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## *Chapter 1*

### *Introduction*



Day by day, there is an increasing requirement for emerging novel materials for an innovative technology-driven up-to-date society. Thus, the focus has been given to control material function via different means i.e., to grow materials with tunable physical properties. In 1865, when James Clerk Maxwell projected four equations governing the dynamics of electric and magnetic fields as well as electric charges, it was clear that the magnetic communications and motion of electric charges are fundamentally united to each other. However, from modification in relativistic covariant form, these equations were reduced to only two equations for the electromagnetic field tensor, which successfully shows the unification of magnetism and electricity. Actually, magnetism and ferroelectricity are the most important parts of current technology such as for spintronics devices. Thus, nowadays people are focused on the new mission i.e., multiferroic materials, where electrical properties can be controlled by magnetic fields and vice-versa. Such magnetic ferroelectricity, showing an extraordinary sensitivity to applied magnetic fields, happens in a ‘frustrated system’ due to different competing interactions among spins and multifaceted magnetic orders. We will summarize key experimental findings and the theoretical understanding of these phenomena, which will create an intense understanding of potential switchable multifunctional devices.

## 1.1 Magnetic property

Magnetism is a force, basically originated as a result of the movement of electrical charges i.e., electrical current, by which magnetic materials attract or repel each other. As a matter of fact, every material consists of a tiny entity called atoms and each atom has a core called the nucleus, around which electrons are circulating and spinning. Electrons are electrically charged particles and hence their motions give rise to an electrical current and

hence each atom behaves as a microscopic magnet. The magnetization of any material is exclusively depending on the electronic configuration of its constituent ions. In most substances, equal numbers of electrons spin in opposite directions, which cancels out their magnetization thus leading to zero magnetic moments, but if there exists any unpaired electron then the system will possess a net magnetic moment. That is why materials such as cloth or paper are said to be weakly magnetic. In substances such as iron, cobalt, and nickel, most of the electron's spin is in the same direction. Thus, leaves the atoms strongly magnetic in these substances but overall materials are not yet magnets. The material could be magnetized only if another strong magnet must enter the magnetic field in the material. Depending upon their behaviors in an external magnetic field, the magnetic materials have been divided into mainly two parts. Firstly, the materials, which get weakly magnetized in the opposite direction of the applied external magnetic field. These materials are characterized as diamagnetic with a negative susceptibility. It will be easier to understand the diamagnetism using Lenz's law classically. As we all know the electrons in atoms are continuously revolving around the nucleus in an orbit making a close loop. Under the external applied magnetic field, there will be a change in the magnetic flux through the loop. According to Lenz's law, the orbital motion of electrons opposes any changes in magnetic flux thus creating a back electromotive force. Nevertheless, quantum mechanically, every material intrinsically displays weak diamagnetism owing to orbital motion. In absence of any external magnetic field in the diamagnetic materials, electrons are paired or the orbital shells are completely filled with zero net magnetization. Secondly, the materials, which get magnetized in the direction of the applied external magnetic field with a positive susceptibility. Depending on their capability of magnetization these

materials are characterized into numerous types, viz., paramagnetic, ferromagnetic, antiferromagnetic, and ferrimagnetic. Below, they have been described in detail.

## 1.1.1 Paramagnetic material

The paramagnetic materials possess at least one unpaired electron. They have small but positive magnetic susceptibility. Due to the spins of the unpaired electrons, the atoms/molecules/ions of paramagnetic materials have a permanent magnetic moment. These moments are randomly oriented in absence of external magnetic fields since spins of atoms do not interact or very weakly interact with the spins of neighboring atoms, giving rise to zero net magnetic moments. The application of an external magnetic field in these materials causes alignment of spins in the direction of the applied magnetic field, thus leads a net attraction in the direction of the magnetic field. They will demagnetize as soon as we removed the external magnetic field. The magnetization of the paramagnetic materials depends on the strength of the applied external magnetic field as well as it depends on the temperature. The magnetic field will tend to align the spin moment of each atom while the temperature will randomize the moment of spins due to thermal energy.

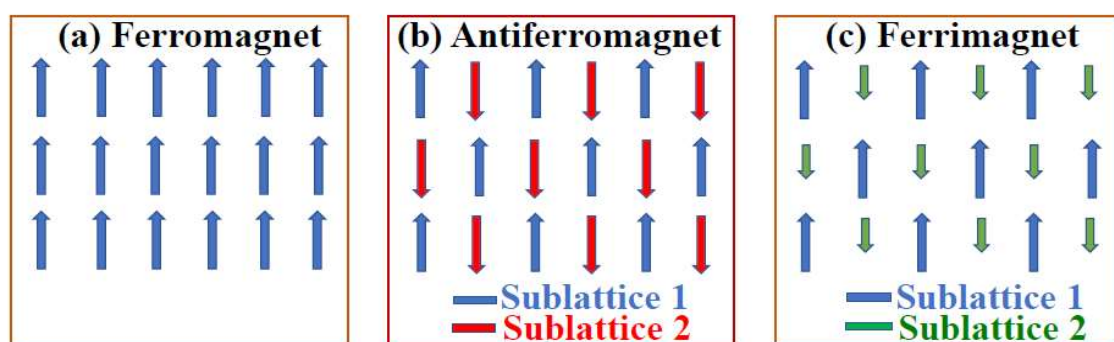
## 1.1.2 Ferromagnetic material

The ferromagnetic materials also possess unpaired electrons but they have very large and positive magnetic susceptibility and they have the capability to remain magnetized even when the magnetic field is removed. The special properties of ferromagnetic materials are that it forms tiny magnetized regions (known as magnetic domains) spontaneously to minimize their free energy. Within a domain of a ferromagnetic material, spins are aligned in a single

direction even in absence of external magnetic fields, however, the domains are oriented randomly with respect to each other. Under the application of a magnetic field, the magnetic domains become parallel to the field direction, leading the material to be strongly magnetized. When we remove the magnetic field, there still exist a few domains with moments aligned in the same direction. Thus, ferromagnetic materials exhibit large remanent magnetization and hysteresis.

