In this chapter we briefly review the literature on multiferroic materials. The chapter starts with an introduction on ferromagnetic, ferroelectric and ferroelastic materials. Multiferroic materials, their classification, and magnetoelectric coupling are introduced. Landau theory and spin current model associated with spin frustrated multiferroics are discussed. The chapter is concluded with motivation and the questions that the present thesis seeks to answer.
1.1 Introduction

Several recent discoveries involving magnetism driven ferroelectricity and new insight into the intertwined states of electric, magnetic and elastic order parameters have redefined the broad scope of research in multiferroic materials [1, 2, 3, 4, 5]. Such multifunctional materials are of great technological significance; potentially it could lead to eight-state memory devices, magnetic field sensors, gate ferroelectrics based field-effect transistors, and electric field controlled magnetic resonance devices [6, 7]. Furthermore, because of the associated rich magnetic-electric-elastic phase diagram, new functionalities and their theoretical foundations are under intense investigation [3].

The concept of multiferroic materials owes its origin to the discovery magnetoelectric (ME) effect, over a century ago, by P. Curie [8] and its material verification in PbFe0.67W0.33O3 by Smolenskii et al. [9]. By definition, these materials can sustain induced magnetization with the application of electric field and electric polarization by means of magnetic field. This ME interdependence occurs because of pronounced interplay between various subsystems of crystal structure that lead to coupling between ordered ferroelectric and (anti)ferromagnetic phases [5, 10, 11]. However, practical application of devices based on ME effect remain hindered by the small electric polarization, low onset temperature and lack of a comprehensive understanding of the microscopic origin of multiferroicity. The current revival of interest in these materials is assigned to a seminal work by Spaldin; Why are there so few magnetic ferroelectrics? [5] This was further consolidated by discovery of multiferroicity in a new class of materials where ferroelectricity is caused by non-collinear magnetic ordering [1, 2, 3, 12, 13].

From practical application point of view it is important to search for materials having substantial ME coupling at room temperature. In this thesis, we have studied this possibility by choosing Bi2Fe4O9 which has a frustrated antiferromagnetic (AFM) spin structure close to room temperature (∼ 265 K). Also, due to competing magnetic interactions, large number of degenerate ground state can arise at low temperature. Depending on the spin configuration of the particular ground state one can have ferroelectricity [1, 2]. Towards this end we have studied Ni3V2O8. The value of spontaneous polarization (Ps) for most of the spin frustrated multiferroic materials is very low (Ps ∼ 0.01-few μC/cm²) as compared to the
conventional ferroelectrics ($P_s \approx 26 \mu C/cm^2$ for BaTiO$_3$ at 300 K). Tuning and enhancing the ME coupling in multiferroics is another important research area. This aspect is studied by depositing lattice mismatched thin film of hexagonal YMnO$_3$ on sapphire substrate with Zn$_{0.90}$Ga$_{0.01}$O buffer layer. Towards a better understanding of the microscopic origin of multiferroicity in spin frustrated systems we have studied temperature and magnetic field dependent neutron diffraction in the prototype hexagonal YMnO$_3$ and its doped variants.

1.2 Ferromagnetic, ferroelectric and ferroelastic materials

Magnetic and ferroelectric materials pervade every aspect of modern science and technology. *Ferromagnetism* involves spontaneous magnetization below a critical temperature that can be switched and saturated ($M_s$) along the direction of external magnetic field ($H$). There is a remanent magnetization ($M_r$) once the field is removed and applications of these materials are determined by the values of the remanent magnetization ($M_r$) and coercivity ($H_C$). For example, a square-shaped hysteresis loop with high remanent magnetization and high coercive field is needed for permanent magnet applications, while materials with narrow hysteresis loops are needed for recording media. The fundamental and application issues associated with magnetic random-access memories (MRAMs) and related devices have been pursued intensely [14, 15, 16, 17].

*Ferroelectricity*, on the other hand, is the phenomenon that involves electrical polarization. A ferroelectric material undergoes a phase transition from a high-temperature phase (paraelectric state) above the Curie temperature ($T_C$) to a low temperature phase (ferroelectric state) that has a spontaneous polarization along a preferred direction. As electric field is applied, ferroelectric materials exhibit a saturation polarization ($P_S$) along the direction of the applied electric field. Once saturation is reached, remanent polarization ($P_r$) remains in the absence of an external electric field. This polarization direction can be reversed by switching the external electric field. The sensor and actuator industry relies on ferroelectric materials because most ferroelectrics, especially perovskite oxides, are high-performance ferroelastics or piezoelectrics with spontaneous strain [14, 15, 18]. The coexistence of strain and polarization allows these materials to be used in broad applications in which elastic energy
is converted into electric energy and vice versa. Since the discovery of ferroelectricity in Rochelle salts (KNaC₄H₄O₆·4H₂O) in 1920 [19], a great number of ferroelectric compounds have been found and investigated.

