1 Chapter 1

1.1 Motivation

Increasing digitalization of day-to-day routines is leading to ever increasing demand of fast, robust and low power consumption higher data storages memory devices [1 - 5]. The ferroelectric (FE) or ferromagnetic (FM) materials based memory devices has been demonstrated owing to their switchable polarization (magnetization states) [1-5]. In commercially available magnetic memory device (MRAM), data is stored (or write operation) by switching the magnetic states (+ M) by applying a magnetic field and the data is read through variation of magneto resistance in the magnetic states [1-3, 5]. For the memory devices a fabricated using ferromagnetic material which has high coercivity, switching the magnetic states is difficult and results in consume a large amount of energy [1-3, 5]. On the other hand, ferroelectric random access memories (FeRAMs) exhibits faster writing speed due to polarization switching and consume a small amount of energy in the switching process [1-3, 5]. But, these devices show some limitation such as slow read out because of their destructive read operation and later reset operations [1-3, 5].

It is very important to note that the mutual control of electric and magnetization polarization in Multiferroic has many technological prospects because of their application in magneto electric (ME) multiferroic devices. Wood and Austin suggested several types of applications of ME materials [6] such as (1) modulation of amplitudes, polarization and phase of optical waves, (ii) ME data storage and switching, (iii) optical diodes, (iv) spin-wave generation, (v) amplification and (vi) frequency conversation etc. [6-11].
Therefore, the faster writing speed and smaller energy consumption in switching of magnetic states are utmost necessary. In general, memory device comprises of ferroelectric materials for data write operation and ferromagnetic materials for read operation [1-3, 5]. Also, many multifunctional devices like multiple state memory elements, spintronic and transducers can be fabricated using multiferroics material.

1.2 Material selection criterion for multiferroic materials

The quest for suitable Multiferroic material in which more than one ferroic order coexist in single phase has brought attention of researcher worldwide so that the ultimate memory devices can be realized. Interestingly, in the recent years, multiferroic materials has brought a lot of attention because of their unique properties like coexistence of more than one ferroic order (ferroelectric, ferro-elastic and ferromagnetic/antiferromagnetic) in single phase as depicted in figure 1.1.

![Schematic diagram showing the relationship between magneto electric and Multiferroic materials (a) and different types of coupling (b), respectively[12, 13].](image)

Moreover, device miniaturization is expected to enhance the data operation (write and read) speed and reduction of the energy consumption. Probably, the fabrication of these devices with optimal performance has brought attention of researcher across the world to realise the
multiferroic and magnetoelectric memory devices which is expected to open a new avenue (or possibilities) towards the many folds increment in data densities. The multiferroic systems are often superior as compared to conventional materials because they give freedom to mutually control the coupling between ferroic order parameters due to the interaction between spin and charge. Moreover, multiferroic is materials show very interesting phenomenon called as magnetoelectric (ME) coupling effect where ferroelectric polarization can be controlled by a magnetic field and contrary the magnetization via an electric field[14, 15].

Note that due to the chemical incompatibility and mutual exclusiveness of electric and magnetic ordering the multi ferroics materials are rare in nature. To realize the coupling between the magnetic and electric order in the same phase is one of the biggest challenge since its inception. There are few materials, such as YMnO₃[16], TbMnO₃[17], BiMnO₃[2, 18], BaTiO₃[19], Pb(ZrTi)O₃[20], BiFeO₃[21-24] etc., are known to exhibit Multiferroic properties. To the best of our knowledge BiFeO₃ (BFO) is only material that shows multiferroic properties with very high Curie temperature [(Tₐ)~ 1103K] and G-type antiferromagnetism up to 640 K (Tₐ), Neel temperatures [(Tₐ)~ 640 K][21, 25, 26]. BFO has distorted rhombohedral crystal structure with R₃c space group symmetry which permits anti-phase octahedral orientated and ionic displacement from the centro-symmetric position [21, 25, 27]. In BFO, the neighbouring magnetic spins are oriented antiparallel to each other. In addition, it makes a spiral spin structure with a large period of ~ 620 Å precise throughout the crystal [28].

1.3 Dielectric material and their properties

Dielectric materials are essentially an electrical insulator which exhibits polarization effect when subjected to an electric field. In externally applied field the centre of the negative charge in a material is displaced relative to the centre of the positive charge and dipole moment is induced in the material. In some cases, due to crystallographic non-centro
symmetry such polarization may arises which is termed as spontaneous polarization. Such phenomenon is observed in perovskite structure where the position of anion and cation are in non-Centro symmetric position.

1.3.1 Dielectric polarization

One of the important electrical properties of dielectric material is permittivity. If we consider the parallel plate geometry of the capacitor which is filled with the dielectric medium, the permittivity (\( \varepsilon \)) of medium can be determined purely on the basis of electrostatics and Gauss law as given below[29]

\[
\varepsilon = \frac{\sigma_s}{E}
\]

(1)

where \( \sigma_s \) is the surface charge density on the capacitor plate and \( E \) is the electric field.

The dielectric constant depends strongly on frequency of alternating electric field (or the rate of change of varying field), crystallographic structure and defects of the materials. The dielectric material shows the polarization effect under the applied electric field. Mathematically, the dielectric polarization of a material can be written as[29]:

\[
P = N\alpha E,
\]

(2)

where \( \alpha \) is the polarizability and \( N \) is concentration of atoms(molecules) per unit volume of the material. Relative permittivity (\( \varepsilon_r \)) can also be written in terms of electrical susceptibility as[29]

\[
\varepsilon_r = \frac{\varepsilon}{\varepsilon_0} = 1 + \chi
\]

(3)
where \( \chi = \frac{N\alpha}{\varepsilon_0} \) is the electrical susceptibility and \( \varepsilon_0 \) is the permittivity of free space.

