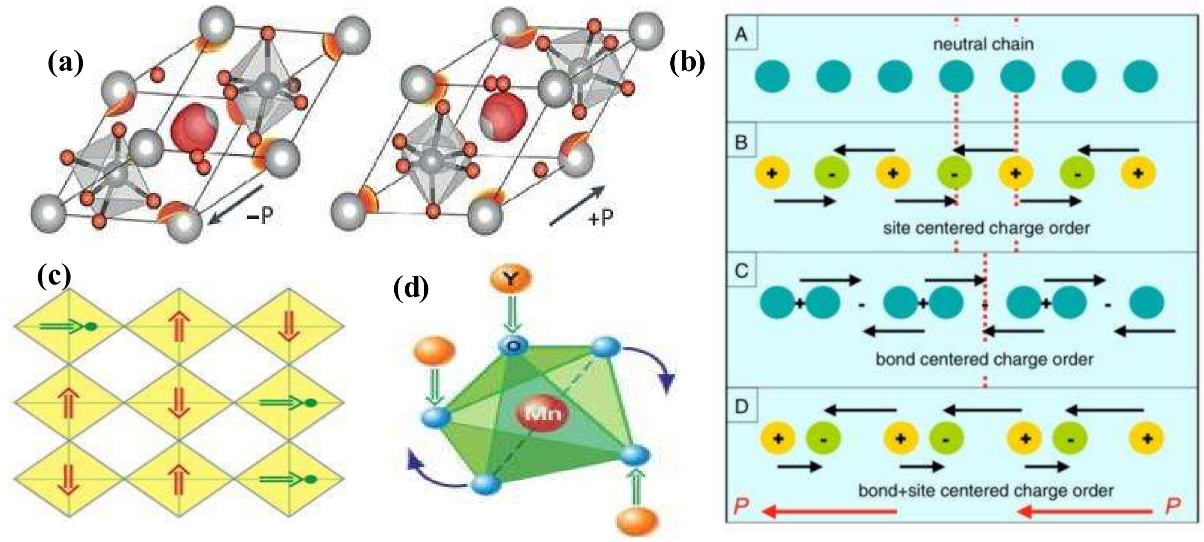


Figure 1.6: *Ferroelectric behavior-promoting processes are shown schematically.*

Perovskites like $BaTiO_3$ and $Pb(ZrTi)O_3$ (PZT) are perhaps the most well-known ferroelectrics[15]. In these materials, the origin of ferroelectricity is linked to transition metal ion off-center movements. which, using their empty d (d^0) states, create strong covalent connections with one (or three) oxygens, whereas magnetism is due to the presence of dn states. As shown in mixed perovskite, actual d^n ions (represented by red circles) are responsible for the magnetism, but ferroelectricity is created by the off-center movement of d^0 ions (represented by green circles) from the center of O_6 octahedra (represented by yellow plaquettes), resulting in polarization and magnetic moments (indicated by red arrows)[14].

1.6.1.4 Geometrically Driven Ferroelectricity

In multiferroics, frustrated geometry in type-I multiferroicity can produce permanent dipoles and ferroelectricity as a geometric byproduct of increased packing density. Inversion symmetry is broken by long-range dipole-dipole interactions and oxygen rotations in this type of system. This class includes non-magnetic K_2SeO_4 and hexagonal $YMnO_3$ (h-YMO). For instance, in YMnO3, the primary contributor to ferroelectricity is the tilting of the rigid MnO_5 block rather than the magnetic Mn^{3+} ion. This tilting occurs to provide closer packing, and as a result, the oxygen ions move closer to the relatively small Y ions. Because of the tilting, the Y-O bonds form dipoles (indicated by green arrows), and there are two "up" dipoles for everyone "down" dipole, resulting in the system becoming ferroelectric (and multiferroic when Mn spins order at low temperature)[16].

1.6.2 Type-II Multiferroics

In type-II multiferroics, a strong connection between the magnetic and electric properties occurs due to their magnetically induced ferroelectricity, resulting in enhanced magnetoelectric coupling in these materials. The achievement of ferroelectricity is theoretically dependent on crystal structural phase transitions, but it is not an essential requirement for magnetic order. The majority of manganites from rare earth fall into this category, for example, $TbMnO_3$ (T_{FE}~28 K, T_C=41K, P~0.1 μC/cm2), $TbMn_2O_5$ (T_{FE}~38 K, T_C=43K, P~0.06 μC/cm2), etc[17,18]. Additionally, they exhibit weak polarization due to their centrosymmetric structure, which is greatly impacted by an external magnetic field. They are divided into two categories based on their multiferroic mechanism:

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

1.6.2.1 Spiral Type-II

By breaking the inversion symmetry in these systems, ferroelectricity is induced in magnetic phases with spiral magnetic structures. The orthorhombic multiferroics exhibit a range of magnetic ordering, and $TbMnO_3$, $Ni_3V_2O_6$, and $MnWO_4$ all possess this characteristic. In $TbMnO_3$, all of the spins below T_{C1} = 41 K point in the same direction, and the magnetic structure is a sinusoidal spin-density wave, while the local moment size changes periodically in space. The Mn spins arrange themselves below T_{C2} = 28 K in such a way that the spins' tips sweep out cycloid particles. Based on the understanding of a phenomenological technique developed by Mostovoy, and a microscopic technique developed by Katsura, Nagaosa, and Balatsky, it was demonstrated that in a cycloidal spiral, a polarization (P) develops, which is given by:

$$P \sim rij \times [Si \times Sj] \sim [Q \times e]$$

where Q is the wave vector representing the spiral, e~ [Si × Sj] is the spin rotation axis, and rij is the vector connecting adjacent spins Si and Sj.