Ferroelasticity is a phenomenon which involves spontaneous deformation (ε). In ferroelastic materials, by applying stress (σ) (in the ferroelastic phase), transition from one phase to another with an equally stable structure but of different orientations is achieved. This process involves motion of twin boundaries, and these stress-induced phase changes result in spontaneous strain in the material. The shape memory effect and superelasticity are important phenomena which involve ferroelasticity.

1.3 Multiferroic materials

The trend toward device miniaturization necessitates incorporation of multiple functions into a single material. Driven by numerous industrial applications of magnetic and ferroelectric materials, it is obvious to pursue a new generation of memory, sensor, and actuator devices with materials that combine magnetism, ferroelectricity and ferroelasticity (as shown in Fig 1.1). The coexistence and interplay between several order parameters (spin, lattice, charge and orbital degrees of freedom) in complex oxides offer such possibilities for new device functions [10, 20].

By definition, multiferroics are the multifunctional materials in which at least two ferroic orders coexists within the same system. This signifies that they can possess a spontaneous magnetization which can be reoriented by an applied electric field and a spontaneous polarization, which can be reoriented by a magnetic field [21, 22, 23, 24, 25]. Conventional antiferromagnets such as IrMn, NiO, and CoO do not have the ability to be tuned with an electric field; but oxides such as YMnO₃, Bi₂Fe₄O₉, Ni₃V₂O₈, and BiFeO₃ offer exactly such an opportunity so as to gain magnetic control of ferroelectric polarization [26, 27]. But the materials showing this multifunctional character are rare and the systems where these two disparate order parameters exhibit significant coupling are still rarer [5, 32, 3]. This is figuratively discussed in Figure 1. Figure 1(a) shows that the electric field (E), magnetic field (H) and stress (σ) independently control the electric polarization (P), magnetization (M), and strain (ε) respectively. In multiferroics, the coexistence of at least two ferroic forms
of ordering leads to additional interactions [33, 34]. As indicated in Fig 1(b), only a small subgroup of all magnetically and electrically polarizable materials are either ferromagnetic or ferroelectric, and fewer materials simultaneously possess both these order parameters. It is to be noted that ME features can also be indicated due to magnetoresistance, but these are not true multiferroics [35, 36, 37].

![Diagram](image)

Figure 1.1: (a) Relationship between ferroelectricity (polarization $P$ and electric field $E$), magnetism (magnetization $M$ and magnetic field $H$) and ferroelasticity (strain $\varepsilon$ and stress $\sigma$) [21]. (b) Phase diagram of magnetic and ferroelectric materials. Multiferroics exists only in the phase of joint magnetically and electrically ordered systems [11].

The multiferroics addressed in this thesis represent one such subgroup of materials that allows opportunities to develop efficient control of magnetization or/polarization by an electric field or/magnetic field (Fig 1.1). Historically, the discovery of multiferroic materials can be attributed to three independent events:

1. In 1865, J. C. Maxwell proposed four equations governing the dynamics of electric fields, magnetic fields and electric charges, which are known as Maxwell’s equations and showed that magnetic interactions and motion of electric charges, which were initially thought to be two independent phenomena, are intrinsically coupled to each other [38].

2. In 1888 Röntgen discovered that a moving dielectric became magnetized when placed in an electric field [39], which was followed by observation of the reverse effect—polarization of a moving dielectric in a magnetic field [40].

3. In 1894 Curie pointed out the possibility of intrinsic ME behaviour of (non-moving)
1.3 Multiferroic materials

crystals on the basis of symmetry considerations [8]. The basic idea of multiferroicity was introduced for the first time by Curie in 1920 after the discovery of switching behaviour in ferroelectric Rochelle salt by Valasek. The first theoretical understanding of ME coupling was proposed by Dzyaloshinkii, and Cr$_2$O$_3$ was predicted to be ME. This material was studied by Astrov but it was proved to be paraelectric and AFM, making microelectronic applications impractical [41].

In material science, magnetism and ferroelectricity are generally studied as two unrelated phenomena. But, in a sense ferroelectricity is an electronic version of magnetism which is associated with the polar arrangement of charges. In conventional industrial ferroelectrics such as BaTiO$_3$, or PbTiO$_3$, the requirement is to have empty $d$-orbital of transition metal ions. These positive charged ions make coordinate bonds with negative oxygen ions and collective shift of anions and cations inside the lattice results in a non-centrosymmetric crystal structure leading to bulk polarization. On the other hand, magnetism requires cations with partially filled $d$-orbitals, as completely filled or empty $d$-orbital have no role in magnetic ordering. The difference in filling of $d$-shells required for ferroelectricity and magnetism make them mutually incompatible.

