CHAPTER 1

INTRODUCTION

1.1 MULTIFERROIC MATERIALS

The term “multiferroic” was introduced by Schmid in 1994 to define the materials that have simultaneous coexistence of at least two ferroic properties in the same phase; (anti) ferromagnetism, (anti) ferroelectricity and (anti) ferroelasticity. Previously, the term ferroelectromagnets was used to describe the same materials (Smolenskii & Chupis 1982). An important group of materials are the “magnetoelectrics”, which possess long range magnetic ordering, but no spontaneous polarization though electrical polarization can be induced by applying a magnetic field.

One more class of materials that are neither Magnetoelectrics (ME) nor Multiferroics (MF) such as MnO (Seehra & Helmick 1981) and MnF$_2$ (Seehra & Helmick 1984) are called “magnetodielectrics”. In these materials, the coupling exists between the dielectric constant and magnetization of ferromagnetic (SeCuO$_3$) or antiferromagnetic (TeCuO$_3$) materials (Lawes et al 2003). These materials exhibit dielectric anomalies at magnetic phase transition temperatures or finite magnetocapacitance; change of the capacitance under applied magnetic field.

Among these materials, MF and ME with the simultaneous presence of polarization and magnetization can find application in Ferroelectric Random Access Memory (FeRAM) and Magnetic Random Access Memory (MRAM) independently to store binary data. The coupling between the electrical ($\pm P$) and the magnetic ($\pm M$) order parameters in these
materials provides a possibility of possessing additional functionalities such as electrical (magnetic) control of magnetization (polarization) (Kimura et al 2003a) enabling the design of futuristic multistate memory devices with electrical writing and non-destructive magnetic reading operations (Bibes & Barthelemy 2008; Chen et al 2006). Schematic representation of the relationship between multiferroic and magnetoelectric materials is shown in Figure 1.1. However, the materials with the strong coupling between the electric and the magnetic states, the available switchable states, namely (+P, +M), (+P, −M), (−P, +M) and (−P, −M) are not absolutely independent of each other and the only the combinations that are independently achievable are either (+P, +M) and (−P, −M) or (+P, −M) and (−P, +M).

![Figure 1.1](image)

**Figure 1.1** (a) Relationship between multiferroic and magnetoelectric materials (b) Schematic illustration of different types of coupling present in multiferroic materials (Martin et al 2010)

Thus, the memory device is restricted to two states similar to that of conventional ferroelectric or magnetic memories (Scott 2007). Nevertheless, this problem can be solved by forming a ferromagnetic-magnetoelectric tunnel junction with the combination of electroresistance and magnetoresistance that can result in four state memory effect (Gajek et al 2007a).
1.1.1 Ferroelectricity (FE)

Ferroelectric materials are ordinary dielectrics at high temperature phase and have spontaneous polarization at low temperature phase, wherein the direction can be switched by applying the electric field (Hill & Filippetti 2002). The two main types of ferroelectric behaviour are: displasive and order-disorder. The displasive type occurs with the displacement of ion from its equilibrium position and acquisition of permanent dipole moment. At high temperatures $T>T_c$ (where $T_c$ is ferroelectric Curie temperature), the thermal energy is sufficient to move the ions randomly, so there is no fixed asymmetry. When the temperature is below $T_c$, the ion is frozen in an off-center position giving rise to a net dipole moment.

![Figure 1.2 Ferroelectric hysteresis loop of a ferroelectric material](image)

In order-disorder ferroelectrics, each unit cell has a dipole moment, but at high temperatures, dipoles point in random directions. Upon lowering the temperature, the dipoles are aligned in the same direction within a single domain. According to their symmetry, crystals are divided into 32 point groups with 11 of them being centro-symmetric (non-polar) and 21 lacking an inversion center (polar). This lack of inversion center is a requirement for the piezoelectric behaviour of the crystal. In the centro-symmetric crystals, the
centers of the charges (positive and negative) would always coincide, and so no electric dipole is generated, but the crystal lacking a centre of symmetry would have an electric dipole. Further, first-principles density functional theory calculations have contributed significantly to understand the origin of ferroelectric behaviour, particularly in perovskite structure oxides (Hill 2000). Ferroelectric hysteresis loop, as shown in Figure 1.2 (Ferrater 2012), is characteristic of a ferroelectric material. Application of an external direct current (dc) electric field (E>E_c) to a polydomain ferroelectric crystal causes the polarization in the direction of the field via domain wall movement.

The minimum dc field required to move the domain walls is called coercive field (E_c). The initial value of saturated polarization (P_s) in a polydomain crystal increases with the increasing dc field to a maximum that is characteristic of the material. Reversing the electric field, domain wall movement occurs in the reverse direction resulting in reverse polarization. At zero applied field, the crystal would have a remnant polarization (P_r) which is smaller than the spontaneous polarization. The hysteresis loop is a function of the work required to displace the domain walls which is closely related to the defects present in the crystal and the energy barrier separating the different orientational states.