### 1.1.3 Anti-ferromagnetic and ferrimagnetic material

An antiferromagnetic material has two ferromagnetic sub-lattices with having equal magnetic moments, whose magnetic moments are pointed in opposite directions. Thus, the magnetization is cancelled out in an antiferromagnetic material giving rise to net-zero magnetic moments. The ferrimagnetic material has also two anti-aligned magnetic sub-lattices but the magnitude of the magnetic moments is different. Thus, there is a net magnetization in a ferrimagnetic material.



**Figure 1.1:** A representation of spin alignments within a domain of (a) a ferromagnet material (b) an antiferromagnet material (c) a ferrimagnet material below magnetic ordering temperature.

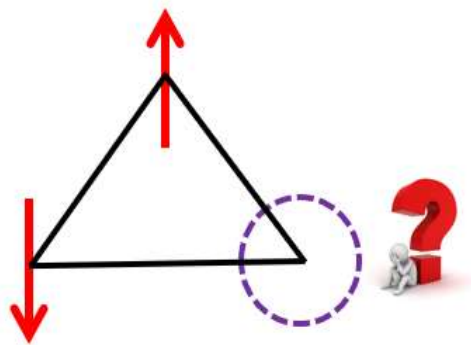
## 1.2 Frustration

Psychologically, frustration is a mental state in life where a different opposing situation arises due to some opposition in achieving a particular goal or there are different ways to achieve the same goal and it is difficult to decide to choose a better path. Generally, higher levels of frustration cause controversial/problematic behavior in humans and may lead to violent reactions against opposing factors. However, in extraordinary cases, the mental frustration/unrest builds its way and finds a suitable path to solve existing problems without any social/physical harm. In physics, frustration is common in systems of competing interaction as each interaction tries to favor its own characteristic correlations. Thus, the system cannot minimize its total energy by minimizing the pair-by-pair interactions [1]. However, a little frustration may lead to some interesting physical properties due to different competing interactions.

### 1.2.1 Spin/magnetic frustration

The spin frustration is observed in magnetism from a conflicting situation, where a single spin has multiple ground states. Such frustrated magnetic systems present a diverse set of physical properties. The spin frustration is mainly driven by the disorder present in the system and the geometry of the system. When magnetic ions are randomly distributed on their crystallographic sites, the spin interactions of the magnetic ions become random and at lower temperature spins get frozen in random directions rather than achieving a single ground state. A spin-glass (SG) state, where magnetic moments are frozen in random directions, has been found in the system when disorder/randomness brings frustration [2]. Disorder-driven spin frustrations are extensively found in perovskite and double perovskite materials. This type of

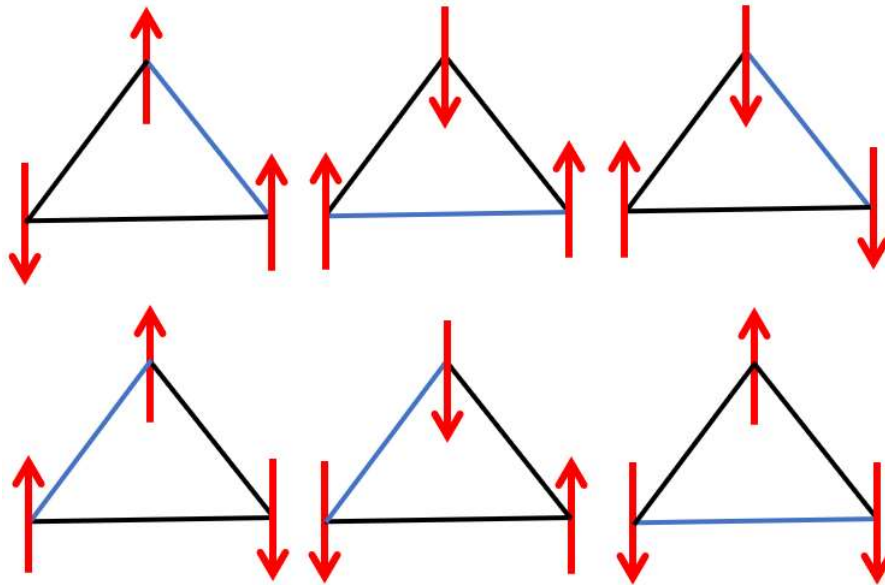
spin frustration leads to different magnetic phenomena viz. low-temperature spin glass or re-entrant spin glass or cluster glass, Griffiths like phase, exchange bias, magneto-dielectric coupling, metamagnetic transition, magneto-resistance, etc [3–10]. However, the geometrical spin frustration occurs due to the relative arrangement of spins on the geometrical sites of the lattice, where it is impossible to have all interactions favorable and restrict the formation of a collinear magnetic ordered state. One example is two-dimensional triangular lattices where three spins lie on the corners of the lattice (Fig. 1.2). The energy of the system will be minimum



**Figure 1.2:** Showing 2D triangular lattice which does not satisfy all the nearest neighbor antiferromagnetic interactions simultaneously: An example of geometrical spin frustration.

if each spin is antiferromagnetically coupled. However, here each spin has two possible neighboring spins by which it can pair antiferromagnetically. Once two spin anti-aligned, the third one gets frustrated as it has two options, up or down, with the same energy. Similar situation arises for the rest two spins and thus there is total six possible ground state (with same energy) for this arrangement [11]. In this regard, pyrochlore materials are very promising [12–14]. The inherent geometrical spin frustration in pyrochlores leads different low-temperature exotic states by means of proper balance among the different competing exchange interactions, dipolar interactions, and crystal field effect [12,13].