The renaissance of research in ME multiferroics started around year 2000 and it can be attributed to three facts. First, the techniques, especially that of preparing and studying thin films of oxides was developed significantly. This permitted very good quality thin films of ferroelectric materials, and opened an avenue to use these systems. In 2003, R. Ramesh group successfully grew thin films of one of the most popular multiferroics, BiFeO$_3$ [3] with high saturation polarization. The multiferroic properties of bulk BiFeO$_3$ are fairly weak, but in thin-film form they are greatly enhanced. Second, several new multiferroic systems were discovered [2, 43, 44] with rather spectacular properties, in particular, very strong coupling between ferroelectric and magnetic degrees of freedom. In 2003, Tokura and Kimura discovered a new multiferroic compound TbMnO$_3$ [45, 46], Cheong discovered TbMn$_2$O$_5$ [47], and in 2008 we showed magnetodielectric effect near room temperature in Bi$_2$Fe$_4$O$_9$ [48]. These new multiferroics are in turn proving to be rich source for exploring the fundamental science of phase control and ME interactions, partickularly with regard to ferroelectricity derived from spin frustration [2]. And third is probably a much broader
realization that with these new technical facilities and with novel materials, one can think of many interesting and very promising applications [49, 50, 51].

1.4 Spin frustration

Frustrated spin systems have always attracted considerable attention because of their novel magnetic and multiferroic properties [30, 31]. This frustration is caused either by competing interactions or lattice geometries, which disallow the energy minimization of all spin pairs simultaneously, and thus leading to a large number of degenerate spin configurations. In principle, there is no long range spin ordering in strongly frustrated magnetic systems. However, magnetic frustration can often be lifted by a symmetry-reducing lattice distortion at finite temperature that allows long-range magnetic order at lower temperatures [52, 53].

![Figure 1.2: Geometrically frustrated (a) equilateral triangle (b) tetrahedron and (c) Kagomé lattices](image)

By definition, spin frustrated magnets are materials in which localized magnetic moments or spins, interact through competing exchange interactions that cannot be simultaneously satisfied, giving rise to a large degeneracy in the ground state of the system. The simplest case of spin frustration is provided by three antiferromagnetically coupled spins at the corners of an equilateral triangle; if two spins are antiparallel to each other, the third spin cannot be antiparallel to both of them (Fig 1.2 a). Situation of spin frustration gets even more complicated for AFM interactions between spins at the corners of a tetrahedron. In this case, two of the bonds are frustrated (Fig 1.2 b). Another well known example of spin frustration is Kagomé lattice which is formed by corner sharing triangles in two dimensions.
Most of the spin frustrated systems, when cooled below certain temperature, acquire a long range ordered state that reflects non-collinear or compromised spin configurations. For example in a triangular lattice the three spins are aligned at 120° (Fig 1.3a). The corresponding compromised configuration for the tetrahedral lattice is the 109° structure and is shown in Fig 1.3(b). In both cases there are other ways to achieve these non-collinear configurations which introduces degeneracy in the ground state. In spite of intensive investigation of the properties of insulating magnetic materials, relatively little is known about compounds for which the long-range magnetic ordering of strongly interacting spins is frustrated by their geometric arrangement in the crystal lattice [54].

Figure 1.3: Compromised non-collinear magnetic structures: (a) the 120° structure on a triangular lattice, (b) the 109° structure on a tetrahedral lattice and (c) the 120° structure on a Kagomé lattice.

Such materials are unique in a way that they allow the study of a spin system which remains magnetically disordered when cooled well below the ordering temperature expected from the strength of the pairwise spin interaction. Study of frustrated systems relies mainly upon observation of their bulk properties, namely neutron diffraction, magnetic susceptibility and specific heat capacity. In the paramagnetic state, bulk magnetic interactions are governed by the Curie-Weiss Law:

$$\chi = \frac{C}{T - \Theta_{CW}}$$  \hspace{1cm} (1.1)

where $\chi$ is the molar magnetic susceptibility, $C$ is the Curie constant, $T$ is the temperature and $\Theta_{CW}$ is the Curie-Weiss constant. By fitting the inverse susceptibility versus temper-
1.5 Magnetoelectric coupling in multiferroics

In the most general way, the control of magnetic order parameter by electric field or electric order parameter by magnetic field is defined as ME coupling. Attempts to combine the dipole and spin orders into one system started in the 1960's [55, 56], and some multiferroics, including boracites (Ni$_3$B$_7$O$_{13}$I, Cr$_3$B$_7$O$_{13}$Cl) [56], fluorides (BaMF$_4$, M = Mn, Fe, Co, Ni) [57, 58], magnetite Fe$_3$O$_4$ [59], (Y/Yb)MnO$_3$ [60], and BiFeO$_3$ [61] were identified in the following decades. The first successful observation of the ME effect was realized in Cr$_2$O$_3$, and the ME coupling coefficient was 4.13 ps m$^{-1}$ [62]. To realize the ME coupling for application point of view it is important to have materials whose different degrees of freedom are coupled strongly. In single phase materials, ME effect is described by writing the Landau

\[ C = \frac{Ng^2\beta^2S(S+1)}{3k_B} \]  

(1.2)

and

\[ J = \frac{3\Theta_{CW}k_B}{2S(S+1)} \]  

(1.3)

Fitting the inverse susceptibility versus temperature for a non-frustrated antiferromagnet yields a value $\Theta_{CW}$ that is similar in magnitude to the observed Néel transition temperature, $T_N \sim \Theta_{CW}$. In the spin frustrated system, however, the observed $T_N$ is significantly smaller relative to $\Theta_{CW}$ because fluctuations among highly degenerate states suppress the transition to long range order. Ramirez defines a frustration parameter, $f$, as an empirical means of quantifying frustration.

\[ f = \frac{|\Theta_{CW}|}{T_N} \]  

(1.4)
1.6 Classification of multiferroics

The free energy $F$ in terms of magnetic field $H$ and applied electric field $E$, i.e.