### 1.1.2 Ferromagnetism (FM)

The overall magnetic property a crystal depends upon two factors: magnetic response associated with each atom/ion and interactions between these magnetic moments. It is necessary to consider ferroelectric materials displaying the magnetic ordering based on the interactions between the magnetic dipoles. These materials exhibit the properties: Paramagnetism (PM), Ferromagnetism (FM), Antiferromagnetism (AFM) or Ferrimagnetism (FIM). In a paramagnetic material, alignment of adjacent dipoles is not observed due
to thermal fluctuation. Ferromagnetic material consists of parallel aligned adjacent dipoles. Antiferromagnets consist of antiparallelly aligned equal dipoles ensuring zero net magnetization, so these materials do not find wide applications in magnetic technologies. Ferrimagnetic materials also comprise antiparallel and unequal dipoles resulting in non-zero net magnetization, which tend to concentrate magnetic flux in their interiors offering broad applicability.

At low temperature, the antiferromagnets possess a small canting of the spins away from antiparallel alignment, which is described by the term “weak ferromagnetism”. The origin of ferromagnetic properties has been successfully explained by the Curie-Weiss localized moment theory and the Stoner band theory of ferromagnetism.

Ferromagnetic materials undergo a phase transition from a high-temperature phase, which does not have macroscopic magnetic moment, to a low-temperature phase which has spontaneous magnetization even in the absence of an applied magnetic field (Hill 2000). They have large positive permeability that leads to many applications such as transformer cores, permanent magnets, data storage and electromagnets, wherein large magnetic fields are required (Ncube 2012). Magnetic permeability, which defines the degree of magnetization of a material in response to an external magnetic field, is a good indication of magnetic properties.

Magnetism of a material is characterized by transition temperature or Curie temperature ($T_c$). Above $T_c$, the material has paramagnetism and below $T_c$, it has ferromagnetism which is characterized by hysteresis response in applied magnetic field as shown in Figure 1.3. As seen from the figure, when the magnetic field increases in the positive direction, the magnetization also increases from zero to a saturation value ($M_s$) due to the movement and the growth of the magnetic domains (Wang 2013). When the field is reduced
to zero after saturation, the magnetization decreases from $M_s$ which is called residual magnetization or retentivity ($M_r$). The reverse field required to reduce the magnetization to zero is called coercivity ($H_c$). The suitability of ferromagnetic materials for a particular application is determined largely from the characteristics of hysteresis loops. For example, magnetic data storage applications require a square-shaped hysteresis loop with two stable magnetization states while a small hysteresis loop is adequate for a transformer core.

![Ferromagnetic hysteresis loop of a ferromagnetic material](image)

**Figure 1.3** Ferromagnetic hysteresis loop of a ferromagnetic material

**1.2 MAGNETOELECTRIC COUPLING**

In multiferroics, coupling between (anti) ferroelectricity and (anti) ferromagnetism leads to the magnetoelectric effect which means magnetic (electric) polarization would be induced by applying an external electric (magnetic) field. The effects can be linear or non-linear with respect to the external fields. The magnetoelectric coupling can be described thermodynamically. The Free energy ($F$) of a magnetoelectric material is given bellow (Fiebig 2005; Martin et al 2010).
The magnetoelectric effect can be obtained from the differentiation of the $F$ of a material leading to the polarization in the $i$ direction that can be given by

$$
P_i(E, H) = \frac{\partial F}{\partial E_i} = P_i^s + \epsilon_0 \epsilon_{ij} E_j + \alpha_{ij} H_j + \frac{1}{2} \beta_{ijk} H_j H_k + \gamma_{ijk} H_j E_k - ... \quad (1.2)
$$

and to the magnetization in the $i$ direction is represented by

$$
M_i(E, H) = \frac{\partial F}{\partial H_i} = M_i^s + \mu_0 \mu_{ij} H_j + \alpha_{ij} E_j + \beta_{ijk} E_i H_j + \frac{1}{2} \gamma_{ijk} E_j E_k - ... \quad (1.3)
$$

where $E$ and $H$ are the electric and magnetic field, $F_0$ is the ground state free energy, subscripts $(i, j, k)$ refer to the three components in spatial coordinates, $P_i^s$ and $M_i^s$ are the components of spontaneous polarization ($P^s$) and magnetization ($M^s$), $\epsilon_0$ and $\mu_0$ are the dielectric and magnetic susceptibilities of vacuum and $\epsilon_{ij}$ and $\mu_{ij}$ are the second order tensor coefficients. $\alpha_{ij}$, $\beta_{ijk}$ and $\gamma_{ijk}$ are the components of tensor $\alpha$, $\beta$ and $\gamma$, which are used to define the ME effect. In addition, it can be shown that the magnetoelectric response is limited by the relation $\alpha_{ij}^2 < \epsilon_{ii} \mu_{jj}$ or more rigorously $\alpha_{ij}^2 < \chi^e_{ii} \chi^m_{jj}$ where $\chi^e$ and $\chi^m$ are the electric and magnetic susceptibilities. This means that the magnetoelectric effect can only be large in ferroelectric or ferromagnetic materials. When the magnetic and ferroelectric parameters are coupled, the magnetic order is coupled to the polarization and consequently to the dielectric permittivity, the origin of which can also be understood from the Ginzburg-Landau theory (Kimura et al 2003b).
1.3 PATHWAYS TO MULTIFERROISM