**Figure 1.3:** Showing six possible degenerate ground state for three identical spins situated on a simple 2D triangular lattice [11].

### 1.3 Dielectric property

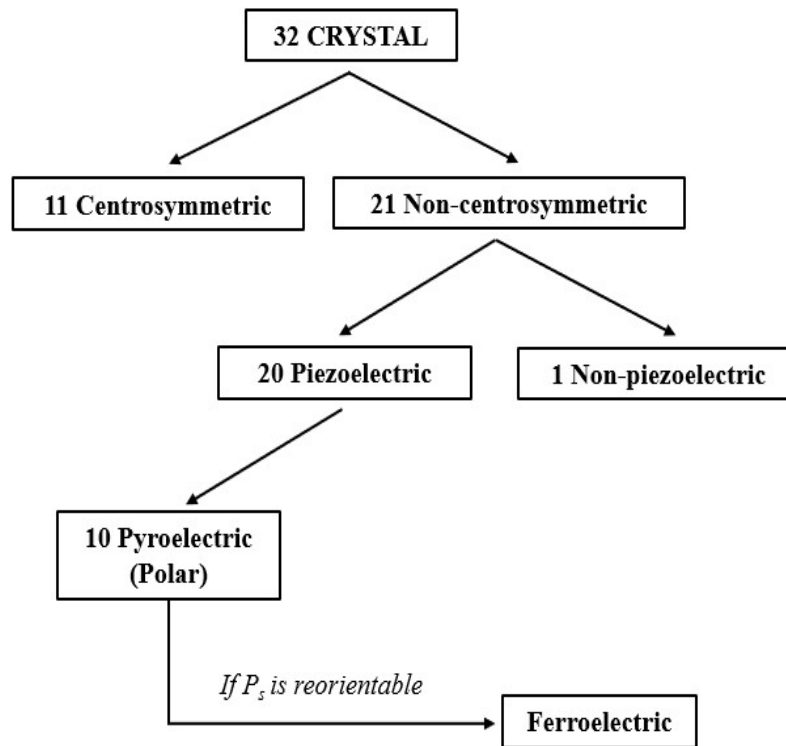
Dielectric materials are basically insulators that allow the electric field/flux through them, but not electric charge with the application of an external electric field. However, under the influence of the electric field, the electric charges get slightly shifted from their stable positions, giving rise to net dielectric polarization. From the technological point of view the different dielectric properties, like dielectric strength, relative permittivity (dielectric constant), and the dielectric loss of materials play a much important role. The static charges in materials depend on their resistivity and the electrical resistivity is the function of the permittivity of the materials. Thus, it is more likely to study the relative permittivity of the materials. The relative permittivity of the materials can be calculated from the capacitance (C) measurement, using the relation,

$$k = Cd/k_0A \quad (1.1)$$

Where  $d$  is the separation of plates and  $A$  is the cross-sectional area of the material. Further, the dielectric constant can be represented in terms of real ( $\epsilon'$ ) and ( $\epsilon''$ ) imaginary components, i.e.,  $\epsilon^* = \epsilon' - i\epsilon''$  and another physical quantity i.e., loss tangent (dielectric loss) defined as,  $\tan\delta = \epsilon''/\epsilon'$ . The dissipation of dielectric occurs due to different reasons like hindrance between electrical signal and polarization, crystal symmetry, phonon interactions, and many others, which are measured as a tangent loss.

## 1.3.1 Ferroelectric material

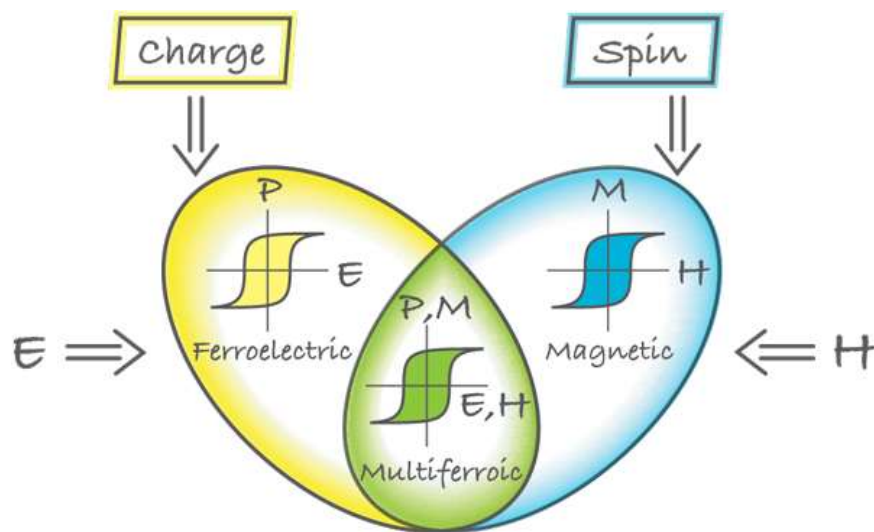
Ferroelectric materials are those materials that possess spontaneous electric polarization even when there is no applied electric field. The orientation of spontaneous polarization could be changed using an externally applied electric field. The ferroelectricity in material depends on the periodic arrangements of atoms on the lattice sites. Based on the periodicity of a lattice we have 7 crystal systems and these crystal systems are divided into 32 classes known as point groups depending upon symmetry. Ferroelectricity mainly arises in non-centrosymmetric materials, where the center of positive charges and negative charges do not coincide. As the basic crystal systems have been classified into 32-point groups based on their symmetry operations where 21-point groups are non-centrosymmetric. Out of these 21 non-centrosymmetric point groups, 20 are piezoelectric where 10-point groups exhibit pyroelectricity (which is basically polar material). Ferroelectric materials are a special category of spontaneously polarized pyroelectrics whose polarization ( $P_s$ ) can be reversed with the help of an external electric field (see Fig. 1.4).