The spin-orbit interaction contributes to the microscopic mechanism causing this polarization. Spiral magnetic ordering in an insulator can be triggered by magnetic frustration. The microscopic process leading to magnetically induced ferroelectricity that has received attention is the inverse Dzyaloshinskii-Moriya interaction, but it is certainly not the only reason. As a result, these type-II multiferroics are typically discovered in frustrated systems. This is a nice illustration of how research on magnetic frustration, an exciting subject in and of itself, has produced new results with potentially very significant implications.

1.6.2.2 Collinear Spin Ordering

The existence of spin-orbit coupling is not necessary for this mechanism; it is based on magnetostriction and can also take place in collinear magnetic structures. Magnetostriction in $HoMnO_3$ leads to multiferroic behavior resulting from the existence of a periodic collinear spin pattern of the up-up-down-down type, which can produce electric polarization via an exchange-striction process. Considering there is frustration in the magnetic ion's spin when the spins are parallel, the bond length and bond angle are shorter, which is advantageous for energy reduction, and the converse is true when the spins are antiparallel.

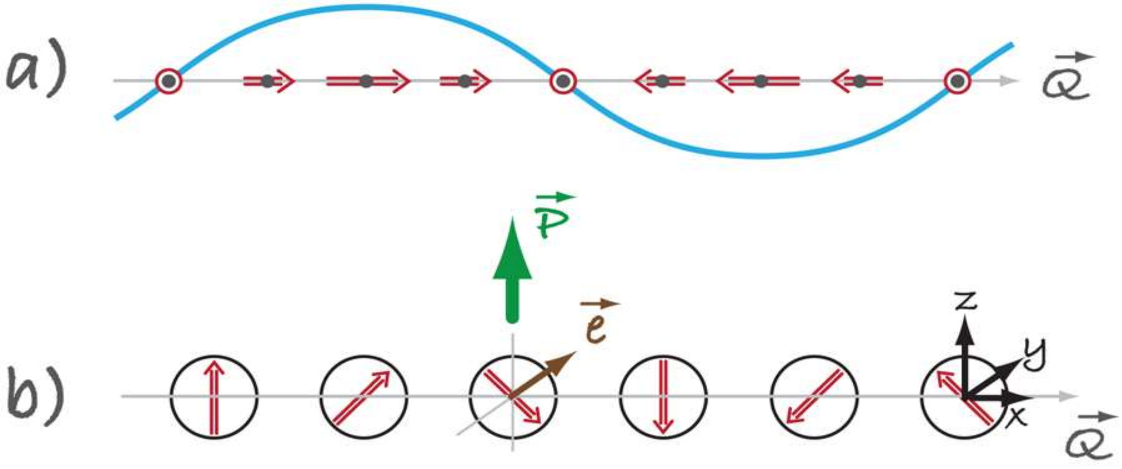


Figure 1.7: *Different types of spin structures relevant for type-II multiferroics. (a) Sinusoidal spin wave, in which spins have to point along one direction but vary in magnitude. This structure is centrosymmetric, and consequently, the value of ferroelectricity is zero. (b) The cycloidal spiral with the wave vector $Q = Q_x$ and spins rotating in the (x,z)-plane. It is in this case where one finds non-zero polarization, $P_Z \neq 0$.*

1.7 Perovskite Structure

A vast family of crystals with structures resembling those of the material Calcium titanium oxides ($CaTiO_3$) is referred to as "perovskite". The name "Perovskite" was given after the Russian mineralogist Count Lev Aleksevich von Perovski. It was discovered and named by Gustav Rose in 1839 from samples found in the Ural Mountains. The “A” cation in the original Perovskite mineral ($CaTiO_3$) is divalent, while the “B” cation is tetravalent. As demonstrated in the Figure, the perovskite structure is represented by ABX_3, in which “X” anions form corner-linked octahedra with "B" cations at their centers and "A" cations in the interstices formed by the anion octahedra. In general, the "A" cation has 12-fold cuboctahedral coordination, whereas the "B" cation has X-cation-octahedral coordination[6,19]. The A cation has a valence of +1 to +3, whereas the B cation has a valence of +3 to +6. The "A" atoms have higher ionic radii than the "B" atoms, and X is commonly an oxygen or fluorine ion. Cubic symmetry (space group Pm¯m) with a lattice constant of ~ 4 Å is the ideal perovskite structure. The cations may occupy 1a or 1b positions, and the oxygens occupy 3c or 3d Wyckoff positions. As shown in Figure 1.8, by shifting the origin (0, 0, 0) to (½, ½, ½), there are two different views of the unit cell offered by the two possibilities of occupation. For all perovskites, the cubic prototype structure is always expected at high pressure and high temperatures. Due to the coupling of spin, charge, and orbital ordering which offers a wide range of magnetic, electric, transport, and multiferroic properties, perovskites have attracted much attention.