There are number of pathways through which one can achieve multiferroism in materials that have been classified into two types: Type-I and Type-II (Khomskii 2009). Type-I multiferroics are the materials in which ferroelectricity and magnetism rely on two independent mechanisms. These multiferroics like the perovskites (ABO$_3$), in one way make use of the stereochemical activity of an A-site cation with a lone pair, i.e. 6s electrons in Bismuth (Bi) or Lead (Pb) to induce a structural distortion and ferroelectricity while inducing magnetism with the B-site cation (Martin et al 2010). For example, the most widely studied single phase multiferroics are BiFeO$_3$ (Wang et al 2003) and BiMnO$_3$ (Son et al 2010).

Another way to achieve Type-I multiferroics is through geometrically driven effects where long-range dipole-dipole interactions and anion rotations drive the system towards a stable ferroelectric state in materials like YMnO$_3$ (Van Aken et al 2004). Finally, there can also be charge ordering

Figure 1.4 (a) Ferroelectric material (BaTiO$_3$) under spatial inversion symmetry (b) Representation of a particle with spin angular momentum under time reversal operation (Langenberg Perez 2013)
driven multiferroics where non-centrosymmetric charge ordering results in ferroelectricity in magnetic materials like LuFe$_2$O$_4$ (Ikeda et al 2005). This kind of Type-I multiferroics tend to show much higher ferroic transition temperatures at the expense of small magnetoelectric coupling.

In contrast, Type II multiferroics are the rare earth manganites, in which magnetism causes ferroelectricity; ferroelectricity exists only in a magnetically ordered state implying a strong coupling between the two order parameters. The ideal examples for this sort of behaviour are TbMnO$_3$ (Kimura et al 2003a) and TbMn$_2$O$_5$ (Hur et al 2004) where ferroelectricity is induced by the formation of a symmetry-lowering magnetic ground state that lacks inversion symmetry. The reasons for the scarcity of multiferroism in materials can be summarized as follows (Hill 2000; Martin et al 2010; Wang et al 2009):

i) Magnetic materials can be either insulating or conductive, whereas ferroelectric materials can exclusively be insulating, otherwise an applied electric field would induce an electric current rather than switching ferroelectric domains. These factors restrict the search for multiferroics, explicitly the magnetic materials that should possess the insulating nature.

ii) From crystal symmetry considerations ferroelectricity breaks the spatial inversion symmetry, which requires non-centrosymmetric structures for ferroelectric order to occur. Conversely, magnetism breaks time-reversal symmetry (Van Aken et al 2007) which is shown in Figure 1.4.

iii) Combination of two symmetry restrictions leaves only 13 point groups (among 233), that would enable ferroelectricity and magnetism to coexist.
Since most of the ferroelectrics and a large number of magnetic materials are transition metal oxides with ABO$_3$ perovskite structure, more attention is reasonably drawn to this structure for achieving the multiferroism. In the Bi containing multiferroic perovskites, the cation A gets displaced from the centre of the surrounding oxygen octahedra breaking the centrosymmetry and creating an electric dipole. However, this condition requires that the cation A should have empty d orbitals to minimize the Coulombian electrostatic repulsion of the surrounding oxygen anions. Magnetism in transition metal perovskites arises from magnetic superexchange interactions or double exchange for conductive magnetic oxides of the B cations mediated by the adjacent oxygen ions, which is possible only when the d orbitals of the B cation are partially occupied (Hill 2000).

### 1.4 PEROVSKITE STRUCTURE

One of the most promising multiferroic materials usually is transition metal perovskite. Chemical formula for a typical perovskite structure is ABO$_3$ where A and B are different size cations. In the ideal cubic unit cell, 12-coordinated cations A$^{a+}$ where 'a' varies from 1 to 3 sit on the corners of the cube, octahedral O$^{2-}$ ions on the faces and the cations B$^{b+}$ where 'b' varies from 3 to 6 is in the center of the octahedral cage as shown in Figure 1.5(a). Due to the flexibility of the corner-sharing octahedra, the perovskite structure can be easily distorted to adapt a wide range of valence states on both the A and B sites by expanding or contracting the lattice or by rotating the bond angles. The resulting symmetry of the distorted perovskite could be tetragonal, orthorhombic, rhombohedral or monoclinic (Wang 2013).