**Figure 1.4:** Demonstrating the classification of point groups for electrical property [taken from the source; <http://125.22.54.221:8080/jspui/bitstream/123456789/167/2/Thesis.pdf>].

## 1.4 Multiferroic material

The ‘multiferroic’ term was firstly used by Schmid in 1994 [15]. Those single-phase materials in which more than one ferroic/anti-ferroic ordering (like ferromagnetic, ferroelectric, ferro elastic, etc.) coexist simultaneously, known to be multiferroic [15–17]. An example of a multiferroics is magnetoelectric (ME) compounds (Fig. 1.5) which possess both ferromagnetic (or anti-ferromagnetic) and ferroelectric (or anti-ferroelectric) ordering in a single phase [18]. In general, the isothermal magnetization curve of a ferromagnetic material exhibits usual M-H hysteresis loop (blue, right side) whereas a ferroelectric displays similar P-E hysteresis loop (yellow, left side). If it is possible to synthesis a material which shows



**Figure 1.5:** Diagrammatic representation of a multiferroics from the combination of ferroelectric and magnetic properties [16].

ferromagnetic and ferroelectric property simultaneously (green, middle, intersection of ferromagnetic and ferroelectric region), then the magnetization can be tune using an electric field and/ vice versa, polarization can be tune using a magnetic field. In this way four 4-state logic state can be made using the combinations, (P+/M+), (P+/M-), (P-/M+) and (P-/M-).

## 1.5 Electrical resistivity

The electrical resistivity ( $\rho$ ) of a material can be estimated from the electrical resistance (R) measurement using the relation,  $\rho = RA/L$ , where L is the length of the sample and A is the cross-sectional area. The electrical resistivity of a system can be measurements with the with varying various external environments like magnetic field, pressure, temperature, etc. For the case of semiconducting materials, the temperature dependent resistivity can be analyzed by thermally activated Arrhenius and Mott variable-range-hopping (VRH) models.

## 1.5.1 Arrhenius model

According to Arrhenius, in a semiconducting material the resistivity ( $\rho$ ) varies with temperature (T) according to the equation,

$$\rho = \rho_0 \exp[E_A/k_B T] \quad (1.2)$$

Where,  $\rho_0$  is a pre-factor,  $E_A$  is the energy required to activated carrier from valence band to conduction band (i. e. activation energy) and  $k_B$  is the Boltzmann constant.

## 1.5.2 Variable range hopping (VRH) model

According to this model the hopping resistances among neighbours become large than the distant species. Only those carriers participate in conduction whose energies are close to the Fermi level and the resistivity varies as [19–23],

$$\rho = \rho_0 \exp[(T_0/T)^{1/n+1}] \quad (1.3)$$

Where,  $n$  is the dimension of the system and  $T_0$  is Mott's characteristics temperature. For the 3-D case, parameter  $T_0$  is related to the localization length ( $1/\alpha$ ) of the wave-function and with the density of states ( $N(E_F)$ ) near Fermi level with the relation,

$$T_0 = 24\alpha^3/\pi k_B N(E_F) \quad (1.4)$$

Moreover, the polaron hopping energy ( $W$ ) at any temperature (T) can also be estimated with the help of the Mott's characteristics temperature using relation,

$$W = 0.25 k_B T_0^{0.25} T^{0.75} \quad (1.5)$$

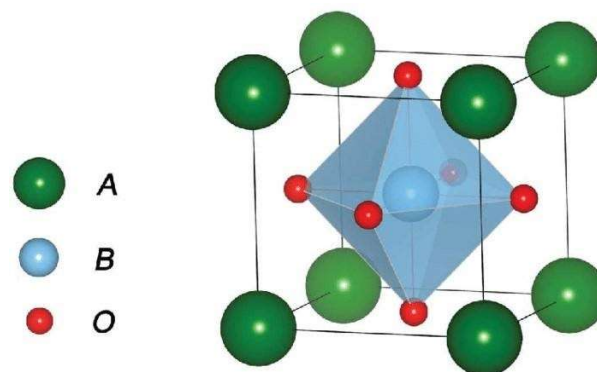
With a probable hopping length (D),

$$D = \left[ \frac{9}{8\pi\alpha k_B N(E_F)} \right]^{1/4} = \left[ \frac{9T_0}{192\alpha^4} \right]^{1/4} \quad (1.6)$$

And the VRH model will be valid only if  $W > k_B T$  (thermal energy) and  $\alpha R > 1$ .