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

(1.5)

Here $H_i$ and $E_i$ are the $i^{th}$ component of magnetic ($H$) and electric ($E$) field respectively. $P^S$ and $M^S$ denote the spontaneous polarization and magnetization respectively; $\varepsilon_0$ and $\mu_0$ are the permittivity and permeability of free space respectively. Differentiating free energy (Eq. 1.5) with respect to $E_i$ and then setting $E_i = 0$, we get,

$$P_i(E, H) = - \frac{\partial F}{\partial E_i} \bigg|_{E_i=0} = P^S_i + \alpha_{ij} H_j + \frac{1}{2} \beta_{ijk} H_i H_k + \ldots$$

(1.6)

The complementary operation involving $H_i$ gives us,

$$M_i(E, H) = - \frac{\partial F}{\partial H_i} \bigg|_{H_i=0} = M^S_i + \alpha_{ij} E_j + \frac{1}{2} \gamma_{ijk} H_i E_j + \ldots$$

(1.7)

Here $\varepsilon_{ij}$ and $\mu_{ij}$ are relative permittivity and permeability respectively, and are second rank tensors. The second rank tensor $\alpha_{ij}$ represents the induction of polarization (magnetization) by magnetic (electric) field and is termed as linear ME coupling. The third rank tensors $\beta_{ijk}$ and $\gamma_{ijk}$ are higher order (quadratic) ME coupling terms. The magnitude of first order ME response of a material is governed by the relation: $\alpha_{ij}^2 \leq \varepsilon_0 \mu_0 \varepsilon_{ij} \mu_{ij}$ [11, 22]. This relation is a key implication toward the fact that ME coupling can only be large in ferroelectric and/or ferromagnetic materials.

1.6 Classification of multiferroics

On the basis of microscopic origin, all the multiferroics can be broadly categorized in two classes: type-I multiferroics and type-II multiferroics [4, 63].

1.6-1 Type-I multiferroics

This group contains the materials in which the origin of ferroelectricity and magnetism are independent of one another. The ferroelectric transition temperature is generally much higher than the magnetic transition temperature and as a result a very weak ME coupling exists. The spontaneous polarization is $\sim 10$ - $100 \mu C/cm^2$, which is rather large. The
major challenge for this group of material is to enhance the ME coupling without affecting its positive features. This group of materials can be divided into following major subclasses:

1.6-1.1 Multiferroic perovskites

In many magnetic perovskite and perovskite ferroelectrics the magnetism and ferroelectricity are mutually exclusive. As already mentioned, for magnetism, partially filled $d$-shell of transition metal and empty $d$-shell for ferroelectricity are required. This is called $d^0$ versus $d^n$ problem [5, 4]. Multiferroic perovskites were grown for the first time in 1958 by Smolenskii’s group, by substituting noble gas shell in ferroelectrically distorted perovskite lattices with magnetically active $3d$ ions [64]. This leads to ferroelectric AFM compositions like PbFe$_{0.5}$Nb$_{0.5}$O$_3$ (PFN), PbFe$_{0.5}$W$_{0.5}$O$_3$ and PbFe$_{0.5}$Ta$_{0.5}$O$_3$. In some such systems transition temperatures are rather high, e.g. in PbFe$_{0.5}$Nb$_{0.5}$O$_3$ $T_{FE} = 387$ K and $T_N = 134$ K. A saturated polarization as high as $\sim 65 \mu C/cm^2$ in epitaxial PFN thin films was also reported, demonstrating excellent ferroelectric property [65]. However, the coupling between ferroelectric and magnetic subsystems is rather weak due to the fact that different ions are responsible for ferroelectricity and magnetism; and ferroelectricity has nothing to do with the presence of transition metal ion.