#### 1.4.1 Structure of BiMnO$_3$ System

BiMnO$_3$ (BMO) acquires monoclinic crystal structure with C2 space group at Room Temperature (RT). The monoclinic unit cell is shown in
Figure 1.5(b). The reported cell parameter values are: $a = 9.532\ \text{Å}$, $b = 5.606\ \text{Å}$, $c = 9.854\ \text{Å}$ and $\beta = 110.7^\circ$ (Atou et al 1999). To understand the physics of this material, it is often helpful to view it as having a perovskite structure. Indeed, the triclinic distortion from the ideal perovskite structure is quite small.

Figure 1.5  
(a) Ideal cubic perovskite structure ($\text{ABO}_3$)  
(b) Monoclinic unit cell of $\text{BiMnO}_3$ (Ozawa & Kang 2004)
The cell parameters of pseudo-perovskite phase of BMO are: 
a = 3.950 Å, b = 3.995 Å, c = 3.919 Å, α = 90.7º, β = 90.9º and γ = 91.0º  
(Faqir et al 1999). The structure of this pseudo-perovskite unit cell of BMO is  
the same as that of the ideal cubic perovskite containing one formula unit as  
shown in Figure 1.5(a). Upon cooling from high temperatures, BMO  
undergoes several phase transitions (Hassink 2004).

1.5  FERROELECTRICITY IN BiMnO₃ SYSTEM

In BiMnO₃, stereochemical active cation Bi³⁺ sits on the perovskite  
A-site induce ferroelectricity due to lone-pair electrons and magnetic cation  
(Mn) located on the B-site. The electronic configuration of Bi³⁺ is  
[Xe]⁴f¹⁴⁵d¹⁰⁶s²⁶p⁰ with empty 6p-states and the two 6s outer lone-pair  
electrons do not participate in chemical bonds as revealed in Figure 1.5(a). In  
the absence of interactions, the lone-pairs are nearly spherically distributed,  
but when surrounded by oxygen anions, they shift away from the  
centrosymmetric position due to the Coulombic electrostatic repulsion. Thus,  
the lone-pairs form an electric dipole which breaks the spatial inversion  
symmetry leading to the ferroelectricity (Langenberg Perez 2013; Schmidt et  
al 2013).

At high temperatures, BiMnO₃ undergoes two phase transitions at  
~450 K and ~770 K (Kimura et al 2003b). The first structural change is from a  
low temperature (~450 K) non-centrosymmetric monoclinic C2 structure to a  
high temperature non-centrosymmetric monoclinic C2 structure, i.e. still  
allowing ferroelectric order. Instead, the phase transition occurring at ~770 K  
leads to a centrosymmetric structure at higher temperatures corresponding to a  
orthorhombic structure which no longer allows spontaneous polarization.  
Hence BiMnO₃ is considered to be ferroelectric upto ~ 770 K well above room  
temperature.
1.6 FERROMAGNETISM IN BiMnO₃ SYSTEM

Magnetic behaviour of BiMnO₃ arises from the magnetic superexchange interaction Mn³⁺ - O - Mn³⁺ where Mn³⁺ is a d⁴ transition metal ion. Following the Hund’s rule, the four electrons occupy the d-orbitals and maximise the total spin, i.e. Mn³⁺ d-orbital configuration is (t₂g, e₉) (Langenberg Perez 2013). The BMO system reduces its energy slightly by elongating the MnO₆ octahedron, as it decreases the Coulombic electrostatic repulsion of the surrounding oxygen anions over the occupied e₉ orbital, so-called Jahn-Teller distortion. This distortion causes splitting of energy levels (d level) into two energy states: two high-energetic (e₉) and three low-energy (t₂g) orbitals (Tokura & Nagaosa 2000).

![Figure 1.6: Representation of super exchange interaction in BiMnO₃ (Langenberg Perez 2013)](image)

The nature of ferromagnetic interaction, whether it is ferromagnetic or antiferromagnetic, depends on the filling of the e₉ orbitals based on the Goodenough-Kanamori’s (GK) rules. According to GK rules, filling of electrons in the BiMnO₃ system is as follows: Mn³⁺ (empty e₉ orbitals)-O-Mn³⁺ (half-filled e₉ orbitals) give rise to ferromagnetic interactions as represented in Figure 1.6. Moreover, these GK rules are inferred in the simplest scenario of an ideal perovskite ABO₃ where the B-O-B bond angle is 180°. Distorted perovskites, rotation of the oxygen octahedral and different
B-O-B bond angles may give rise to different magnetic interactions (Goodenough 1963). In fact, Mn-O-Mn bond angles are significantly smaller between 140º and 160º than the ideal 180º (Atou et al 1999). On the one hand, the p orbitals of oxygen couple with the d orbitals of magnetic ions (Mn$^{3+}$) form a covalent bond, with p orbitals of Bi$^{3+}$ simultaneously. On the other hand, oxygen anions are responsible for the lobe-like distribution of the lone pair electrons of Bi$^{3+}$. Hence the magnetoelectric coupling indirectly exists between the two ferroic properties in BiMnO$_3$ (Langenberg Perez 2013).