## 1.6 Double perovskite material

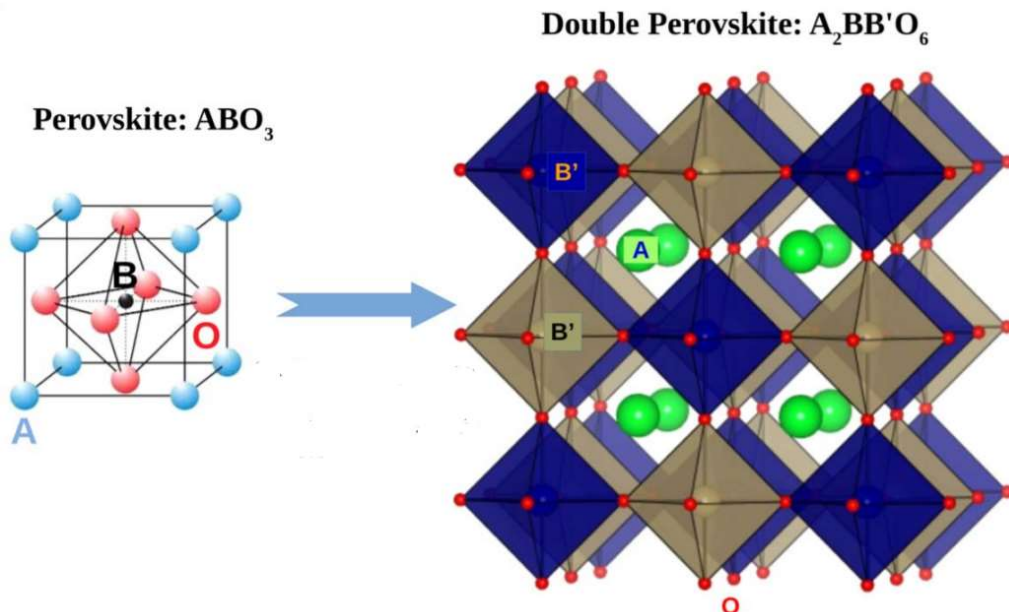
Here, I would like to start with the parent perovskite system  $ABO_3$ . Perovskite material was first found in the Ural Mountains in Russia by Gustav Rose in 1839 and named after Russian mineralogist Lev Aleksevich von Perovski. The widely investigated perovskite material is one that has the structure of the form  $ABO_3$  similar to mineral perovskite  $CaTiO_3$ . The basic structure of ideal cubic  $ABO_3$  with space group  $Pm-3m$  (221) is shown in Figure 1.6. In the perovskite system, A lies in a +1 to +3 oxidation state while B in +3 to +6 state. In lattice arrangement the cation of type A (usually alkaline/rare earth element) is present at the corners of the cube (0, 0, 0), while the center (0.5, 0.5, 0.5) of the cube is occupied by B (generally 3d, 4d, or 5d transition elements) atoms and the oxygen (O) anions lie at the face (0.5, 0.5, 0) of



**Figure 1.6:** Unit cell of an ideal (cubic) perovskite ( $ABO_3$ ) structure.

the cube. Further 'B' ions are surrounded by six oxygen (O) anions forming  $BO_6$  octahedral and 'A' is coordinated cubo-octahedrally via  $BO_6$  polyhedral. Thus, the  $BO_6$  octahedra form a

corner-shared network, where A cations remain in the voids formed by the corner-shared network of  $\text{BO}_6$  octahedra. Most importantly, the  $\text{BO}_6$  octahedra can contract/expand/tilt on substitution of different elements on A/B-sites to compensate for strain developed due to non-ideal ionic size ratios. Besides this, the octahedra can distort and cation may shift to a non-ideal position to compensate for electronic instabilities. Thus, its crystallography is very interesting as well as challenging where a slight structural variation may have a significant effect on the various physical properties. They can be explored by different elemental substitutions on the A and B-sites to optimize their technological applications. The substitution of B' for B, where B and B' has different charge/or size gives solid solution  $\text{AB}_{1-x}\text{B}'_x\text{O}_3$ . For the case  $x = 0.5$  (Fig. 1.7) the ordering of B-site cations may occur and we can write modified formula  $\text{A}_2\text{BB}'\text{O}_6$ , which is described as double perovskite (DP) [24,25].



**Figure 1.7:** The doubling of a perovskite unit cell to a double perovskite unit cell [24].

Thus, we can define that DPs are perovskites, where half of the ‘B’ ions are substituted with other B’ ions. The doubling of ideal perovskites leads to another cubic structure, with doubled unit-cell edge relative to  $ABO_3$ , while  $BO_6/B'O_6$  octahedral tilting results in a lower-symmetric phase. Moreover, we can tune the physical properties of DPs via substitutions of A-site cations with other A’ cations as it modifies the B-O-B’ bond angle and bond length. Additionally, many theoretical and computational efforts are given to predict the possible structures of DPs [26]. They tried on many DPs and found that they can acquire different structures viz. cubic, hexagonal, monoclinic, orthorhombic, tetragonal, trigonal, etc., depending on the type of elements on A/B-sites. The structural stability of the DP  $(AA')BB'O_6$  can be decided using the Goldschmidt tolerance factor ( $t$ ), which is defined as [27],

$$t = \left[ \frac{R_A + R_{A'}}{2} + R_O \right] / \left[ \sqrt{2} \left( \frac{R_B + R_{B'}}{2} + R_O \right) \right] \quad (1.7)$$

Where R stand for ionic radii and subscripts denotes corresponding elements. Ideally, case  $t = 1$  corresponds to a perfect cubic geometry and the deviation of  $t$  from 1 causes structural transition from ideal cube to some lower symmetric phase. The larger difference in ionic radii of A ( $R_A - R_{A'}$ ) and B ( $R_B - R_{B'}$ ) elements cause lower values of tolerance factor and hence larger octahedral distortion. Moreover, the ordering of the B-site cations matters much in determining the exact space symmetry of double perovskites. In the perfect ordered state, the B and B' cations are distributed in a regular fashion at their sites. However, according to Valasa et al., disordering among cations takes place due to two reasons [28]. 1) Anti-site defect (ASD), which arises by means of interchange of B and B'-site cations and 2) Anti-phase boundary (APB), where at the boundaries of two ordered domains, the B/B'-sites occupancies are reversed. It has been observed that smaller difference in oxidation state ( $\Delta Z_B$ ) of B and B'



favors disordered stacking as in this case both cations have similar chemical activity and will try to occupy both sites interchangeably [26]. This statement can also be understood with the help of thermodynamic law according to which for similar B and B' cations, the system will try to maximize its entropy and thus become disordered. While for the large ( $\Delta Z_B$ ) values, highly charged cations favor less charged cations at its neighboring site to reduce Coulomb energy, thus leading to ordered state [28,29]. Other than this, the smaller difference in ionic radii ( $\Delta R_B$ ) of B/B' atoms favors disordered structure of double perovskites and larger  $\Delta R_B$  favors ordered structure assisted by induced strain [29,30]. It has been concluded that the system with,  $\Delta Z_B = 4$  and  $\Delta R_B \geq 0.1 \text{ \AA}$  favors ordered state whereas  $\Delta Z_B = 0$  and  $\Delta R_B \leq 0.1 \text{ \AA}$  favors disorder.