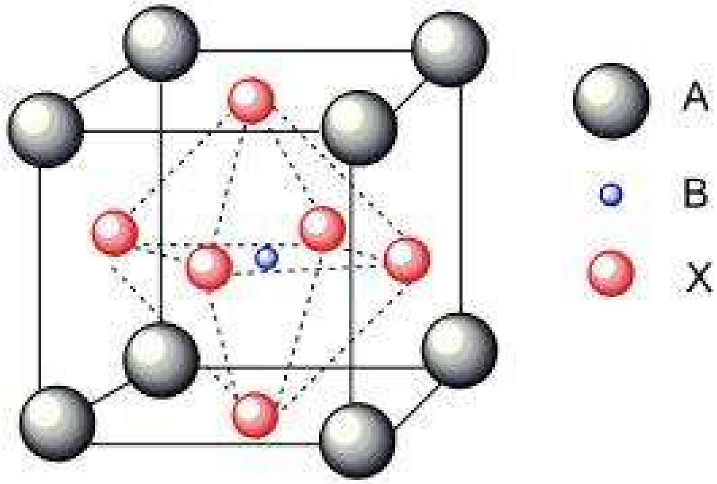


Figure 1.8: *ABX$_3$ perovskite structure.*

According to the literature, a majority of the materials have the orthorhombic Pnma (or Pbnm) distorted structure at ambient temperature. It is also feasible for further distortion to occur, producing a rhombohedral structure with the space group R3c. The appearance of the hexagonal P63cm structure signifies further deformation. After the hexagonal structure, further distortion will emerge in a cubic bixbyite (space group Ia3) structure.

The ideal perovskite structure is constructed from hard spheres, and each cation is of a suitable size to be in touch with an oxygen anion[20]. The ions' radii can then be connected as given:

$$R_A + R_O = \sqrt{2}(R_B + R_O)$$

On the other hand, as the A cation size decreases (due to distortion), the cations become too small to remain in contact with the anions in the cubic structure. The aforementioned equation has been modified by adding a constant, t, that allows for this distortion:

$$R_A + R_O = t * \sqrt{2}(R_B + R_O)$$

Where t is the tolerance factor, and its ideal value is one for the cubic structure.

Perovskite materials have a wide range of exciting features, both theoretically and practically. Magnetic and transport properties, charge ordering, superconductivity, spin-dependent transport, colossal magneto-resistance, optoelectronic properties, high thermopower, and the interplay of structural features are typically observed in this family. These substances are suitable for memory devices and spintronics applications

1.8 Bismuth Ferrite ($BiFeO_3$)

Bismuth ferrite (BiFeO3) is a multiferroic material that exhibits both ferroelectricity and ferromagnetism at room temperature. It is a multifunctional material with remarkable physical and chemical properties, making it a promising candidate for a wide range of applications in electronics, data storage, and sensors. $BiFeO_3$ (BFO) is a perovskite-type oxide with a distorted crystal structure that gives rise to its multiferroic properties. At room temperature, it has a rhombohedral crystal structure with spontaneous polarization arising from the displacement of Bi and Fe ions from their ideal positions in the crystal lattice, resulting in its ferroelectric properties. BFO also exhibits antiferromagnetic, where the magnetic moments of the iron ions in the crystal align in an antiparallel manner. However, at low temperatures, it can exhibit ferromagnetism, thought to arise from defects in the crystal structure. As a ferroelectric and antiferromagnetic material, BFO exhibits a range of useful properties, including piezoelectricity, multiferroicity, and magnetoelectric coupling.