1.7 LITERATURE REVIEW ON BiMnO$_3$

1.7.1 BiMnO$_3$ -Bulk

Multiferroic BMO with a highly distorted perovskite structure is synthesized at a high pressure of 6 GPa by (Chi et al 2005). The synthetic ceramics is observed to display ferromagnetic and ferroelectric orderings simultaneously. Multiferroic perovskite BMO is also synthesized (Montanari et al 2005a) under high pressure, which decomposes when it is heated from RT to 500-650 ºC. X-ray Diffraction (XRD), Electron Diffraction (ED), thermal analysis and magnetic investigation reveal the existence of a complex pathway to decomposition depending on the heating rate, pressure and atmosphere that involves different metastable phases. In particular, the as-prepared monoclinic phase (I) transforms to a second monoclinic form (II) at 210 ºC and then to an orthorhombic phase (III) at 490 ºC. These phase transitions occur fast and are reversible upon heating.

Magnetic and specific heat measurements made (Belik & Takayama-Muromachi 2006) for single-phase BMO powder sample prepared at 6 GPa and 1383 K. The appearance of a “spin-glass-like” state in BMO and the existence of ferromagnetic spin waves are identified. Atomic arrangements in bulk BMO have been studied by (Belik et al 2006) and it is found that the
system is very close to centrosymmetric. It confirms that the structural distortion cannot be the origin of ferroelectricity. Structural properties of polycrystalline single-phase BMO samples have been described by (Belik et al 2007). Selected Area Electron Diffraction (SAED) and Convergent Beam Electron Diffraction (CBED) results show that BMO crystallizes in the centrosymmetric space group C2/c at 300 K. The crystallographic parameters are: a = 9.541 Å, b = 5.6126 Å, c = 9.863 Å, β = 110.658 ° at 300 K and a = 9.586 Å, b = 5.5990 Å, c = 9.742 Å, β = 108.601° at 550 K with space group C2/c. The theoretical calculations are also done by (Baettig et al 2007) which suggest that the ground state of perovskite-structure BMO is centrosymmetric with space group C2/c and zero ferroelectric polarization. Further, the ultrafine stoichiometric BMO particles are prepared by (Samuel et al 2007) at 80–100 °C under refluxing conditions. Single-phase multiferroic BMO ceramic is synthesized via solid-state reaction route by (Chi et al 2007). It is established that BMO has monoclinic substructure. The magnetic hysteresis loop is manifested with Tc around 105 K and saturated ferroelectric hysteresis loops are also observed at RT.

The structure of BMO at RT through ED, High Resolution Transmission Electron Microscopy (HRTEM) and theoretical simulations have been analyzed by (Yang et al 2008a). ED data also reveal that BMO crystallizes in the centrosymmetric C2/c structure. This is confirmed by further calculations of ED patterns and HRTEM images. BMO ceramics are synthesized under high pressure and their RT structures are also investigated using Transmission Electron Microscopy (TEM) and theoretical simulations by (Yang et al 2008b). The samples get crystallized in the centrosymmetric C2/c structure and possess weak ferroelectric polarization. (Chou et al 2008) have studied magnetic field dependent dc magnetization and the pressure dependent (Pm ~ 16 kbar) ac susceptibilities χp(T) on both powder and bulk multiferroic BMO samples.
A clear ferromagnetic transition is observed at $T_C$ around 100 K which increases with magnetic field. Ac susceptibility data indicates that both the FM peak and its $T_C$ decrease simultaneously with the increasing pressure. These features can be considered to have originated from the complex interplay of the magnetic and orbital structure of BMO which is affected by pressure. Jahn–Teller distortion and associated orbital order in BMO at RT have been observed by (Belik et al 2009). Octahedral distortions occur above 473K and the structural feature originates from the highly distorted monoclinic structure. (Hatt & Spaldin 2009) also have investigated the effect of epitaxial strain on the electronic ordering and symmetry of BMO to determine whether strain effects could explain the apparently contradictory experimental results regarding ferroelectricity. No significant polarization or re-ordering of Bi lone-pairs is found under experimentally achievable strain values and it is concluded that BMO remains centrosymmetric and non-polar. (Chou et al 2009) have examined the magnetic phase variations under hydrostatic pressure on multiferroic BMO. It is observed that the variations of crystal structure are influenced by the external pressure.