The double perovskites are very attractive owing to their rich physics and technological applications. Slight changes in different factors in DPs affect crystallography and may interfere with their physical properties. For example, there may be anti-site disorder due to the exchange of the B/B' site ions or oxygen vacancy depending on synthesis condition and size of ions. The ideal (cubic) structure of a DP has three-dimensionally connected linear arrays of corner-sharing BO<sub>6</sub> and B'O<sub>6</sub> octahedra where A cations reside in the voids among the octahedral [31,32]. However, depending on the ionic radii of A and B site cations, they have structures having lower symmetries. Their physical properties are mainly depending on the ordering of the B-site cations. Many ordered DPS has been reported to exhibit FM insulating ground state owing to 180° positive of B<sup>2+</sup>-O<sup>2-</sup>-B<sup>4+</sup> super-exchange interactions, which can be explain by Goodenough-Kanamori rules [10,33,34]. Furthermore, presence of B<sup>3+</sup>/B<sup>13+</sup> ions lead competing AFM) interactions in the materials. Depending on the distribution of B & B' ions on their crystallographic sites, most of the DPs crystallize mainly either in an ordered

monoclinic phase (with space symmetry P21/n) or in a B-site disordered orthorhombic phase (with space symmetry Pnma) [35–38]. Till now there is around thousands of DPs reported in literature. A brief review on rare earth-based DPs with Co/Mn on B-site has been discussed below.

## 1.6.1 A brief literature survey on $R_2CoMnO_6$ double perovskites

The recent studies on various rare earth-based DP with B sites occupied by Co and Mn, that is  $R_2CoMnO_6$  (R = La to Lu; rare earth elements), have received extensive attention due to their various interesting functional properties, viz., electrical and optical properties [39,40], defect-induced modulation of physical properties [41], tunable magnetization steps [42], magnetocaloric effect and pyro-current [23,43], magnetoresistance [21], exchange bias [44–46], magnetocaloric and magnetodielectric effects [47,48], Griffiths-like and non-Griffiths-like clustered phase [49,50], spin-phonon coupling [51], Hopkinson effect [52], multiferroicity [53], etc. The slight change in rare-earth size in the  $R_2CoMnO_6$  family, instigate significant changes in the Co-O-Mn bond length and bond angle; thus, modifying magnetic and electronic ground states via modification of super-exchange interactions. In these DP oxides, the  $CoO_6$  and  $MnO_6$  octahedral are alternately located at corners of the lattice. A ferromagnetic ordering arises due to dominant  $Co^{2+}$  and  $Mn^{4+}$  super exchange interactions, where the ordering temperature,  $T_C$ , linearly decreases from 204 K (for  $La_2CoMnO_6$ ) to 48 K (for  $Lu_2CoMnO_6$ ), as the ionic radii of the rare-earth elements decreases from La to Lu [54]. However, due to random distribution of Co/Mn ions, anti-ferromagnetic ordering also arises owing to  $Co^{2+}-O^{2-}-Co^{2+}$  and  $Mn^{4+}-O^{2-}-Mn^{4+}$  super exchange interaction along with dominant ferromagnetic phase. Moreover, the rare earth ions may lead to additional magnetic ordering

at lower temperatures, thus resulting moderation of the magnetic properties [54]. For example, in  $\text{Er}_2\text{CoMnO}_6$ , a ferrimagnetic behavior have been seen below 30 K due to the long-range ordering of  $\text{Er}^{3+}$  moments with Co/Mn sublattice, other than the ferromagnetic ordering of the  $\text{Co}^{2+}$  and  $\text{Mn}^{4+}$  moments below 70 K [55,56].

Among the  $\text{R}_2\text{CoMnO}_6$  family of double perovskites, the  $\text{La}_2\text{CoMnO}_6$  has been the most investigated. It is a ferromagnetic insulator with magnetic transition temperature around 225 K, when B-site atoms are perfectly ordered [10,57,58]. However, due to partial anti-site disorder,  $\text{La}_2\text{CoMnO}_6$  exhibits two successive ferromagnetic around 210 K (corresponding to  $\text{Co}^{2+}-\text{O}^{2-}-\text{Mn}^{4+}$  super exchange interaction) and 150 K (corresponding to  $\text{Co}^{3+}-\text{O}^{2-}-\text{Mn}^{3+}$  super exchange interaction).

The  $\text{Y}_2\text{CoMnO}_6$  is another well studied member of the  $\text{R}_2\text{CoMnO}_6$  double perovskite family. It was much attracted owing to their meta-magnetism and ferroelectricity driven by magnetostriction effect due to the E-type magnetic ordering of  $\text{Co}^{2+}-\text{Mn}^{4+}-\text{Co}^{2+}-\text{Mn}^{4+}$  spin chain [59–62]. However, the sharp steps in isothermal magnetization (meta-magnetic transition) have been credited to the anti-phase boundary among the magnetic moments emerging owing to presence of anti-site disorder in the system. Later, it has also been supposed that the multiferroicity in the  $\text{Y}_2\text{CoMnO}_6$  originated owing to defect dipoles, trapped charges or any other extrinsic effects rather than the E-type magnetic ordering [5]. Other than this,  $\text{Y}_2\text{CoMnO}_6$  also manifests multi-caloric effects simultaneously such as magneto-caloric and electro-caloric effect around its ferroic ordering temperature ( $\sim 75$  K) [61].