1.6-1.2 Ferroelectricity due to lone pair

The compounds which belong to this group have general formula ABO$_3$ and the multiferroicity originates from combining A-site (lone pair) ferroelectricity with B-site magnetic order. Bi and Pb based perovskites (BiFe$_3$, BiMn$_3$, and PbVO$_3$) fall in this group [66, 67, 68]. The properties of this group are largely determined by the $6s^2$ lone pair of non magnetic Bi$^{3+}$ which is “stereo-chemically active” and is the main driving force for off-center distortion [4, 63, 68]. Recently, the role of the lone pair in driving the antiferroelectric transition in the ordered double perovskite Pb$_2$MgWO$_6$ has been studied [69]. Because the ferroelectric and magnetic orders in these materials are associated with different ions, the coupling between them is weak. For example, BiFe$_3$ shows a ferroelectric Curie temperature $T_C \sim 1100$ K, and AFM transition temperature $T_N \sim 643$ K, below which the two orders coexist. BiMn$_3$ is another unique compound, in which both M and P are reasonably large. It has a monoclinic perovskite structure, and shows a ferroelectric transition at $T_C \sim 800$K accompanied
by a structure transition with the remnant polarization of $\sim 16 \mu C/cm^2$, and a ferromagnetic transition at $T_{FM} \sim 110K$, below which the two orders coexist.

1.6-1.3 Ferroelectricity due to geometrical constraints

Hexagonal multiferroics $RMnO_3$ ($R = Ho - Lu or Y$) fall into this category and are often cited as typical examples that violate the "$d^0$-ness" rule. Hexagonal $YMnO_3$ is a well known example from this class with $T_{FE} \sim 950 K$ and $T_N \sim 70 K$ [70, 71]. Ferroelectricity in $YMnO_3$ is driven by electrostatic and size effects of Y cation. Off-centering of Mn ion is energetically unfavourable and ferroelectricity arises from buckling of $MnO_5$ trigonal bipyramids [72]. The Mn spins undergo long-range ordering at $T_N$ by forming a non-collinear configuration with a $120^0$ angle between neighbouring spins. The spin configuration of hexagonal $YMnO_3$ is frustrated and easy plane anisotropy of Mn spins restricts the moments strictly on the ab-plane. Therefore, $YMnO_3$ is an excellent example of a quasi-two-dimensional Heisenberg magnet on a triangular lattice with a spin frustration generated by geometric constraint. In contrast to the case of perovskite multiferroics, relatively few examples of element substitution have been reported for hexagonal manganites thus far. A detailed study of hexagonal $YMnO_3$ and doping at Y site is presented in chapter 6 and 7.

1.6-1.4 Charge ordered multiferroics

This class of compounds were first discovered by Khomskii and co-workers. When $LaMnO_3$ ($Mn^{3+}$) and $CaMnO_3$ ($Mn^{4+}$) are alloyed, then the resulting arrangement of $Mn^{3+}$ and $Mn^{4+}$ ions can be ordered, which is called as charge ordering [73]. Charge ordering is very common in materials containing narrow band transition metal ions with strong electronic correlation. At low temperatures these charge carriers are localized and form periodic superstructures. If somehow these charges order in a non-symmetric manner, electric polarization is induced. The well known example of this class of materials are $RFe_2O_4$ ($R= Y, Lu, Eu$, etc) [74], $Ca_3CoMnO_6$, $TbMn_2O_5$, and $RNiO_3$ [75, 76]. $Pr_{1-x}Ca_xMnO_3$ is another member where the coexistence of bond-centered and site-centered charge ordering leads to a non-centrosymmetric charge distribution and a net electric polarization [73]. Unfortunately, these proposed charge-ordered multiferroics are unlikely to be of immediate practical use because the electric polarization is very small and the magnetic ordering is essentially AFM. Also,
the electric and magnetic ordering temperatures are far below room temperature [77, 78].

1.6-2 Type-II multiferroics

These multiferroics are relatively newly discovered as compared to type-I multiferroics. These are also called as magnetically driven ferroelectrics where the macroscopic electric polarization is induced by magnetic long-range order. In general, magnetic frustration is the microscopic source of multiferroicity in these systems. Due to high tuneability of electric dipoles by applying magnetic field, these compounds are considered as the best candidate for useful multiferroics. A necessary but not sufficient condition for the appearance of spontaneous electric polarization is the absence of inversion symmetry. In these materials inversion symmetry is broken by magnetic ordering. Such a symmetry breaking often occurs in frustrated magnets, where competing interactions between spins favour unconventional magnetic orders [79, 80, 81]. Due to this the ME coupling in type-II multiferroics is larger as compared to type-I. However these materials usually show very small ferroelectric polarization ($\sim 10^{-2}$ $\mu$C/cm$^2$) which appears at very low temperatures. The major challenge in this group of materials is to enhance the magnitude of ferroelectric polarization as well as ferroelectric transition temperature without affecting its ME coupling features. This group of materials can be divided into two major subclasses, and they are as follows:

1.6-2.1 Spiral spin structure multiferroics

This class of compounds are also called as spin driven ferroelectrics where the appearance of a spiral (non-collinear) magnetic structure is accompanied by ferroelectric order. But not all spiral magnetic structures induce ferroelectricity in the system. These materials belong to a Mott insulators with an integer number of electrons per site. The term spiral is defined as the spin vectors lying within a plane, such that the components of the spin along two axes at right angles in the plane have a periodic variation along some arbitrary direction in the crystal. Figure 1.4 schematically represents the collinear (I), and non-collinear (II-IV) spiral spin structures. The nature of angle between spin rotation axis and propagation vector makes the spin arrangement to be in (I) sinusoidal, (II) screw spiral, (III) cycloidal spiral, (IV) conical (1), and (V) conical (2). When the spins on the adjacent atomic sites
are canted from each other (Fig 1.4 II-V), their symmetry is lost along the horizontal mirror plane leading to possible generation of polarization along the vertical direction via spin-orbit interaction [1, 2, 45]. The discovery of ferroelectricity in TbMnO$_3$ in 2003 opened a recent boom of spin driven ferroelectrics.