Mechanochemical synthesis of single phase BMO have been introduced by (Brankovic et al 2010) using a planetary ball mill. The system has a tetragonal structure with lattice parameters $a = 3.923 \, \text{Å}$, $c = 3.920 \, \text{Å}$ and a crystallite size of 17 nm. Microscopic theory of improper multiferroicity in BMO have been presented by (Solovyev & Pchelkina 2010): (i) the ferroelectric polarization is driven by the hidden antiferromagnetic order or centrosymmetric C2/c structure and (ii) the relativistic spin-orbit interaction is responsible for the canted spin ferromagnetism. The study explicitly shows how electric polarization can be controlled by the magnetic field and that BMO is a rare and a potentially interesting material wherein ferroelectricity and ferromagnetism can exist together.
Ferroelectricity in BMO ceramics have been studied by (Goian et al 2012). No ferroelectric polarization is observed upto electric field of 20 kV/cm and the number of detected IR and Raman active phonons corresponds to centrosymmetric $C2/c$ than to non-centrosymmetric $C2$ space group. (Zhang et al 2012) have utilized BMO perovskite for selective catalytic reduction of NO with NH$_3$ at 100–240 °C. In addition, BMO also acts as a resistant to water vapour and to a mixture of H$_2$O and SO$_2$.

The orbital structure and magnetic ordering of multiferroic BMO have also been theoretically investigated by (Gonchar et al 2013). It is shown that the orbital structure depends not only on the nearest neighbour oxygen environment of manganese ions but also on their next-to-nearest neighbours. This orbital structure significantly influences the magnetic order that has been formed as a result of the competition between ferromagnetic and antiferromagnetic exchange interactions.

Similarly, (Subramanian et al 2014) have investigated the crystal structure and magnetic ground state of monoclinic BMO using first principle calculations. The calculation reveals that BMO stabilizes to monoclinic $C2/c$ (centrosymmetric) with ferromagnetic ground state. (Mickel et al 2014) have employed the coupling of ferroelectric polarization to applied strains in multiferroic BMO. Moreover, dielectric characterization shows that the onset of the strain coupling coincide with the relaxer ferroelectric freezing temperature. (Toulemonde et al 2014) also have reported the temperature dependence of the phonons and crystallographic parameters in BMO single crystals. The crystallographic structure of the sample is refined from RT to liquid helium temperature in the centrosymmetric $C2/c$ space group, i.e. a group which does not allow ferroelectricity. In addition, the lattice dynamics is probed by Raman spectroscopy down to liquid nitrogen temperature (below the ferromagnetic transition). The result indicates the absence of a structural
phase transition at the ferromagnetic ordering or any other temperature. (Molak et al 2014) also have used the sintered BMO ceramics. The crystal lattice symmetry is monoclinic and centrosymmetric. Electrical conductivity has been measured in the 85-770 K range and the ceramics show semiconductor properties and charge order transition.

1.7.2 BiMnO₃ - Thin films

Growth of BMO thin films using pulsed laser ablation method have been reported by (Kim et al 2005). Nano-size bits of ferroelectric polarization on the BMO thin film grown on (111)Pt/TiO₂/SiO₂/Si substrate can be easily written and read by Kelvin Force Microscope (KFM). The preferentially oriented BMO thin film is identified to be a potential candidate for high-density data storage device. (Eerenstein et al 2005b) also have described the preparation of epitaxial BMO films on SrTiO₃ (001) substrates using Pulsed Laser Deposition (PLD). Optimization of growth parameters has resulted in highly resistive films of resistivity $5 \times 10^7 \, \Omega \, \text{cm}$ and dielectric constant of 1400. These findings pave the way for magnetoelectric measurements and further optimization for memory devices.

Epitaxial thin films of BMO grown on SrTiO₃ substrates have been studied by (Yang et al 2006). Orbital ordering and magnetic properties of the thin films are identified. This peculiar orbital order inherently contains magnetic frustration. (Grizalez et al 2007) have studied magnetic and electrical properties of BMO thin films deposited by Radio Frequency (RF) magnetron sputtering on SrTiO₃(001) substrates. The films have monoclinic structure and polycrystalline nature. The observed $M_s$ of the film is $2.8 \mu_B$ per Mn ion, smaller than that of the bulk ($3.6 \mu_B$) at 5 K, which is decreasing with the increasing temperature. Epitaxial thin films of BMO deposited on SrTiO₃ substrates have also been reported by (Yang et al 2007). Long range ordering
of the Mn$^{3+}$ orbitals is probed with Mn K-edge resonant X-ray scattering. The inter-relation between the orbital, magnetic and ferroelectric degrees of freedom are given. In the same way, (Kaul et al 2007) have proposed the deposition of BMO thin films on SrTiO$_3$ substrates by RF sputtering. The film possess monoclinic structure and do not contain ferromagnetism below the bulk $T_C = 105$ K.

Optimized growth conditions for stoichiometric BMO thin film on SrTiO$_3$ (001) substrate using PLD have been explored by (Moriien 2008). The optimal substrate temperature and oxygen partial pressure are found to be 620 °C and 25 mTorr. The evidence of ferroelectricity in BMO films synthesized using RF magnetron sputtering method on (100) oriented SrTiO$_3$:Nb 0.1% and Pt/TiO$_2$/SiO$_2$/Si substrates have been given by (Grizalez et al 2008; Grizalez et al 2009a). The P-E loops show that $P_s$ of 40 nC/cm$^2$ and 25 nC/cm$^2$ at 105 K and 300 K respectively indicate that this is a very robust insulating material. Magnetic and ferroelectric properties can be very sensitive to the oxygen pressure. The ferromagnetism is observed with two transitions around 50 and 125 K and magnetic moment of 3.2 $\mu_B$.