There are four primary mechanisms for polarization of a dielectric medium and interestingly each one of them involves a short range motion of carriers. These four dielectric polarization mechanism are given below [29]

1. **Electronic polarization**: The electronic polarization arises when an external electric field applied to the dielectric. Due to the applied external electric field, the electron cloud displaced from their position relative to the position of positive charge (i.e. nuclei) and results in the formation of electric dipole in material[29].

2. **Atomic or ionic polarization**: The ionic polarization occurs in solids where the ionic bonding voluntarily having dipoles (i.e. displacement of positive and negative ions in ionic molecule) [30].

3. **Dipolar polarization**: This dipolar polarization occurs only in polar molecules which possess permanent dipole moment. When electric field applied on polar molecules, the randomly oriented dipoles align (or orient) themselves along the direction of applied field [30]. The dipolar polarization is a slow process as compared to ionic polarization and it depends on the temperature and frequency [30].

4. **Space charge/interfacial polarization**: The space charge or interfacial polarization arises due to accumulation of the charge carrier at the interface. The ions get diffuse over appreciable distance and redistribution of charge carries take place when external electric field is applied. There can be two possible ways for space charge 1) hopping polarization, and 2) interfacial polarization. In dielectric material, localized charge (ions and vacancies, holes and electrons) may accumulate from one site to neighbouring site which is called as hopping polarization [31, 32]. Whereas, the interfacial polarization occurred due to the separation of moving positively and negatively charged particle in applied field. These charge particle form positive and
negative space charge in the bulk of the material or at the interface between different materials [31, 32].

1.3.2 Ferro-electricity

The Ferro-electricity was discovered by J. Valasek in 1921 [33]. The material which shows ferro-electricity is termed as ferroelectric materials. These materials possess spontaneous electric polarization which can be switched hysterically by applying electric field [34, 35]. These materials exhibits a para electric phase at high temperature ($T>T_c$) while at low temperature ($T<T_c$) the ferroelectric phase at low temperature [36, 37]. Interestingly, these materials possess a switchable spontaneous polarization ($P_s$) [38, 39]. These materials possess permanent dipole moments and show a hysteresis loop of polarization as well electric displacement with the application of externally applied electric field as shown in figure 1.2 [40, 41].

![Diagram](image)

Figure 1-2: Systematic representation of ferroelectric (P-E) hysteresis loop[36].
The formation of ferroelectric (P-E) hysteresis loop can be explained as follow: As the applied electric field increases the dipoles in the materials start switching the direction and at sufficiently high electric field the most of the dipole moments align themselves along the field direction. When the polarization value stops increasing with increasing field the polarization state is called as saturation state and it is denoted by $P_s$. On the other hand, if we reduce the electric field (from maximum electric field to zero fields) value the material may still show non vanishing polarization and it is called as remnant polarization ($P_r$) which is generally smaller than the spontaneous polarization ($P_s$). In order to remove this remnant polarization we have to reverse the field in opposite direction (from zero to some negative value of field). The value of electric field at which the remnant polarization reduces to zero is called as coercive field ($E_c$) [42-44]. There are large number (more than 700) of ferroelectric materials such as BaTiO$_3$, Pb(Zr,Ti)O$_3$, BiFeO$_3$, RMnO$_3$ (R=Ho, Yb, In, Tb and Y) and, TbMn$_2$O$_5$, and Ni$_3$V$_2$O$_8$, etc., are reported in literatures [45-54]

1.4 Magnetic materials and their classification

Material consists of atoms and atom contains electron and nucleus. Therefore, properties of both electron and nucleus influence the materials behaviour. In general, the magnetism takes place in a material where material properties are governed by the magnetic moment of electrons, atoms and ions[55, 56]. In general, there are two types of motion of electron namely orbital motion and spin motion. In materials, the orbital and spin motion leads to formation of orbital magnetic moment and spin magnetic moment. When materials consist of more than one valence electron then the net magnetic moment of a material is quite large. Whenever a finite magnetic moment material is placed in an external magnetic field then it behaves in a special manner. The materials are magnetized ($M$) in presence of magnetic field. Mathematically the response of materials to the applied magnetic field ($H$) can be written[55, 56] as
\[ B = \mu_0 (H + M) \]  

(4)

where the M is the magnetization of the material. For a magnetic material of volume \( V \) and the net magnetic moment \( m_i \), then the magnetization is defined magnetic movement per unit volume given below[55, 56].

\[ M = \frac{\sum m_i}{V} \]  

(5)

The Magnetization (M) is the property of the materials and depends on together the individual magnetic moment of constitutes ions, atoms (or molecules), where \( \mu_0 \) is the permeability of free space and \( \mu \) is the magnetic permeability (the ratio of B to H) and. The \( \mu_0 \) and \( \mu \) are related through relative permeability \( (\mu_r) \) where \( \mu_r = \frac{\mu}{\mu_0} = 1 + \chi_m \) is the relative permeability of medium and \( \chi_m \) is the magnetic susceptibility of materials[55, 56] and define as ratio of magnetization (M) and magnetic field (H), give below [55-58].

\[ \chi_m = \frac{M}{H} \]  

(6)

Therefore, depending on the magnitude of the magnetic moment, materials are classified in two categories: (1) Nonmagnetic material - materials whose net magnetic moment vanishes are called non- magnetic materials and (2) magnetic materials - materials whose net magnetic moment is finite are called magnetic materials. The magnetic material can be further classified into five main categories, namely (1) paramagnetic (2) ferromagnetism (3) antiferromagnetic, (4) canted antiferromagnetic (or weak ferromagnetic) and (5) ferrimagnetism [55, 57-59] as shown in the figure 1.3.
Figure 1-3: The schematic representation of spin alignment for several common magnetic behaviours, namely paramagnetic (a), ferromagnetic ordering (b), antiferromagnetic ordering (c), canted antiferromagnetic (or weak ferromagnetic) (d), and ferrimagnetic ordering (e), respectively [60].