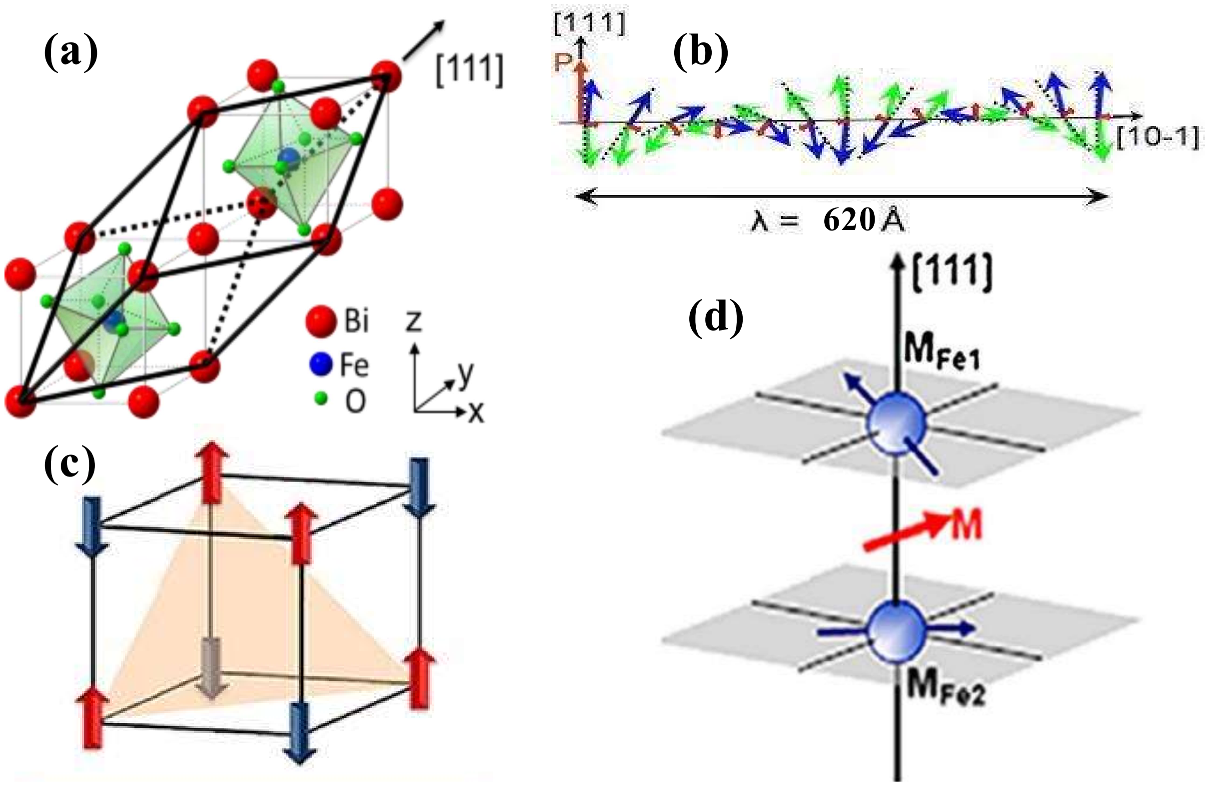


Figure 1.9: *BFO structures and the elements which influence it. (a) Diagram illustrating the BFO crystal structure (unit cells). (b) Schematic diagram of the spin cycloid. A net magnetic moment (purple arrows) is produced by the canted antiferromagnetic spins (blue and green arrows), and it is caused by cycloid rotation, which averages down to zero. (c) An illustration of a G-type antiferromagnet is shown. In the (111) plane, spins are ferromagnetically aligned. (d) Using a schematic to show how the canting spin cycloid structure results in weak magnetism.*

In addition, BFO has a high Curie temperature, low toxicity, and good chemical stability making it attractive for use in various technological applications such as energy storage, sensors, memory devices, and spintronics[2,21]. The crystal structure of BFO results in many interesting physical phenomena, such as polarization switching under an electric field, spin-canting under a magnetic field, and the exchange bias effect. Understanding these phenomena is crucial for the design and optimization of BFO-based devices. Despite significant progress in the study of BFO, several fundamental issues remain unresolved, such as the origin of the large polarization in BFO, which is still a subject of debate, and the relationship between the structural distortions and the magnetic properties, which is not well understood. Moreover, the synthesis of high-quality BFO films with controlled crystal orientation and defect density remains a challenge.

Due to its potential applications, BFO has been extensively studied in magnetic data storage, spintronics, and sensors. It also has potential applications in energy harvesting and as a photocatalyst for water splitting. However, further research is needed to optimize its properties and develop practical applications.

1.9 $GaFeO_3$

The element gallium iron oxide (GaFeO3) has currently received extensive research for its possible use as a magnetoelectric ferrimagnet due to its magnetic and piezoelectric characteristics[22,23]. $GaFeO_3$ (GFO) possesses an orthorhombic symmetry and corresponds to the Pc21n space group. At 300 K, the standard lattice parameters are a = 8.7193(2), b = 9.3683(8), and c = 5.0672(3). Because of the coexistence of ferroelectric polarization and spontaneous magnetization characteristics at room temperature, $GaFeO_3$-type oxides are potential multiferroic materials. The four distinct cation positions in the crystallographic unit cell are identified as Ga1, Ga2 (mostly occupied by gallium), and Fe1, Fe2 (primarily inhabited by iron)[24,25]. The physical properties, particularly magnetism in GFO, are greatly influenced by the technique of synthesis and are highly associated with the cation distribution among the four crystallographic sites[26–28].

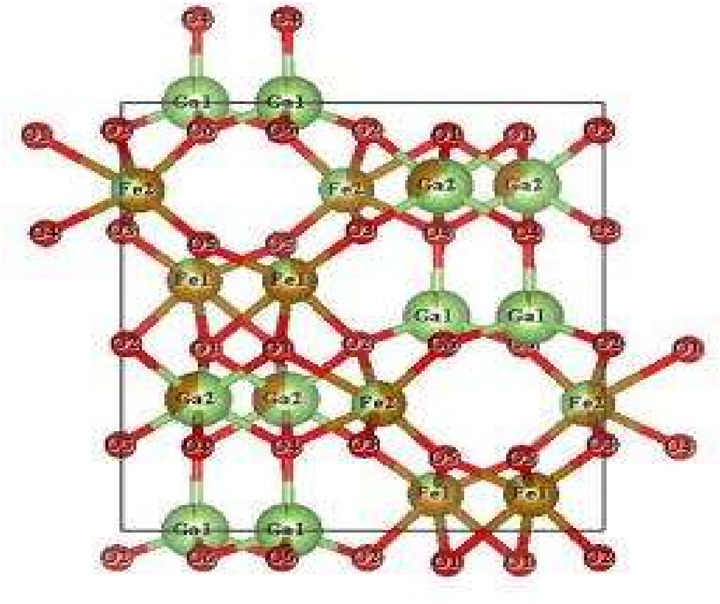


Figure 1.10: *Crystal structure of GaFeO3 at room temperature.*

1.10 Literature Review

H. Schmid introduced the word "multiferroic" in 1994. According to his explanation, multiferroics are single-phase materials that concurrently exhibit two or more basic ferroic characteristics. The term "multiferroic" is presently employed for a wide range of materials that include spontaneous electric polarization, long-range magnetic ordering, and/or Ferro-elasticity. The recent reemergence of interest in multiferroics was sparked by the identification of substantial magnetic and electric coupling in orthorhombic TMO and $TbMn_2O_5$. Multiferroics, which include rare-earth manganites and ferrites such as TMO, $LuFe_2O_3$, and $HoMn_2O_5$, often fall under the category of perovskite transition metal oxides. There are other non-oxides as well, such as $BaNiF_4$, spinel chalcogenides, $ZnCr_2Se_4$, as well as the bismuth complex and $BiMnO_3$. These alloys show rich phase diagrams combining different heterostructures exhibiting more than one ferroic order parameter, which has been extensively studied. Multiferroics have the potential to be used as new kinds of electronic memory devices, actuators, switches, magnetic field sensors, or actuators.