High quality BMO thin films with double SrTiO$_3$ buffer layers on Pt/Ti/SiO$_2$/Si substrates have been fabricated by (Son et al 2010) for the reduction of leakage current. The BMO films exhibit a ferromagnetic transition with $T_c$ of about 105 K. The film also shows FE with a $P_r$ of about 9 $\mu$C/cm$^2$. Adsorption controlled growth of BMO films using Molecular Beam Epitaxy (MBE) have been depicted by (Lee et al 2010) and its direct band gap is determined as 0.1 eV.

Growth and properties of epitaxial thin films of BMO using PLD on SrTiO$_3$ (001) substrates have been studied by (Jeen et al 2011). The films have a ferromagnetic $T_C$ of $85 \pm 5$ K and $M_s$ of 1 $\mu_B$/Mn. The P-E plot shows a clear
hysteresis that confirms the multiferroic nature of the thin films. Further, high quality BMO thin films on Nb-doped SrTiO$_3$ substrates with (100), (110) and (111) orientations have been prepared by (Jung et al 2013) using PLD. All the films with different orientations undergo ferromagnetic transitions at the temperature of around 105 K as that of the bulk BMO. The result accomplished proves that the FE of the films may not be an intrinsic property.

Mechanisms for establishing magnetic and ferroelectric order in Bi containing perovskite oxide thin films have presented by (Schmidt et al 2013). Epitaxial growth of BMO thin films by PLD and its structural, magnetic, ferroelectric properties and ME coupling parameters are included. Its result reveals the weak coupling effects of up to 2% near the magnetic transition $T_C$ around 100 K.

1.8 MOTIVATION FOR THE RESEARCH

Magnetic and ferroelectric materials are widely used in many devices. The former materials play an important role in the storage devices such as hard disks, magnetic RAMs as well as sensors, read heads and so on. The latter materials are used in sensors and transducers because of their large piezoelectric response in capacitors and their high dielectric permittivity. They are also used in storage data devices like ferroelectric RAM’s. Thus, multiferroics receives much attraction not only because they exhibit the same properties and same applications as their ‘parents’ (ferroelectrics and magnetics) but also because of the interplay between magnetism and ferroelectricity, which gives an extra degree of freedom providing additional functionalities (Langenberg Perez 2013).

Some of the additional applications could be the four-state memories wherein the multiferroics are used to encode the information in either four resistive states (Gajek et al 2007a; Ju et al 2007; Scott 2007) or the
electric control of magnetic RAM, if the magnetoelectric coupling is prominent allowing high density and low-energy consuming magnetic RAM’s. Moreover, electrically controlled magnetic sensors, electrically tunable microwave applications such as filters, oscillators and phase shifters, selective catalytic reduction of nitrous oxide with ammonia and the other kinds of applications in magnetoelectronics and spintronics have also been proposed for multiferroic materials (Béa et al 2008; Scott 2007; Wang et al 2009). However, there is a practical difficulty in the development of high quality multiferroics with good coupling between the electric and the magnetic order parameters. Only a very few multiferroics are found to exist in nature and some of them have been synthesized in laboratory. As it is noted by (Hill 2000), one of the materials developed in laboratory is BMO.

BMO is perhaps the most fundamental multiferroic material and is referred to a “hydrogen atom” of multiferroics (Hill & Rabe 1999). This compound has been intensively studied both theoretically and experimentally. From the overview of BMO, it is found that Bi ions are responsible for FE while Maganese (Mn) ions are responsible for FM. The off-center displacement of the Bi ions leads to the hybridization between Bi-6s and O-2p orbitals driving ferroelectricity while the Mn cation has four 3d-electrons giving ferromagnetism (Rao et al 2000). However, under certain conditions, structural distortion or strain might take place in BMO thin films due to the displacement of ions or tilting of structure during the film growth. This structural distortion could change the original symmetry of the material and unit cell parameters. Evidently, these are essential for ferromagnetism and ferroelectricity that occur simultaneously (Hill 2000). For tensile strain larger than 2.8%, the BMO has a large electric polarization \( P > 80 \, \mu\text{C/cm}^2 \), FM with a large saturated magnetic moment \( 4 \, \mu_B/\text{Mn} \) and a high magnetic \( T_c \) between 169 K and 395 K. It is inferred that the BMO under tensile strain has the highest \( T_c \) among all the ferromagnetic and ferroelectric multiferroics.
Usually, heating the mixture of bismuth oxide and manganese oxide at ambient pressure leads to the formation of more stable Bi$_{12}$MnO$_{20}$ and Bi$_2$Mn$_4$O$_{10}$ compounds than the metastable perovskite BiMnO$_3$ (Montanari et al 2005b). Stabilized single phase high quality bulk and thin films of BiMnO$_3$ are difficult to achieve because of their tendency of multiphase formation, incompatible partial pressure of oxygen and the volatility of bismuth at a high growth temperature (Fujino et al 2007; Gajek et al 2005; Gajek et al 2007b; Havelia et al 2009; Moreira dos Santos et al 2004). Indeed, the conventional synthesis of bulk BiMnO$_3$ requires high pressure and high temperature of 6 GPa and 1100 K (Moreira dos Santos et al 2004). In order to get stable and high quality, thin films of BMO can be grown by ensuring a low mismatch between the substrates and the films which reduces mechanical stress on the films (Langenberg et al 2007). To do so, n-type silicon (100), n-type silicon (111) and platinized silicon [Pt(111)/Ti/SiO$_2$/Si(100)] substrates are used, which offer a lower percentage of strain on the BMO films.