Figure 1.4: Schematic illustration of types of magnetic structure with a long wavelength. (I) Sinusoidal, (II) screw, (III) cycloidal, and (IV, V) conical structures. Geometric configurations of the unit vector connecting the neighboring magnetic moments at $i$ and $j$ sites $\vec{r}_{ij}$ and the vector spin chirality $(\vec{e}_i \times \vec{e}_j)$ are also shown for the respective structures [2].

The spiral spin states are widely seen in complex transition-metal compounds like spinels and perovskites, where competing exchange interactions of the neighbouring spins can produce periodically modulated spin structures. Compounds Cr$_2$BeO$_4$, ZnCr$_2$Se$_4$, orthorhombic RMnO$_3$ (R = Tb, Dy, Eu, Y) [45], Ni$_3$V$_2$O$_8$ [82], MnWO$_4$ [83], CoCr$_2$O$_4$, CuO, and CuFeO$_2$ can be considered in this category. Recent discovery of high-temperature multiferroic coupling in CuO by Kimura et al. opens a new hunting ground in the area of geometrically frustrated spin spiral magnets [12]. Interestingly, the dielectric properties of this class of compounds is very sensitive to the applied magnetic fields as the ferroelectricity is induced by complex spin structure which is the characteristic of frustrated magnets.
1.6-2.2 Collinear spin structure multiferroics

This is another class of compounds, where ferroelectricity is induced by collinear magnetic order without spin orbit interactions. In this mechanism, the ferroelectricity originates from lattice relaxation through exchange-striction, that is associated with the symmetric superexchange coupling. For example, in RMn$_2$O$_5$ (R = Tb-Lu), a nearly-collinear acentric magnetic order with broken inversion symmetry was proposed to be responsible for the ferroelectricity. Another example is the so called E-type magnetic order (e.g. HoMnO$_3$), where collinear order combined with alternating oxygen cage rotations, has been suggested as the origin of ferroelectricity. Ising chain magnet Ca$_3$CoMnO$_6$ is quite unique, because the ferroelectricity (FE) is driven by exchange-striction in a collinear Ising spin chain consisting of charge ordered transition-metal ions [75].

1.7 Theoretical understanding of magnetoelectric coupling

Having listed the different types of materials that show coupling between electric and magnetic orderings, we can summarize some aspects of current theoretical understanding in the field.

1.7-1 Landau theory of phase transition

Landau theory of phase transition is extensively used in order to model the magnetoelectric (ME) coupling in various multiferroics. Magnetocapacitance and anomalies in the dielectric constant due to magnetic ordering are defined as ME coupling. Landau theory is a symmetry based analysis of equilibrium behavior near the phase transition. This theory characterizes the phase transition in terms of an “order parameter”, which is zero in the high-temperature disordered state, and becomes finite continuously or discontinuously as the symmetry is lowered. The free energy is then expanded as a power series in this order parameter. Only terms which are invariant with respect to all symmetry operations are included. The equilibrium state is found by minimizing the free energy with respect to the order parameter. Other thermodynamic properties can be computed by relevant differentiation. In the field of
multiferroics, Landau modelling is mainly used to explain the magnetocapacitance of various samples [67, 84, 85].

Smolenskii defined [55], and Kimura et al. [67] used the order parameters for ferroelectric and magnetic subsystems and added a term $\gamma P^2 M^2$ to account for the ME coupling. Polarization, $P$, is the order parameter for the ferroelectric subsystems, $M$, the magnetization, is the order parameter for the magnetic subsystems, and $\gamma$ is the ME coupling coefficient. In the framework of the Ginzburg-Landau theory for the second order phase transition, the thermodynamic potential $\Phi$ can be written in the form,

$$\Phi = \Phi_0 + \alpha P^2 + \frac{\beta}{2} P^4 - P E + \alpha' M^2 + \frac{\beta'}{2} M^4 - M H + \gamma P^2 M^2$$

(1.8)

where $\Phi$, $\alpha$, $\beta$, $\alpha'$, $\beta'$, and $\gamma$ are functions of temperature. The term representing ME coupling, $\gamma P^2 M^2$, is always allowed regardless of symmetry. Kimura et al. used this free energy expression to calculate the effect of magnetic ordering on the dielectric susceptibility, $\epsilon = \chi_\epsilon + 1$. The dielectric constant can be derived using the relation:

$$\frac{1}{\chi_\epsilon} = \frac{d\Phi}{dP^2} = \alpha + \gamma M^2$$

(1.9)

Consequently, the dielectric constant can be developed for small $\gamma M^2$ values as follows:

$$\epsilon = \chi_\epsilon + 1 = \frac{1}{\alpha + \gamma M^2} + 1 \approx 1 + \frac{1}{\alpha} - \frac{\gamma M^2}{\alpha^2}$$

(1.10)

From the above equation 1.10, one can conclude that the effect of magnetic ordering on the dielectric constant will be proportional to $\Delta \epsilon \sim M^2$.