The recent desire to study bismuth ferrite was primarily prompted by a 2003 paper from Ramesh's group, which demonstrated that it had an unforeseen large remnant polarization, Pr, 15 times higher than previously reported in bulk BFO, along with significant ferromagnetism of approximately 1.0 Bohr magneton (mB) per unit cell (Catalan & Scott, 2009)[28]. They used pulsed laser deposition (PLD) to grow phase-pure BFO thin films with thicknesses ranging from 50 to 500 nm onto single crystal SrTiO3(100) (STO) substrates (Wang et al., 2003)[29]. Among many options, BFO with a distorted rhombohedral perovskite structure belongs to the space group R3c, due to its high ferroelectric transition temperature (T_{FE}~1100K) and antiferromagnetic Néel temperature (T_C=643K). BFO possesses a G-type antiferromagnetic magnetic structure with a modified spiral spin structure and a long periodicity of 62 nm. Due to its multiferroic characteristics and absence of lead, BFO is perhaps the most researched Bi-based multiferroic perovskite, which makes it more appropriate for potential innovative multifunctional applications. The coexistence of electric and magnetic orderings in multiferroic materials offers the possibility of applications in data storage systems, multiple-state memory, high energy density capacitors, and spintronics.

People all across the world are working on improving the magnetic, ferroelectric, and magnetoelectric properties of BFO systems. Based on investigations on BFO thin films as discussed by the Ramesh group, defects contribute to the leakage current in bulk samples. It was later confirmed that the leakage current is caused by the creation of Fe^{2+} and an oxygen deficiency. Its presence may be eliminated using a short sintering period and an exceptionally fast heating rate.

Four key problems must be solved when developing a BFO-based system for application purposes:

(1) Synthesis of BFO is very difficult due to the volatile nature of Bismuth. (2) Leakage current problem and low dielectric constant and high loss. (3) BFO is type-I multiferroic, so weak magnetoelectric coupling at room temperature. (4) The large difference between ferroelectric (T_{FE}=1100 K) and magnetic (T_C=643K) transition temperature.

Recent theoretical and experimental research reveals that destroying/suppressing the spin cycloid can result in the development and improvement of magnetoelectric characteristics of BFO at room temperature.

1.10.1 Chemical Substitution in $BiFeO_3$

1.10.1.1 A-Site substitution

People have been trying to improve the practical application of BFO-based systems for the past two decades. Multiple approaches have been tried out, such as at the A site and B site, and co-doping at both BFO sites. The multiferroic behavior of the system was found to be enhanced by the substitution of some rare-earth (RE) ions at the Bi^{3+} site in BFO. G. L. Yuan et al. in $Bi_{1-x}La_xFeO_3$ (x = 0 - 0.25) multiferroic ceramics addressed the compositional-driven structural modifications that develop weak ferromagnetism and also ferroelectric to piezoelectric phase transition (Yuan et al., 2007)[30]. Zhang et al found that in the $Bi_{1-x}La_xFeO_3$ (x = 0 - 0.40) system, for x = 0.30 doping, a phase transition occurs from rhombohedral to orthorhombic, resulting in enhanced ferroelectric and magnetic characteristics. The increment in ME interaction is attributed to the release of locked magnetization and destruction of the spin cycloid structure (Zhang et al., 2006)[31]. Cheng et al in $Bi_{1-x}La_xFeO_3$ ceramics observed a structural transition from rhombohedral to orthorhombic for x = 0.20 and tetragonal for x = 0.30, along with a reduction in electric leakage current and enhancement in ferromagnetic moment value (Cheng et al., 2008)[32]. V. A. Khomchenko and V. Koval et al. in $Bi_{1-x}Gd_xFeO_3$ and $Bi_{1-x}Tb_xFeO_3$ (x = 0.1 - 0.3) systems, respectively, explained that there is a phase transition from rhombohedral (R3c) to orthorhombic (x = 0.20 Pn21a → x = 0.30 Pnma) and the emergence of spontaneous magnetism, suggesting a potential approach for enhancing the multiferroic property of antiferromagnetic BFO (Khomchenko, Kiselev, et al., 2008; [33,34] et al., 2017). In another report, V.A. Khomchenko et al. explained in Bi1−xAxFeO3 (A = Ca, Sr, Pb, Ba) systems that A-site replacement with ions of the greatest ionic radius efficiently reduces the spiral spin structure of antiferromagnetic BFO, hence enhancing the multiferroic properties (Khomchenko, Kopcewicz, et al., 2008)[35]. S.G. et al. found in the $Bi_{1-x}Ho_xFeO_3$ (x = 0.2, 0.4, 0.6, and 0.8) system that doping improves ferroelectricity by reducing leakage current and also increases the dielectric constant value (Nair et al., 2022)[36]. Catalan et al. explored the $Bi_{1-x}Ca_xFeO_3$ system and noted an increment in Neel temperature. The ionic radius of Ca^{2+} is smaller than Bi^{3+}, so the chemical pressure effect reduces the gap between the magnetic and electric transition temperatures, enhancing the magnetoelectric coupling (Catalan et al., 2009)[28]. P.C. Sati et al. studied the Bi1-xEuxFeO3 (x= 0-0.15) system and found that for x > 0.10, Eu substitution causes a structural transition between two polar phases R3c→Pn21a, and also an enhancement in the dielectric constant value with a decrement in the optical band gap (Sati et al., 2015)[37]. In another study on Dy-doped BFO ceramics, fascinating optical characteristics in the visible light range, as well as enhanced magnetic properties, have been discovered (Chandra Sati et al., 2014)[38]. T. Durga Rao et al. found mixed phases (rhombohedral and orthorhombic) in the $Bi_{0.9}R_{0.1}FeO_3$ (R = Y, Ho, and Er) system, and also observed an enhancement in the coercive field and remnant magnetization, making this system suitable for magnetoelectric devices (Rao et al., 2013)[39].