It is of great interest to investigate Calcium (Ca) modified BMO (Bi$_{1-x}$Ca$_x$MnO$_3$) system as it exhibits insulating behaviour for a broad range of ‘x’ values and the charge ordered phase occurs approximately at $T_{CO} = 325K$ (Bokov et al 1967; Frontera et al 2000; Woo et al 2001). This charge order transition is accompanied by symmetry breaking which may lead to ferroelectricity around the RT. Furthermore, it has been proved that doping with diamagnetic bivalents (Ba$^{2+}$, Ca$^{2+}$, Pb$^{2+}$ and so on) in Bi site of BiMnO$_3$ is an effective way to enhance the magnetism (Khomchenko et al 2009; Khomchenko et al 2007; Kothari et al 2007; Wang et al 2006). By partially replacing Bi$^{3+}$ cations with Ca$^{2+}$, it is possible to hold the same phase as that of BiMnO$_3$ because Ca$^{2+}$ (1.12 Å) has smaller ionic radius than Bi$^{3+}$ (1.24 Å) ions. Moreover, it becomes quite necessary to investigate the structural, magnetic and electrical properties of the BCMO films at RT for efficient application in memory devices.
1.9 OBJECTIVES

The objectives of the present research are

i. To select a suitable substrate for fabricating dense, crack free and high crystalline BMO films under optimized growth conditions by RF magnetron sputtering.

ii. To choose a suitable dopant of different concentrations that has to be added to BMO films for achieving better electrical and magnetic properties towards the application in data storage devices.

iii. To investigate the structural, elemental, magnetic, dielectric, and ferroelectric properties of the pure and doped BMO films for finding the suitability in device applications.

iv. To expose the irradiation like H\(^+\) ions and \(\gamma\)-ray on the surface of the films in order to enhance the properties of pure and doped BMO films.

1.10 ORGANIZATION OF THE THESIS

The present thesis has been divided into seven chapters.

Chapter 1 has introduced the multiferroic materials and their physical background. The coupling between ferroic parameters and the pathway for multiferroism are discussed. The unit cell structure of perovskite BMO system is diagrammed. The origin of FE and FM in BMO system is presented elaborately. The existing experimental researches on bulk and thin films of BMO system are reviewed briefly. Finally, motivations of the current study along with the objectives of the research are highlighted.
Chapter 2 presents the thin film growth techniques, RF magnetron sputtering and thermal evaporation adopted for the deposition of BCMO films and top metal electrode for electrical studies respectively. The procedure for the preparation of BCMO targets by solid state reaction method is specified. In addition, the experimental techniques used to characterize the prepared BCMO films are given in detail.

Chapter 3 investigates the effect of substrates on the structural, morphological, elemental, magnetic and electrical properties of BMO films. The films are grown by RF magnetron sputtering on n-type silicon substrate with two different orientations (100) and (111) at the substrate temperature of 600 °C.

Chapter 4 deals with the growth and characterization of $\text{Bi}_{1-x}\text{Ca}_x\text{MnO}_3$ ($0 \leq x \leq 0.4$) thin films deposited on n-type Si(100) substrate at two different temperatures of 400 and 800 °C.

Chapter 5 elaborates the deposition of $\text{Bi}_{1-x}\text{Ca}_x\text{MnO}_3$ ($0 \leq x \leq 0.4$) films on Pt(111)/Ti/SiO$_2$/Si(100) substrates at 400 and 800 °C temperatures to enhance further the electrical properties of the films. The functional properties of the films are also analyzed.

Chapter 6 provides the effect of H$^+$ ions and $\gamma$-ray irradiation on the structural, elemental, magnetic and electrical properties of $\text{Bi}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$ thin films grown on Si (100) substrate at 400 °C.

Chapter 7 describes the conclusion and the salient features of the research described in this thesis. It gives the scope for potential development in data storage devices in the future.