Another interesting member of  $\text{R}_2\text{CoMnO}_6$  family i.e.,  $\text{Lu}_2\text{CoMnO}_6$  also exhibits ferroelectricity, where magnetically ordered collinear Co-Mn-Co-Mn chains induce electrical

polarization via breaking of the spatial inversion symmetry and this coupling of electrical and magnetic property was rather strong in its single crystal [63–66]. In  $\text{Lu}_2\text{CoMnO}_6$ , a  $\uparrow\uparrow\downarrow\downarrow$  type spin ordering was observed beneath the  $\sim 43$  K, while the ferroelectric ordering was observed below  $\sim 35$  K. In this system,  $\uparrow\uparrow\downarrow\downarrow$  type magnetic ordering was also probed by neutron diffraction measurement [63].

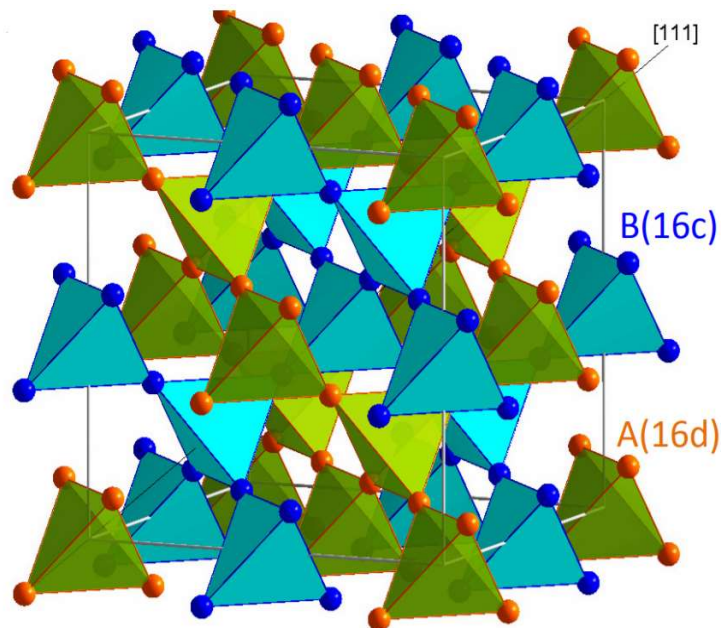
The DP  $\text{Pr}_2\text{CoMnO}_6$ , a ferromagnetic insulator also exhibits a broad range of different interesting properties like exchange bias, Griffiths-like clustered phase, spin-phonon coupling, magneto-dielectric coupling, etc [67]. Similar to other ordered DPs, the  $\text{Dy}_2\text{CoMnO}_6$  also shows many interesting phenomena like metamagnetic transition, magneto-caloric effect, with long range magnetic transition temperature around 85 K related to Co/Mn ordering [68]. The DP,  $\text{Sm}_2\text{CoMnO}_6$  shows long range magnetic ordering below the temperature at  $\sim 135$  K [69,70]. For this system it is described that the transition from an antiferromagnetic metamagnetic state to a spiral metamagnetic state modifies the ferroelectric polarization. The Next system of the  $\text{R}_2\text{CoMnO}_6$  family is  $\text{Nd}_2\text{CoMnO}_6$ , which exhibits various attractive properties [71–74]. The bulk  $\text{Nd}_2\text{CoMnO}_6$  shows magnetic transition around 150 K whereas their epitaxial film shows increase of magnetic transition temperature to  $\sim 175$  K along with a ferroelectric transition above room temperature ( $\sim 585$  K) [71]. This compound has much higher electric polarization (i.e.,  $\sim 1.3 \mu\text{C}/\text{cm}^2$ ) compared to other Co/Mn double perovskites and seemingly driven by anti-site disorder.  $\text{Nd}_2\text{CoMnO}_6$  also shows magneto-dielectric coupling, meta-magnetism and re-entrant glassy dynamics [72,74]. The  $\text{Gd}_2\text{CoMnO}_6$  has also received considerable attention owing to its various interesting magnetic states [47,49,52,75,76]. It also shows magneto-caloric effect, Hopkinson's effect and spin phonon coupling. Latest study on  $\text{Gd}_2\text{CoMnO}_6$  shows a downward trend in inverse DC susceptibility,

which was probed to be due to the presence of non-Griffiths like short range clustered phase in the paramagnetic matrix. The other member  $Tb_2CoMnO_6$  also shows a long-range magnetic ordering temperature  $\sim 100$  K [51,54,77,78]. On lowering the temperature, it shows a re-entrant glassy dynamic owing to the competition of  $Co^{2+}-O^{2-}-Mn^{4+}$  ferromagnetic interaction with  $Co^{2+}-O^{2-}-Co^{2+}$  and  $Mn^{4+}-O^{2-}-Mn^{4+}$  the antiferromagnetic interactions. Moreover, it also shows large dielectric constant near room temperature, spin-phonon coupling, Griffiths phase, magneto caloric-effect.

## 1.7 Pyrochlore material

The name “pyrochlore” comes from its mineral material  $NaCaNb_2O_6F$ , which was first reported by von Gaertner in 1930 [1]. However, the first nomenclature of  $A_2B_2O_7$  pyrochlores was proposed by Hogarth in 1977 [79]. Where the most common pairing valence states of A (Generally rare earth elements) are either 3+ and that of B (Generally transition metal elements) are 4+ [1]. Mostly, they adopt the cubic structure with space group  $Fd-3m$  (No. 227) and each unit cell enclose 8  $A_2B_2O_7$  units (i.e., total 88 atoms per unit cell). Actually, the pyrochlore  $A_2B_2O_7$  system possesses quite stable and ordered structure which is a distinct form of fluorite ( $CaF_2$ ) type structure. The lattice parameters of the pyrochlore  $A_2B_2O_7$  is twice that of  $CaF_2$  [80,81]. In fact, the pyrochlore structure is almost free from any site disorder (<1%) unlike fluorite structure which hosts significant cationic and anionic disorders. In pyrochlore formula unit can be better written as  $A_2B_2O_6O'$ , which shows the two distinct O-sites, where A, B, O and O' are located at 16d (0.5, 0.5, 0.5), 16c (0, 0, 0), 48f (u, 0.125, 0.125) and 8b (0.375, 0.375, 0.375) positions respectively [<https://arxiv.org/pdf/1805.01674.pdf>]. The A & B ions form mixed corner-linked tetrahedral chains in the cubic unit cell along the  $\langle 111 \rangle$