As a response to external magnetic field, the magnetic moment of the domains get aligned in the field direction which in results brings saturation magnetization in $M-H$ curve along with a memory effect. In other words these materials exhibit a hysteresis loop as shown in figure 1.4. As external magnetic field strength increases, the magnetic domains starts aligning themselves along the field direction and at sufficiently high field most of them aligned along the field direction and results in the saturation in magnetization occurs. Note
that the coercivity ($H_c$) is the value of reverse field which is required to bring down the saturation remanence to zero [61, 62].

Figure 1-4: in response to external magnetic field, the domains get aligned in the field direction which results saturation in the magnetization. The key physical quantities of M-H curve are coercivity ($H_c$) and remnant magnetization (Mrs), respectively is depicted in hysteresis loop][61, 63].

The origin of ferromagnetism in the material can be explained in terms of Curie-Weiss phenomenological theory. Mathematically, the Curie–Weiss law for magnetic susceptibility ($\chi$) can be expressed as follows:

$$\chi = \mu_r - 1 = \frac{c}{T - T_c} \quad (7)$$
where $\chi_M$ and $\mu_r$ are the magnetic susceptibility and the relative permeability of the material, respectively, and $C$ is a constant for a given substance and $T_c$ is the ferromagnetic Curie temperature. [61, 64].

On the other hand, in case of antiferromagnetic materials the spins of the atoms are aligned in such a way that the net magnetic moment of the material vanishes. As the temperature increases more than the Neel temperature ($T_N$), these materials show a phase transition from antiferromagnetic to paramagnetic state [55, 62]. The Antiferromagnetic materials can show three types namely A, C and G–type antiferromagnetic.

1. **A-type antiferromagnetic ordering**: In this type of antiferromagnetic ordering, the magnetic ions are ferro-magnetically coupled in the intra-plane while in inter-plane it is coupled anti-Ferromagnetic.

2. **C-Type antiferromagnetic ordering**: In this case, the magnetic ions are coupled antiferromagnetic in intra-plane and ferromagnetic with inter-plane.

3. **G-type antiferromagnetic ordering**: In G-type anti-ferromagnetic ordering the magnetic moment of ions are coupled antiferromagnetic both in intra-plane and inter-plane [65, 66].

### 1.5 Multiferroic materials and magneto-electric effect

Multiferroic is a class of materials in which more than one ferroic order (ferroelectric/ferromagnetism/ferroelastic) coexist in single phase. However, as per modern definition of multiferroic, other long-range orders such as anti-ferromagnetism may also be included in the above listed ferroic orders. Thus, any materials that combine more than one of these properties are described as multiferroics [15, 67-70].

Multiferroic materials may also exhibit the magneto-electric coupling where electric polarization and magnetization is coupled to each other. This is very unusual phenomenon
theoretically predicated by Landau and Lifshitz in 1959 where the magnetic and electric couple to each other to provide a new degree of freedom [71]. In other words, in case of magneto electric multiferroic materials the magnetization can be controlled by an electric field or polarization can be tuned by applying a magnetic field [61, 72-77].

In 1959, Dzyaloshinskii[78] showed the violation of time reversal symmetry in Cr$_2$O$_3$ system and after one year electric field induced magnetization was experimentally confirmed by the Astrov [79, 80]. Just after a year, Rado et al. reported the magnetic field induced polarization in the same system [81, 82]. Similar observation subsequently reported in other materials such as Ni$_3$Br$_2$O$_6$[83], BaCoF$_4$, BaMnF$_4$[84, 85] etc.

To exploit the device prospects for example switching application of magneto electric Multiferroic materials it is utmost necessary to enhance the strength of ME coupling which is in general very weak in these materials. In addition, the polarization or magnetization is often too small. Therefore, the development of new class of Multiferroic materials with new functionality is highly needed [63]. The origin of ME coupling can be explained in terms of Landau theory which is explained in next section. The ME coupling effect is the cross–coupling between electric polarization and magnetization in a material. The ME coupling terms arises in the Landau free energy expansion as a function of $E$ and $H$ [73, 86] as given below:

$$F(\vec{E}, \vec{H}) = F_0 - P_i^*E_i - M_i^*H_i - \frac{1}{2} e_0 e_{ij} E_i E_j - \frac{1}{2} \mu_0 \mu_i H_i H_j - \alpha_{ij} E_i H_j$$

$$- \frac{1}{2} \beta_{ijk} E_i H_j H_k - \frac{1}{2} \gamma_{ijk} H_i E_j E_k$$

(8)

where $E$ and $H$ are the electric field and magnetic Field, respectively. With differentiation of (8) with respect $E$, the information about electrical polarization can be expressed as
\[ P(\vec{E}, \vec{H}) = -\frac{\partial F}{\partial E_i} = P_i^s + \varepsilon_i \varepsilon_0 E_i + \alpha_y H_j + \frac{1}{2} \beta_{ijk} H_j H_k + \frac{1}{2} \gamma_{ijk} H_j E_i + \ldots \]  \hspace{1cm} (9)