1.10.1.2 B-Site Substitution

Several attempts have been made in the recent decade to improve the magnetoelectric (ME) characteristics by adequate chemical replacement of metal and non-metal dopants at the B-site of BFO. P. Mandal et al. synthesized $BiFe_{0.5}Mn_{0.5}O_3$ at high temperature and high pressure and observed magnetization reversal when temperature and magnetic field were varied, along with a structural transition to the orthorhombic phase (Mandal et al., 2010)[40]. S.E. Musavi Ghahfarokhi et al. synthesized $BiFe_{1-x}Mn_xO_3$ (x = 0.0 - 0.30) and found a phase transition from rhombohedral to orthorhombic (R3c→Pnma), as well as a gradual change in the magnetism of the samples from antiferromagnetic to ferromagnetic states as doping increases (Musavi Ghahfarokhi et al., 2020)[41]. E. L. Fertman studied the $BiFe_{0.5}Sc_{0.5}O_3$ system and discovered antiferromagnetic ordering accompanied by a modest ferromagnetic component, and found exchange bias behavior TN (Fertman et al., 2020)[42]. Sosnowska et al. prepared a $BiMn_{0.2}Fe_{0.8}O_3$ composite and studied its crystal structure and magnetic properties, discovering an improvement in magnetic characteristics[43].

1.10.1.3 Co-Substitution at Both Sites

However, partial doping at either the A- or B-site of BFO is effective in enhancing the multiferroic characteristics, stabilizing the perovskite structure, and reducing the leakage current. Several studies have also utilized the concept of co-substitution to further increase the magnetoelectric (ME) coupling. A.K. Ghosh et al. synthesized the $Bi_{0.8-x}Sr_xLa_{0.2}Fe_{0.9}Mn_{0.1}O_3$ (x = 0, 0.1) system with Sr doping, which resulted in enhanced ferroelectric and induced ferromagnetic behavior, and reduced T_C and T_{FE} towards lower temperatures (Ghosh et al., 2012)[44]. M. Gowrishankar et al. synthesized the $Bi_{1-x}Gd_xFe_{1-x}Ti_xO_3$ (x = 0.0 - 0.20) system, which showed structural transitions from orthorhombic rhombohedral (R3c) to orthorhombic

(Pbnm), and then to cubic (P-m3m), along with improvements in multiferroic properties (Gowrishankar et al., 2016)[45]. B. Ishaq et al. prepared the $Bi_{0.75}Cd_{0.25}Fe_{1-x}Mn_xO_3$ (x = 0.0, 0.5, 0.10, and 0.15) system, and observed decreases in coercivity and increases in magnetization, making this material suitable for memory devices and high-density recording media (Ishaq et al., 2016)[46]. Chakrabarti et al. prepared the $Bi_{1-x}Eu_xFe_{1-y}Co_yO_3$ (x = 0, 0.01; y = 0, 0.01) system, and found enhancements in dielectric and magnetic properties, making this system a potential candidate for various applications (Chakrabarti et al., 2012)[47].

1.11 Different Physical Phenomena Related to Our Research

1.11.1 Magnetic Interactions

1.11.1.1 Dzyaloshinsky-Moriya (D-M) Interaction

In a solid, the interaction between spins is quite significant and often responsible for many interesting phenomena. The neighboring spins interact via an exchange interaction, which is purely quantum mechanical and arises due to the electrostatic Coulomb interaction between the electrons and the Pauli exclusion principle. The exchange interaction leads to some kind of long-range magnetic ordering and the possibility of electron transfer from site to site. There are different types of exchange interactions active in materials, such as direct exchange, indirect exchange, double exchange, and superexchange interaction. These interactions are purely spin-spin interactions and hence Heisenberg-like and isotropic in nature.

The Dzyaloshinskii-Moriya (DM) interaction, on the other hand, is anisotropic exchange interaction. Dzyaloshinskii developed a model to explain weak ferromagnetism in solids in 1960, and later Moriya found that the mechanism behind this interaction is partially based on spin-orbit coupling. Thus, the interaction has been named after both these scientists as the DM interaction. It is induced by a lack of inversion symmetry in the crystal and strong spin-orbit coupling. The interaction between the DM vector D, which is proportional to the strength of spin-orbit interaction, and two spins on a lattice bond with no inversion center makes the spins canted by a small angle. The DM interaction for two spins has the Hamiltonian of the form:

$$H_{DM} = D_{ij} \cdot (S_i \times S_j)$$

The vector D_{ij} defines the DM anisotropy, S_i and S_j are spins on the i-th and j-th sites, respectively. Magnetically ordered systems induce a spin canting of otherwise (anti)parallel aligned magnetic moments. Usually, D-M interactions take place in antiferromagnetic systems, and they increase the effective ferromagnetic moment because of spin canting along the antiferromagnetic spin axis' perpendicular direction. It is typically found in orthoferrite systems.