### 1.7-2 Spin current model

Spin current model or the inverse Dzyaloshinskii-Moriya (DM) model is the microscopic quantum theory of ME effect proposed by Hosho Katsura, Naoto Nagaosa, and Alexander V. Balatsky [86] based on the electronic states of the atoms. It has been shown theoretically that the overlap of the electron wave function between the two atomic sites with canted spins generates a genuine electronic polarization \textit{via} the spin-orbit interaction. In other words, spontaneous spin-current flows between the mutually canted spin sites. By analogy to the charge current, producing magnetic field, the spin current produces a fictitious electric field or
electric polarization. According to this model, magnetic ordering results in the hybridization of electronic orbitals producing a polar charge distribution. Here the electronic Hamiltonian is constructed by considering the spin-orbit interaction and spin current. The ME effects are proved to be directly related with the noncollinear spin structure.

For example, let us consider a cycloidal spin structure where spins rotate in the $bc$-plane along the $b$ axis, and focus on two nearest neighbour (NN) spins along the $b$ axis, termed $\vec{S}_1$ and $\vec{S}_2$. The DM interaction Hamiltonian between the two spins is written as:

$$H_{DM} = \vec{D} \cdot \vec{S}_1 \times \vec{S}_2$$  \hspace{1cm} (1.11)

where $\vec{D}$ is the DM vector which is of the order of $\lambda t_{pd}^4/\Delta E^4$. Here $\lambda$ is the relativistic spin-orbit coupling, $t_{pd}$ is the electron transfer integral between NN Oxygen 2$p$ and the transition-metal 3$d$ orbitals. $\delta$ is the energy separation between the ground and excited states. Above the spin ordering temperature, it is assumed that there is a reflection symmetry at the center of the bond connecting sites $i$ and $j$, and $\vec{D} = 0$. With decreasing temperature, a cycloidal spin order sets in at a certain temperature due to frustrated exchange interactions, and the vector chirality $\vec{S}_i \times \vec{S}_j$ becomes finite. Then in order to gain the DM interaction energy in Eq. (1.11), a spontaneous breaking of inversion symmetry along the $c$ axis is induced and $\vec{D}$ becomes finite. This is the inverse process of the usual DM interaction in magnets, where the DM vector is finite, i.e., $\vec{D} \neq 0$, due to the low symmetry crystal structure in all temperature range.

According to the spin-current model or the inverse DM model, the electric polarization $\vec{P}_{ij}$ produced between the mutually canted magnetic moments ($\vec{S}_i$ and $\vec{S}_j$) on the neighbouring sites $i$ and $j$ is given as

$$\vec{P}_{ij} = A_0 \vec{e}_{ij} \times (\vec{S}_i \times \vec{S}_j)$$  \hspace{1cm} (1.12)

Here, $\vec{e}_{ij}$ is the unit vector along the direction from the site $i$ to $j$, and $A_0$ a coupling constant related to the spin-orbit and spin-exchange interactions. This model can explain the ferroelectricity in RMnO$_3$ (R = Tb and Dy), Ni$_3$V$_2$O$_8$, CoCr$_2$O$_4$, LiCu$_2$O$_2$, etc., qualitatively. In these materials, external magnetic field influences the configuration of the magnetic order, leading to changes in ferroelectric or dielectric properties. Spectacular cross-coupling effects,
such as reversible flipping of ferroelectric polarization or drastic changes in dielectric constant in applied magnetic fields, have been recently observed in magnetism-driven ferroelectrics.

Figure 1.5: Schematic view of the inverse Dzyaloshinskii-Moriya interaction mechanism. The cluster model of two transition metal ions R1, R2 separated by oxygen atom is shown. Here $\vec{S}_i$ and $\vec{S}_j$ are the noncollinear spin directions at metal sites R1 and R2 respectively. $\vec{j}_s \propto \vec{S}_i \times \vec{S}_j$ is the spin current due to noncollinear spin directions $\vec{S}_i$ and $\vec{S}_j$. The direction of the electric polarization ($\vec{P}$) is given by $\vec{P} \propto \vec{e}_{ij} \times \vec{j}_s$ where $\vec{e}_{ij}$ is the unit vector connecting R1 and R2 [86].