While 1\textsuperscript{st} order of differential of (8) with respect to magnetic field intensity gives the information about the magnetization as

\[ M(\vec{E}, \vec{H}) = -\frac{\partial F}{\partial H_i} = M_i^s + \mu_y \mu_0 H_i H_j + \alpha_y E_i + \beta_{ijk} E_j H_k + \frac{1}{2} \gamma_{ijk} E_j E_k + \ldots \]  \hspace{1cm} (10)

In (9) and (10), \( P^S \) and \( M^S \) denote the spontaneous polarization and magnetization, respectively, whereas \( \varepsilon \) and \( \mu \) are the electric and magnetic susceptibilities, respectively. In expression (9) and (10), \( \alpha_{ij} \) is a tensor quantity represents the coefficient of ME coupling in the material while \( \beta_{ijk} \) and \( \gamma_{ijk} \) are higher –order coefficient of ME effects [87-89].

### 1.6 Microscopic origin of ferroelectric and ferromagnetic properties

We know from Maxwell equation that a varying magnetic field generates an electric field while a moving electric charge generates magnetic fields. Such similarities can be found in ferro–electric and ferromagnetic materials where these two orders are coupled to each other. For example, the observation of hysteresis loops in materials in presence of the external field [7]. Because of coupling between electric and magnetic orders, both the orders (electric and magnetic) responds to the applied external field and exhibits anomalies at critical temperatures. In ferroelectrics, on the other hand, the virtual hooping of electron from oxygen filled shell to the empty d-shell of the transition metal ion may take place through the hybridization between the B-site cation and anion. Conversely the long range spin order and macroscopic magnetization is originated because of spin exchange interaction between adjacent uncompensated magnetic ions. The spin exchange interaction can be mapped through virtual electron hooping between the adjacent ions [7]. These results leads to think about a situation where these two order parameters can coexist in single phase.
The simplest method to realise the above scenario is to combine the Ferro-electricity and magnetism during synthesis that contain separate functional units. In perovskite oxides A-site provide (ns)² cations of valance electron (e.g. Bi³⁺ or Pb²⁺) which is responsible for the stability of ferro-electricity in distorted crystal structures [90-92]. However, at the same time B–site ions are responsible for magnetism [90-92]. We can say that ferro-electricity is generated due to A-site ions while magnetism is induced due to B–site ions [7, 90-93]. Although, such approach provide an integration of ferroelectric and magnetic orders in one system but they unable to give a stronger ME coupling [7, 90-93]

1.7 Types of Multiferroics

The magneto-electric multiferroics can be divided broadly in to two categories: Single phase and composite multiferroics. Single phase multiferroics exhibit ferro-electricity and ferromagnetism at the same time in single phase whereas in composite multiferroic materials where the ferro-electricity exists only in a magnetically ordered state and is caused by a particular type of magnetism [7, 49, 73, 94, 95].

1.7.1 Type-I Multiferroics

Materials belonging to this class are, in general, exhibits good ferroelectric behaviour and the critical temperatures of the magnetic and ferroelectric transitions are also, in general, found to be well above the room temperature. But, the coupling between magnetic and ferroelectric orders in these materials is very weak. Depending on the mechanism of ferro-electricity in these materials there can be several different subclasses of type-I multiferroics as given,

- **Mixed perovskite:** the perovskite and mixed perovskite are the best ferroelectric materials in which both magnetism and ferro-electricity can be achieved in single phase. For example, PbFe₁/₂Nb₁/₂O₃, where the origins of ferro-electricity is attributed to off-
centring shift of Nb\(^{5+}\) while the magnetism is due to Fe\(^{3+}\) ion. These systems display low ME coupling [94, 96].

- **Ferro-electricity due to lone pair:** The BiFeO\(_3\) and BiMnO\(_3\) are the materials in which ferro-electricity arises due to lone pair. The BFO is the only single phase material which shows Multiferroic phenomena at room temperature with relatively high ferroelectric Curie temperature (T\(_c\) ~1103 K) and anti-ferromagnetic Neel temperature (T\(_N\) ~643 K). In BiFeO\(_3\), the outer 6s\(^2\) lone pair of electrons does not participate in chemical bond and hybridize with an empty p orbital which gives rise to a structural distortion and induces ferro-electricity. This is example of second order Jahn-Teller effect[97]. The origin of magnetism is due to the presences of Fe\(^{3+}\) transition metal ion. Therefore the multiferrocity can be achieved [94, 98].

- **Ferro-electricity due to charge ordering:** this phenomenon of charge ordering appears in transition metal compounds with transition metal ion with different vacancies. If after the charge ordering both site and bond turn out to be in equivalent, and then this gives rise to ferro-electricity .The appearance of magnetism is attributed due to transition metal ion for Example Pr\(_{0.5}\)Ca\(_{0.5}\)MnO\(_3\) [94, 99].

- **Geometrically driven ferro-electricity:** Ferro-electricity in the hexagonal manganites is driven by geometric and electrostatic mechanism. For example, ferro-electricity in YMnO\(_3\) is due to tilting of rigid block of the MnO\(_3\) while magnetism is due to Mn\(^{3+}\) ion [94, 100].