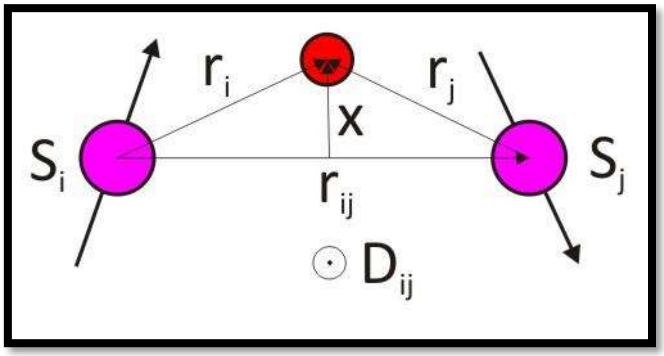


Figure 1.11: *Shows the DM interaction between two neighboring spins.*

1.11.1.2 Exchange Bias Effect

From both a theoretical and technological perspective, the occurrence of exchange bias (EB) has received a lot of attention. In 1956, Meiklejohn and Bean were the first to observe the exchange bias effect in Co/CoO particles and establish a quantitative explanation of exchange coupling. Anisotropy is one of the most crucial elements in exchange bias systems. Conventional exchange bias (CEB) is found when a system with an FM/AFM interface is cooled through the Neel temperature (TN) of the AFM phase in the presence of a magnetic field. The EB effect refers to a shift in the hysteresis loop along the magnetic field axis, and it is a fascinating magnetic phenomenon with a wide range of applications in giant magnetoresistance, electrically controllable spin-polarized currents, ultrahigh density magnetic recording, magnetic sensors, and spin-valve devices.

Explanation of Exchange-Bias Effect

Figure 1.12 depicts the ferromagnetic and antiferromagnetic spin arrangements before and during distinct exchange bias (EB) steps. It should be noted that there is always proximity between atomic magnetic moments at the FM and antiferromagnet AFM interfaces, but thermodynamics determines whether or not this interaction results in unidirectional anisotropy. At a temperature of TN > T > TC, a ferromagnet will become saturated if a sufficiently strong magnetic field is applied, causing all of the ferromagnet's spins to align parallel to the applied magnetic field (H), whereas AFM spins are arbitrarily oriented in a paramagnetic state when a magnetic field is applied. Afterward, when the temperature is reduced below the Neel temperature while applying a constant magnetic field, the monolayer of AFM spins starts to couple at the interface with FM spins due to exchange interaction[48–50]. To complete the AFM order, the subsequent monolayer of the antiferromagnet would naturally align antiparallel to the preceding layer. As a result, the antiferromagnet has zero net magnetization. Due to the uncompensated spins at the FM/AFM interface, a modest finite magnetization occurs at the monolayer. The FM spins attempt to move in the direction of the applied magnetic field when the magnetic field is reversed. Being connected to the stiff antiferromagnet requires a larger force and hence a stronger external field to surpass this coupling and rotate the FM spins.

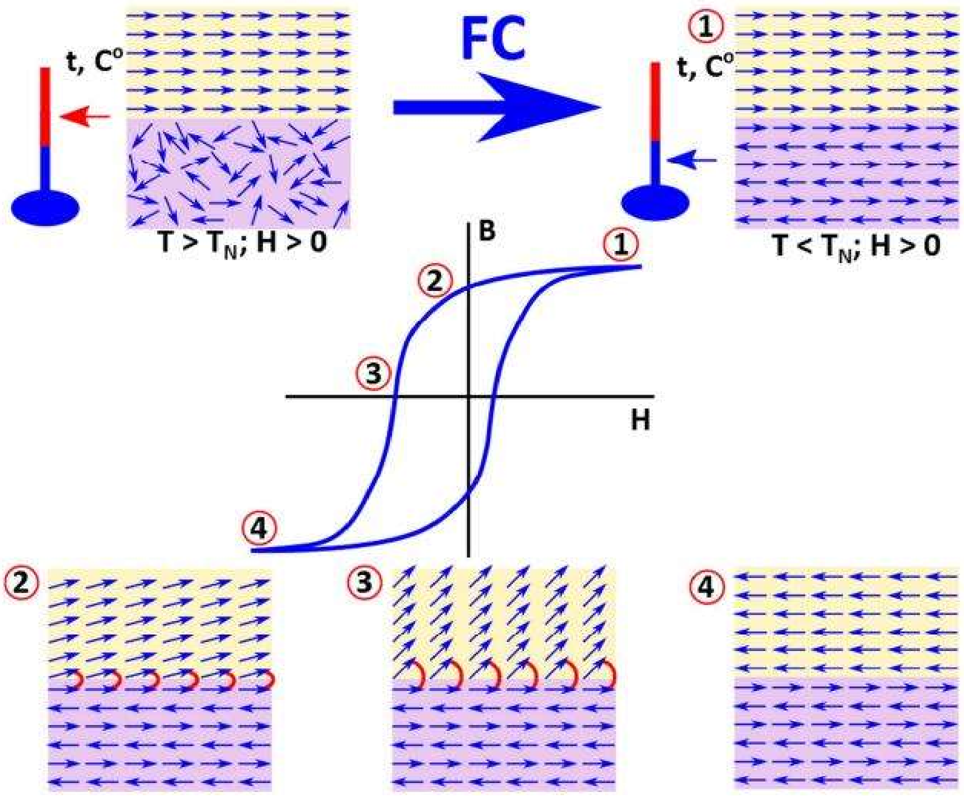


Figure 1.12: *Schematic diagram of the F and AF moments during field cooling and then at different steps of the hysteresis loop.*

As a result, in contrast to the situation where T > TN, a stronger magnetic field is needed to reverse the magnetization in the ferromagnet. Additionally, at the FM/AFM boundary, FM spins turn back antiparallel to the AFM spins. As a result, the FM spins become unidirectional. When a positive field is applied, the FM spins switch quickly, even at low magnetic fields, since they are connected with AFM spins. As a result, the magnetic hysteresis curve moves away from its center and in the direction of the magnetic field that is opposite to that of the applied magnetic field, and this deflection is known as exchange bias[51–54]. The term "conventional exchange bias" (CEB) refers to the type of EB that may be created in the presence of an external magnetic field. Surprisingly, EB has been observed in the absence of any external magnetic fields, meaning that the system exhibits exchange bias spontaneously, and this particular form of EB is referred to as spontaneous exchange bias (SEB)[55,56].