A vastly increasing variety of spin-spiral and geometrically frustrated compounds allowing ferroelectricity according to Eq. (1.12) is at our disposal for multifunctional ME order-parameter control. Systems with conical spin spirals and in-built frustration suggest themselves for electric-field control of a macroscopic magnetization, and the discovery of mechanisms promoting magnetically induced ferroelectricity.
1.8 Motivation and scope of the present thesis

Multiferroic systems that are prone to small external perturbations, such as applied magnetic (electric) field result in a small modulation in the spontaneous polarization (magnetization). However, the complete rotation of ferroelectric domains by magnetic fields has rarely been observed. The main challenge in this area of research is to find materials exhibiting robust magneto-electric properties at room temperature. Through this thesis work, we try to address the following key problems:

1. Most of the reported multiferroic materials are AFM and it has now been established that spin frustration is the basis of multiferroicity in them (discussed in section 1.5). These materials have very limited practical application because frustration induced ferroelectricity tends to exist only at low temperatures and the magnitude of polarization is negligibly small. From technological point of view the relevant question is, whether it is possible to achieve multiferroic properties at room temperature by suitably choosing materials having room temperature noncollinear AFM spin structure? Orthorhombic Bi$_2$Fe$_4$O$_9$ is an example of material having spin frustrated AFM structure below \( \approx 265 \) K. Chapter 3 deals with the discovery of promising ME coupling in Bi$_2$Fe$_4$O$_9$, which shows its magnetodielectric character very near to room temperature. Sample preparation and various characterization techniques of this novel compound are discussed in detail.

2. Ni$_3$V$_2$O$_8$ is also another example of AFM insulator having orthorhombic crystal structure. Below 10 K, it undergoes various phase transitions namely, high temperature incommensurate phase (HTI), low temperature incommensurate phase (LTI) and two commensurate phases (C and C'), which exists for \( T < 2.3 \) K. A ferroelectric phase is identified in LTI magnetic phase. The magnetic structure of C' phase appears to be complex [94]. High field (\( \mu_0 H = 10 \) T) optical measurements on NVO are in conformity with ND experiments and indicate the presence of another additional phase below 2 K [95]. The presence of this new phase also got support from spontaneous polarization measurements above an applied field of 2 T [96]. In chapter 4, phase pure polycrystalline multiferroic Ni$_3$V$_2$O$_8$ is prepared using solid state reaction method. Using
1.8 Motivation and scope of the present thesis

magnetic, dielectric and high field specific heat measurements, the low temperature field induced ferroelectric phase below 2.3 K is confirmed.

3. When a thin film is grown, a significant amount of strain is always present between thin film and substrates. There are several reports on substantial increase of the spontaneous polarization and Curie temperature due to strain. In the similar way, it is possible to affect the saturation magnetization and Neél temperature by the means of strain. An open question that is of current interest is, whether it is possible to tune the ME coupling and AFM transition temperature by strain? In chapter 5, we have chosen hexagonal YMnO$_3$ as our model system deposited on sapphire substrate with Zn$_{0.99}$Ga$_{0.01}$O as bottom electrode. Magnetization and temperature dependent dielectric measurements clearly establish that magnetic and electric order parameters in YMnO$_3$ can be tuned by the means of strain.

4. The understanding of the microscopic origin of multiferroicity in various multiferroic systems is still evolving. Specially, in case of geometrically frustrated hexagonal YMnO$_3$, there is a big debate on whether the microscopic origin is of magnetoelastic or magnetoelectric in nature. Recently, various experimental results have pointed out the existence of "giant" spin-lattice coupling for interplay between magnetic and electric order parameters [97, 98, 99]. The presence of strong spin-lattice coupling is supported by zero field neutron diffraction experiments [100, 101]. It was also shown that electric polarization (dielectric constant) across the AFM transition showed the same temperature dependence as the effective ordered moment assigned to Mn$^{3+}$ state. Chapter 6 sets a question as to whether the magnetic field dependence of dielectric constant in YMnO$_3$ is caused by ME coupling, that necessarily requires an ordered magnetic state, or due to exchange-striction driven magnetoelastic coupling. This is investigated by using temperature and magnetic field dependent ND experiments.

5. The origin of giant magnetoelastic coupling observed in hexagonal manganites is still under intense investigation. Another important aspect of hexagonal RMnO$_3$ is to tune its magnetoelastic coupling by chemical substitution. In hexagonal YMnO$_3$, Y$^{3+}$ is non-magnetic and we have chosen magnetic Dy to dope at Y site. Due to high
neutron absorption coefficient of naturally occurring Dy it is very challenging to study
the crystal and magnetic structure of Dy doped YMnO₃ using ND experiments. In
Chapter 7, a detailed analysis of powder ND studies on polycrystalline Y₁₋ₓDₓMnO₃
(x = 0, 0.05) as a function of temperature is presented. We also study the modification
in magnetic, thermodynamic, and dielectric properties in YMnO₃ due to Dy doping.
Partial replacement of Y by Dy triggers the reduction in the tilting of MnO₅ polyhedra
which causes considerable decrease in T_N as well as ME coupling. Our results points
to the modification in the magnetoelastic coupling due to Dy doping in YMnO₃.

6. In chapter 8, the major findings of the work is summarized and future directions are
outlined.
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