### 1.7.2 Type –II Multiferroics

In type-II Multiferroics materials, FE are caused by the magnetic ordering which leads to the strong coupling. The possible mechanism for observation of ferro-electricity can be explained in terms of Dzyaloshinskii–Moriya (DM) [78] and Magnetostriction effect [14, 69, 73]. The DM interaction exhibits an anti-symmetric and anisotropic exchange coupling
between two spins on a lattice bond $ij$ where the inversion centre is absent. It is originated by a relativistic spin-orbit coupling which has the form $\vec{D}_y \left[ \vec{S}_i \times \vec{S}_j \right]$ where $\vec{D}_y$ is DM vector[7,73]. In this case, the induced electric polarization vector is orthogonal to the propagation vector and lie in the spiral plane. This mechanism successfully explain the ME effect in TbMnO$_3$, NiV$_2$O$_8$, MnWO$_4$, and BaNiF$_4$[101, 102].

In magnetostriction mechanism, the ferromagnetic material may develop a strain in response to the applied magnetic field and with increasing intensity of field the field induced strain on the material also increases. The magnetic field may causes the ferromagnetic materials to expand or contract that is so called magnetostriction effect. As a result of magnetic field, the dipoles and magnetic field boundaries rotate to align with the field. For example, HoMnO$_3$ exhibits magnetostriction effect that gives rise to multiferroic behaviour due to the presence of a periodic collinear spin arrangement of the up-up-down-down type which results in the electric polarization due to exchange–striction mechanism [7, 73].

In recent years there has been much interest in artificially engineered nanostructured composite materials with novel physical properties [14, 103-105]. One of particular interest is the multilayer heterostructures thin films of functional oxides, such as, ferroelectric (FE), ferromagnetic (FM), antiferromagnetic (AFM) and multiferroics (MF), colossal magneto resistance (CMR) and other different order materials [14, 103, 104, 106].

1.8 Multiferroic properties in BiFeO$_3$-CoFe$_2$O$_4$ heterostructures thin films

Heterostructures multilayer thin films are composed of thin layers of two or more different nanostructures that are piled in a well-defined arrangement, which may reveal interesting physical and technological properties as compared to their individual systems [6,7]. In composite systems, the ME coupling is perhaps due to the strain-effect that is originated due to either by magnetostriction in the ferromagnetic or by the piezoelectric effect
in the ferroelectric which is transferred from one component to other component and which ultimately alter the state of polarization or magnetization [107-113].

The enhancement in multiferroic properties and ME coupling of the composite materials may also occur due to interface bonding i.e. displacement of atoms at the interfaces caused by ferroelectric instability after the overlap between atomic orbitals at the interface thus affecting the magnetization [13-14]. Another reason for the nano composites multiferroic materials are due to the charge mediated i.e. an electric field could result in the accumulation of charges (e.g. spin-polarized electrons or holes) at the interface, which produce a change in the interface magnetization as a consequence of spin dependent screening of the electric field [110-113]. Since the strain (interlayers or film-substrate) and interface bonding greatly affect phonon frequencies and their half widths, these can be conveniently estimated by investigating changes in the Raman spectral features of the composite heterostructures films [21, 25, 114].

Zavaliche et al. reported the multiferroic properties in self-embedded BFO-CFO system at room temperature[106]. They reported strong elastic coupling between the two ferroic constituents as the result of the three dimensional heteroepitaxy for a columnar nanostructures of BFO-CFO epitaxially thin films constrained by using pulsed laser deposition technique [7].

Zheng et al.[108, 115] studied the growth kinetics of the BFO – CFO nanostructure reported the growth and control of two phase nanostructure. They observed that the self-assembled perovskite spinal nanostructure of BFO-CFO can be controlled simply by selecting single crystal substrates[108, 115]. The substrate orientation and stoichiometry play important role in formation of CFO nanopillar in BFO matrix [18]. Dix et al. and several other researchers studied the impact of growth temperature on the crystal structure morphology
and stoichiometry of BFO-CFO nanocomposite deposited on SrTiO$_3$(100) and SrTiO$_3$(111)[116-122].

Wu et al observed the effect of constituent layer thickness on the ferromagnetic and ferroelectric behavior of BFO/CFO thin films [123]. The electrical and dielectric behavior of BFO-CFO nanocomposite system have not been carried out extensively[124]. However, the temperature and frequency dependent dielectric behavior and multiferroic properties of the BFO/CFO heterostructures need to be understood for device applications.

In the BiFeO$_3$-CoFe$_2$O$_4$ system, BiFeO$_3$ (BFO) is known to be the only material that exhibits multiferroism at room temperature [21, 54, 114, 125]. In recent years, several BFO based thin film were fabricated on a SrTiO$_3$ (STO) with different orientation and on other substrates [110, 126-128]. Nanostructured thin films of CoFe$_2$O$_4$ widely studied in recent years due to possible potential application in data storage, spintronics and magnetic sensors and high electromagnetic performance[110, 123, 129, 130]. In addition, It also show the properties such as excellent mechanical hardness, high cubic magneto crystalline anisotropy and chemical stability make it promising candidate in the field of high density data recording media, magnetic fluid and audio, video tapes[4, 13, 111, 131-133]. Cobalt ferrites have cubic spinel structure with the space group Fd3m and characterized lowest surface energy of [111] surfaces [134, 135] The Co$^{2+}$ and Fe$^{3+}$ occupy the interstitial sites of either octahedral or tetrahedral and O$^{2-}$ ions form FCC close packing and the super exchange interaction between these two antiparallel sub-lattices through O$^{2-}$ ions form the ferromagnetic structure[129, 130, 134].