1.11.1.3 Spin-Glass/ Cluster Glass Phenomenology

A magnetic state in which the spins are not organized and are frozen randomly at lower temperatures is commonly known as the spin-glass state of a system. The word "glass" refers to the analogy of regular glasses, in which the atoms are randomly positioned and no periodicity is preserved, as compared to ordered crystals. The spins in spin glass are frozen in a non-collinear random pattern, as opposed to ferromagnetic or antiferromagnetic materials, where they are oriented in a certain way. This is because of the conflict between ferromagnetic and antiferromagnetic interactions. In reality, the degenerate multivalley ground states, also known as the spin glass, are produced as a result of the increasing magnetic frustration caused by the conflicting magnetic interactions[57–59].

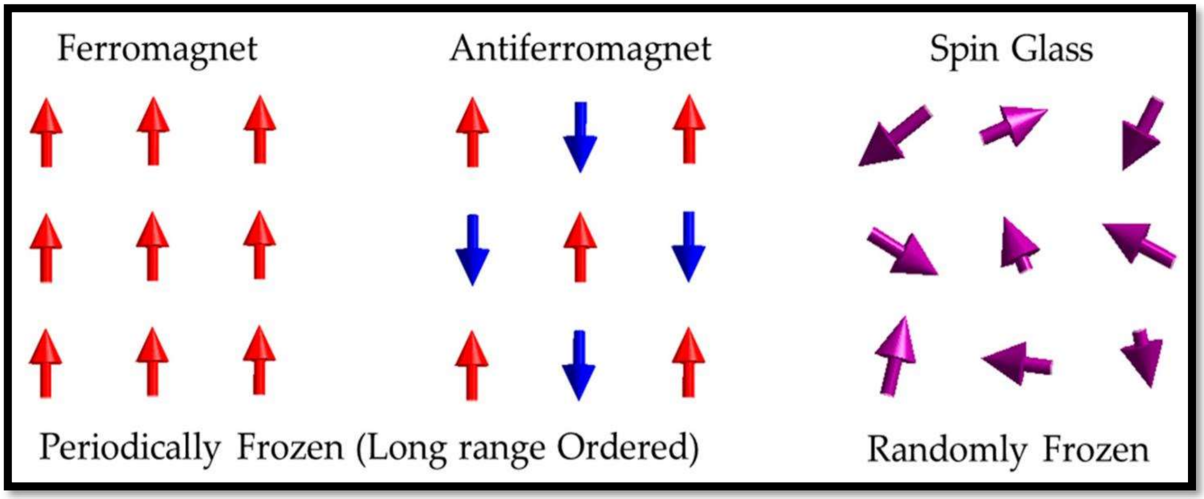


Figure 1.13: *Depicts the spin arrangement in ferromagnetic, antiferromagnetic, and spin glass states.*

Additionally, such states in systems result from geometrical frustration and structural disorder. In the spin glass (SG) condition, the domain barriers of ferromagnet/antiferromagnet (FM/AFM) are pinned by system disorder. Therefore, domain walls in meta-stable states can hop between states using thermal excitation. As a result, the system is unable to reach an equilibrium condition within the time frame of the experiment[60–63]. Due to the delayed spin relaxation, the system enters a magnetic glassy phase. Conversely, the scenario for the cluster glass state (CG) is different. In the CG state, chaos or spin frustration is observed in tiny areas of clusters. The system transitions to the CG state when one component's (FM/AFM) contribution is comparatively greater than that of another component's (AFM/FM).

1.12 Motivations of the Thesis

The latest advancements in materials for many technologies are attracting people to a new class of multifunctional materials. Because of their extraordinary room temperature magnetic ordering, multiferroicity, various types of coupling (such as spin-phonon, magnetoresistance, magnetodielectric, etc.), and many other extraordinary magnetic and electrical properties displayed by these materials, perovskite oxides (described earlier) are very interesting in this regard. This inspired us to further elaborate perovskites. As discussed so far, BFO is type-I multiferroic. It has large electric polarization, order temperatures above room temperature, and indirect coupling between order parameters. The following are a few of the major inherent problems with BFO that have been mentioned previously.

- Synthesize phase pure phase BFO is difficult because of the volatile nature of Bi_2O_3.
- The temperature range for the growth of material is small.
- The high leakage current and dielectric loss.
- For device applications, strong exchange bias must be found close to ambient temperature.
- Weak magnetoelectric (ME) coupling at room temperature.

To address the aforementioned problems, several research studies have been conducted worldwide. Some of these issues still need to be solved despite the fact that many research groups have pursued various approaches. The goals of the current study have been established in regard to the issues, difficulties, and circumstances that are now facing the BFO-based multiferroics. In literature, it has been observed that the $TbMnO_3$ (TMO) is type-II multiferroic with a strong direct coupling between order parameters. The weak indirect coupling is a drawback in BFO and strong direct coupling in TMO is an advantage. So, co-doping of Tb and Mn at A and B sites in BFO may enhance the magnetoelectric coupling (direct coupling).

Moreover, $GaFeO_3$ (GFO) is another well-studied multiferroic material that has a transition temperature near room temperature (i.e., 200-250 K). To enhance the multiferroic property of GFO at ambient conditions many efforts have been attempted by different research groups by the doping, and co-doping methods. If the transition temperature is shifted close to room temperature by the doping method, then GFO can be used at room temperature for different application purposes. In this regard, GFO can be explored via different doping and co-doping.