1.9 Applications of Multiferroics

The magneto-electric (ME) Multiferroic has a lot of interesting physics and shows its importance in perspective of realization of devices for different applications. Multiferroics that demonstrate ferro-electricity and magnetism simultaneously, offer effective approach for
data storage devices. The mutual control of electric and magnetization polarization in Multiferroic is very interesting because their application in magneto electric Multiferroic devices. Wood and Austin suggested as many as 15 types of applications of ME materials [6] such as (i) modulation of amplitudes, polarization and phase of optical waves, (ii) ME data storage and switching, (iii) optical diodes, (iv) spin-wave generation, (v) amplification and (vi) frequency conversation etc., [6-11].

1.10 **Bismuth Ferrite (BiFeO$_3$)**

The BFO is the only single phase material which shows multiferroics phenomena at room temperature with relatively high ferroelectric Curie temperature (T$_c$ ~1103 K) and antiferromagnetic Neel temperature (T$_N$ ~643 K)[2, 22, 136]. BFO has distorted rhombohedral crystal structure with R3c space group symmetry which permits anti-phase octahedral orientated and ionic displacement from the centro-symmetric position [2, 21, 22, 25, 27, 136]. The BFO has many device prospects for their application in ME multiferroic devices [2, 22, 136, 137].

1.10.1 **Crystal structure of BiFeO$_3$**

BiFeO$_3$ belong to space group R3c and has a rhombohedral perovskite structure with unit cell having lattice parameter $a_{\text{Rhomboedral}} = 3.965\text{Å}$ and the rhombohedral angle $\alpha$ is 89.3°- 89.4° at room temperature [25, 137-139]. The crystal structure of the bulk BFO is shown in figure 1.5 which has opposite rotation of successive oxygen octahedral around [111] polar axis where red arrow indicates orientation of Fe magnetic moments in [111] plane [12, 13, 140].
Figure 1-5: (a) Crystal structure of bulk BiFeO$_3$ (BFO) [13, 141]. (b) The part of the BiFeO$_3$ lattice in hexagonal frame of reference with only iron and oxygen ions is shown. The arrows indicate the Fe$^{3+}$ moment direction[28].

BFO may also grow in hexagonal structure with the c axis parallel to the diagonals of the perovskite cube namely [001]$_{\text{hexagonal}}$ | [111]$_{\text{pseudo cubic}}$. In hexagonal symmetry, the lattice parameters are $a_{\text{hexagonal}} = 5.58$ Å and $c_{\text{hexagonal}} = 13.89$ Å[25, 137, 142] While, for an ideal cubic structure the rotation angle of the oxygen octahedral should be $0^\circ$ but in case of BFO this angle is found to be $\sim 11^\circ$ to $14^\circ$ around the polar [111]$_{\text{pseudocubic}}$ axis [25, 137, 138, 143]. The change in the rotation angle distorts the oxygen octahedral that alter the Fe-O-Fe bond angle ($\theta =154^\circ$ to $156^\circ$)[25, 144]. The distortion due to Fe-O-Fe bond angle controls both the magnetic exchange and orbital overlap between Fe and O in the BFO. The tilt in octahedral in the BFO can be estimated from Goldschmidt tolerance factor ($t$) which is defined as,
\[ t = \frac{r_{Bi} + r_O}{\sqrt{2(r_{Fe} + r_O)}} \]  

(11)

For the BFO the tolerance factor is reported to be less than one. In other words, if \( t \) value is less than one, the oxygen octahedral distorts in order to fit to a small unit cell [22, 145-147].

1.10.2 Ferro-electric property of BiFeO₃

In BFO, the ferro electricity generates due to A-site ions (Bi³⁺). The presence of an active lone pair (two valance electrons) of Bi³⁺ ions which is capable of participating in chemical bonds via sp² hybridized states but they do not participate in such bonding[22, 38, 54, 97, 105, 138, 148-150]. In the materials such as BiFeO₃, BiMnO₃ and PbVO₃ where the A-site cation (i.e. Bi⁺³; Pb⁺²) has a stereo-chemically active 6s² lone-pair which causes the Bi 6p (empty) orbital to come closer in energy to the 2p(O) orbitals [93, 97, 150-153] which leads to hybridization between the 6p(Bi) and 2p(O) orbitals and drives the off-centring of the cation towards the neighbouring anion giving rise the Ferro electricity in the system [93, 97, 150-153]. The B-site cation (Fe³⁺) lowers its energy by shifting along one of the [111] directions. Therefore, the direction of ferroelectric polarization in the bulk BFO is along [001] hexagonal/[111] pseudo-cubic of the perovskite structure [38, 97, 138, 144, 148, 150].

In earlier days, the measurement on the bulk ferroelectric materials reveals a small value of the polarization. Teague et al. pointed out the smaller value of polarization could be due to the leakage current in the BFO and the actual polarization value should be an order of magnitude higher than what was recorded in the experiment [114]. Afterwards, Lobo et al., confirmed this prediction in infrared phonon dynamics of a multiferroics BiFeO₃ single crystal [154].
Wang et al., reported enhancement in the room-temperature polarization as large as 50 to 60 μC/cm² which is almost an order of magnitude higher than that of the bulk value (~6.1 μC/cm²) in heteroepitaxial BiFeO₃ thin films [114, 126]. This observation was found to be consistent with the results obtained from first-principles calculations which suggest that a small changes in lattice parameters may result in a large change in spontaneous polarization [141, 155].

Another very efficient approach could be A-site, B-site or both sites doping in to the host lattice of BFO which may help to overcome the above-mentioned challenges [21-22]. The advantage of simultaneous doping on both sites are expected to enhance the magnetic and ferroelectric properties and reduce in the leakage current [23[156]]. Here, enhanced ferroelectric and ferromagnetic properties are supposed to be induced by the internal strain which is due to the coexistence of distorted rhombohedral and tetragonal phase [157].

1.10.3 Magnetic property of BiFeO₃

Origin of magnetism in BiFeO₃ can be attributed to both long-range and short-range magnetic orderings. Sosnowska et al., suggested that the short-range magnetic ordering in BiFeO₃ is G-type antiferromagnetic [21, 28, 158, 159]. In this case each Fe³⁺ spin is surrounded by six antiparallel spins of the nearest neighbours Fe³⁺ ions. In other words the magnetic moments of Fe³⁺ ions are coupled ferromagnetically along the pseudo cubic (111) planes and antiferromagnetic ally between adjacent planes. While, the antiferromagnetic order in BFO is oriented in the [001]ₜ/ [111]ₜ direction and the spin rotation plane is parallel to the [110]ₚ. A schematic representation of the spin rotation and the spiral direction is shown in figure 1.5(b). As a result of tilting the FeO₆ octahedral, the Fe–O–Fe angle reduces from 180° to 154–156° [38, 63, 142, 148, 149, 160]. If the Fe–O–Fe angle was 180° one would expect collinear anti-ferromagnetism [161, 162]. If this angle would be 180° then the BFO is expected to show collinear antiferromagnetic. If the magnetic moments is oriented
perpendicular to the $<111>$ polarization direction then the symmetry also permits a small canting of the moments resulting in a weak ferromagnetic moment due to the Dzyaloshinskii-Moriya (DM) effect [161-164].

![Diagram of spin cycloid](image)

Figure 1-6: Schematic representation of the spin cycloid. The canted antiferromagnetic spins (blue and green arrows) give rise to a net magnetic moment (black arrows) that specially averaged out to zero due to the cycloid rotation. The spins are contained with the plane defined by the polarization vector (red) and the cycloid propagation vector (black) [165].

The canted spins induce a weak magnetic moment that couples with the FE polarization. However, the long range magnetic ordering in BiFeO$_3$ consists of an incommensurate spin cycloid of the antiferromagnetically ordered sub-lattices and the cycloid has a very long period distance of 62 to 64 nm[28]. The spiral modulated spin structure leads to the cancellation of any macroscopic magnetization as shown in Fig 1.6 [28].

Sosnowska et al. used the spin cycloidal ordering model in BiFeO$_3$ structure [28]. The average R3e space group permits the linear magneto-electric effect but at the same time it is excluded by the spin cycloid [28]. Many experimental results has been reported on observation of cycloidal ordering model in BiFeO$_3$ structure [26, 28, 144, 166]. Recently,
Zaleskii et al., proposed that a simple cyclid could be distorted at low temperatures [159, 167]. The spiral spin structure may be suppressed by using various strategies such as

The application of high magnetic field (>20T) [168].

Apply the external stress or due to epitaxial constraints in thin films [127].

Finite sized effect in nano-sized BiFeO$_3$[169] and due to imposition of structural modification introduced by appropriate cation doping [170, 171].

Chemical substitution of various transition metals or rare earth at A-site, B-site or both sites doping in to the host lattice of BFO [171-175].

1.10.4 Dzyaloshinskii-Moriya (DM) Interaction

The DM interaction is a process like to super exchange, where the intermediate process is through spin-orbit interaction compared to oxygen ion. In this the excited state is not associated with the oxygen but is produced by spin-orbit interaction in one of the magnetic ions [78, 161, 162, 164]. This is an anti-symmetric exchange interaction which essentially contributes to the total magnetic exchange interaction between two neighbouring magnetic spins $S_i$ and $S_j$. The effect of DM in magnetically ordered systems is to provide spin canted of otherwise (anti) parallel aligned magnetic moment and thus is a source of weak ferromagnetic behaviour in an antiferromagnetic [73, 93, 161, 162]. The DM exchange interaction occurs between the excited state of a magnetic ion and the ground state of the neighbouring ion. For spin $S_i$ and $S_j$ Dzyaloshinskii Moriya interaction can be mathematically expressed [78, 102, 164, 165]as follows:

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

(12)
where \( H_{DM} \) is the Hamiltonian and \( D_{ij} \) is the DM vector and its orientation is constrained by symmetry. When, the crystal field does not have inversion symmetry with respect to the centre between \( S_i \) and \( S_j \) the vector \( D_{ij} \) can have finite value. The form of the interaction is such that it tries to force \( S_i \) and \( S_j \) to be at right angles in a plane perpendicular to the vector \( D_{ij} \) to ensure that the energy is negative. Therefore, its effect often canted (i.e. slightly rotate) the spins by a small angle which can be observed in \( \alpha \)-Fe\(_2\)O\(_3\), MnCO\(_3\), CoCO\(_3\), and BiFeO\(_3\) etc[102, 161].

![Diagram](image)

Figure 1-7: Determination of the orientation of the Dzyaloshinskii-Moriya (DM) vector from the local geometry [78, 102, 161, 162, 165, 176].

In order to understand the magnetism induced electric polarization in multiferroics the antisymmetric exchange coupling is very important. The general tendency of the system is that its magnetic interaction energy increases on the cost of lattice energy. Therefore, a small shift in the position of the ligand ions may be induced with the magnetic ordering and this mechanism is known as “inverse Dzyaloshinskii-Moriya effect” [161, 177].

### 1.10.5 Magneto-electric coupling in BiFeO\(_3\)

One of the great advantages of bismuth ferrite is the coupling between the electric and magnetic order parameter in single phase and this degree of freedom can be exploited in form
of the high performance magneto electric Multiferroics devices [178, 179]. Due to the cycloid modulation of the spiral spin structure, the BiFeO₃ possess a weak ferromagnetism as it prevent the observation of the linear ME effect. The cycloid modulation may be suppressed at very high magnetic fields which may leads to the observation of linear magneto-electric coupling [168, 179]. The Cycloid spin structure in BiFeO₃ attributed due to the coupling between ferro-electricity and magnetism in BiFeO₃ [178, 180]. The spiral modulated spin structure may permits the second order ME coupling in the BiFeO₃. According to Dzyaloshinski-Moriya theory, domain wall of BiFeO₃ might show very small ferromagnetism (magnetic moment ~ 0.3 emu/g) with ferroelectric material [49, 167, 179].Theoretically the BiFeO₃ proposed that the magnetic moment can be reversed by antiferro destructive rotation of FeO₆ octahedral [104]. The overlapping of ferroelectric and anti-ferromagnetic domains in the BiFeO₃ originates strong coupling between ferroelectric and magnetic orders. Which first shows the magnetic order control at room temperature by electric voltage [49]. The mechanism of magneto-electric (ME) coupling is not yet detailed clear [176, 178]. Furthermore, the coupling between magnetic and FE order parameter in the BiFeO₃ has been experimentally observed by using the X-ray photoelectron microscope and piezoelectric-force microscope together [181].

Although, the BiFeO₃ has many device prospects but it shows some challenges such as (i) presence of impurity phase in BFO, (ii) low rearmament polarizations (iii) high leakage current (iv) wide gap between the transitions temperatures and (v) weak magneto-electric (ME) coupling. In order to exploit the excellent device prospects of the BFO, it is highly necessary to address these issue so that the multifunctional devices with better performance can be fabricated using these materials.

1.11 Objective of the thesis

The thesis is mainly focussed on to synthesize the pure phase BiFeO₃ powder and thin film phase along with the BFO/CFO heterostructures on diverse substrates to improve the
multiferroic properties of BiFeO₃ through co-doping and surface engineering for their potential application in multifunctional devices. This work is also intended to get insight about the role of surface geometry to govern the phase transition, dielectric, magnetic, magneto-dielectric ferroelectric and surface morphological behaviour of thin film samples using analysis of fractal geometry approach. Application of Fractal geometrical approach to analyse the surfaces of multiferroic materials is found to be very efficient tool to extract various surface parameters of samples in resolution independent manner. This study is aims to resolve the few existing challenges of the BiFeO₃ and to open a door for the fabrication of multifunctional devices by utilizing the BiFeO₃ based multiferroics materials.

1.12 Organization of the thesis

This thesis is divided in to seven chapters. A brief description about the different chapters is given below:

Chapter 1 present the introduction of basic concepts of magneto-electric and multiferroics followed by a detailed review of previous work on multiferroics BFO. This chapter contain a brief account on multiferroic phenomenon focusing on the conceptual, theoretical and material aspect.

Chapter 2 is divided into two sections. The section (section-1) describes the sample preparation and details about the various characterization techniques. (Section-2) provides the details about the theoretical background for fractal geometry and the way for their utilization for the characterization of different kind of nanostructured thin film surfaces.

In Chapter 3, we have investigated the effect of (Yb, Co) codoping on structural, magnetic, ferroelectric, dielectric properties and magneto-dielectric properties of the BFO powder prepared using sol-gel method.
Chapter 4 presents detailed description about the effect of Lanthanum (La) and Cobalt (Co) co-doping in the BFO \([\text{Bi}_{1-x}\text{La}_x\text{Fe}_{1-y}\text{Co}_y\text{O}_3\ (x = 0.00, 0.01, 0.03, 0.05, 0.10)]\) ceramics structural, electrical, magnetic and magneto-dielectric properties.

Chapter 5 is focused on investigation of surface topography, structural, electrical properties and Fractal characterization of the BFO thin films deposited using pulsed laser deposition(PLD) technique on different substrates [i.e. Si, SrTiO\(_3\) (STO) and Al\(_2\)O\(_3\) (AlO)]. In order to get deeper insight about the role of surfaces on governing Multiferroics properties of these samples, the fractal characterization technique is employed on these samples.

In Chapter 6, the Multiferroics properties in BiFeO\(_3\)/CoFe\(_2\)O\(_4\) hetero-structures thin films deposited on SrTiO\(_3\) (111) using pulsed laser deposition technique is systematically investigated.

Chapter 7 gives overall summary of the major finding of the research work carried out for this thesis. In conclusion, this thesis work is focused on synthesis of pure and co-doped bismuth ferrite (BiFeO\(_3\)) bulk nanostructure thin films. We have also prepared the BiFeO\(_3\)/CoFe\(_2\)O\(_4\) composite thin films. The surface morphology, structural, electrical, magneto-dielectric and multiferroics properties of these materials are systematically investigated to obtain the deep insight mechanism about the nature of magneto-dielectric coupling in nanostructured and composite thin films. The co-substitution studies revealed that electrical, ferromagnetically and ferroelectric properties of BFO significantly enhanced compared to pure BFO samples.