crystallographic direction (Fig 1.8). These two sublattices are positioned at a distance  $a/2$  relative to one another (where  $a$  is the dimension of unit cell i.e., lattice parameter) along the unit cell edge. The site “A (16d)” ions prefer octahedral coordination while the site “B (16c)” ions prefer forming tetrahedral coordination with oxygen ions. This is in strong contrast with the fluorite structure where both the sites prefer to be in octahedral coordination. The symmetries of the  $\text{BO}_6$  octahedron depend on the value of the x-coordinate (i.e., variable  $u$ ) of 48f sites and for the  $u = 0.3125$  perfect octahedral symmetry was found. For most pyrochlores the value of  $u$  lies in the interval  $0.3125 \leq u \leq 0.375$ . Such ordered structure is always very desirable as it offers the ideal platform for investigating the geometry driven spin frustration leading to theoretically predicted novel ground states viz., spin liquid, spin ice etc [12].



**Figure 1.8:** Showing  $A^{3+}$  and  $B^{4+}$  sublattices in the unit cell of the  $A_2B_2O_7$  pyrochlore.

### 1.7.1 A brief literature survey on $R_2Ti_2O_7$ pyrochlores

Among all possible pyrochlores, the rare-earth based titanates ( $R_2Ti_2O_7$ ; R = rare earth elements) family is very attractive owing to their diverse and novel physical properties. In this family only magnetic elements are rare earth ( $R^{3+}$ ) ions while others ( $Ti^{4+}$  and  $O^{2-}$ ) are diamagnetic. One example of this family is  $Dy_2Ti_2O_7$  which shows complex magnetic behavior like multiple spin freezing owing to spin frustration [82–85]. In this compound  $Dy^{3+}$  ions make classical Ising spins chain on lattice of corner-shared tetrahedra, thus leading to magnetism in the system [86]. The magnetic interaction in this system leads to a canonical spin-ice state, where the spins alignment obeys two-in two-out configurations. In normal ice configuration the oxygen ions try to develop a periodic structure whereas H-atoms remain disordered due to the presence of two dissimilar “O–H” bonds and the theoretical calculations suggest that these in-equivalent bonds originate macroscopically degenerate ground states [85]. Hence, the system possesses some finite entropy even when we move to absolute zero temperature. However, these degeneracies have not been seen experimentally as the dynamics of H-atoms cannot be investigated without including motion of oxygen atoms. The magnetic degeneracy of the pyrochlore  $Dy_2Ti_2O_7$  is analogous to this ice configuration, where the spins play the role of H-atoms. Thus, the system cannot minimize the dipolar interaction and hence ends up in a disordered, non-collinear and frozen state at lower temperatures, below 4 K. The spin entropy (using specific heat measurement) of the  $Dy_2Ti_2O_7$  system is estimated to be around  $0.67R\ln 2$ , interestingly it is close to ( $\sim 0.71R\ln 2$ ) the entropy of water ice. Thus,  $Dy_2Ti_2O_7$  is a well-known spin ice system. Among all the spin ice pyrochlores only  $Dy_2Ti_2O_7$  has a high temperature spin- freezing (around 16 K) related to single ion freezing in addition to interlinked low-temperature spin-ice freezing at 4 K. Other than this systematic investigation of its

electrical property shows presence of magnetoelectricity in  $\text{Dy}_2\text{Ti}_2\text{O}_7$  along with multiple ferroelectric transitions [87].

Similar to  $\text{Dy}_2\text{Ti}_2\text{O}_7$ , the  $\text{Ho}_2\text{Ti}_2\text{O}_7$  is also known for its low-temperature dipolar spin ice state but it does not show high temperature ( $\sim 16$  K) single ion spin-freezing [88–90]. However, in another study of the dielectric spectrum of both systems,  $\text{Dy}_2\text{Ti}_2\text{O}_7$  and  $\text{Ho}_2\text{Ti}_2\text{O}_7$ , shows two diffused dielectric relaxations near 90 K and 36 K [91]. The estimated value of activation energy from dielectric response shows that these relaxations are inherently related to the lattice distortions at the anionic sites. In these systems the crystal field splitting is coupled with structural order parameters which induces structural distortion at 48f and 8b sites of the oxygen, thus leading to ferroelectricity.

Another interesting example of the  $\text{R}_2\text{Ti}_2\text{O}_7$  family is  $\text{Tb}_2\text{Ti}_2\text{O}_7$ , showing a spin-liquid state where spins remain dynamic down to lowest measured temperature [92–95]. In  $\text{Tb}_2\text{Ti}_2\text{O}_7$ ,  $\text{Tb}^{3+}$  spins do not form any long-range spin-ordering down to 50 mK temperature; rather it exhibits antiferromagnetic interactions only with neighboring spins below 50 K [95]. This characteristic makes  $\text{Tb}_2\text{Ti}_2\text{O}_7$  to behave like a classical spin liquid where the spins are correlated but remain dynamic even down to  $T \rightarrow 0$  K. More interestingly, the presence of a spin-liquid state originates strong crystal field-phonon interaction in  $\text{Tb}_2\text{Ti}_2\text{O}_7$  [96]. Similar interesting magnetic properties of other  $\text{R}_2\text{Ti}_2\text{O}_7$  ( $R = \text{Gd}, \text{Er}, \text{Yb}, \text{Sm}, \text{Eu}$ ) has been reported extensively [12,80,81,97–99]. However, the electrical and optical properties of above-mentioned titanate pyrochlore are very less reported, thus they can be further explored.



## 1.8 Some important physical phenomena related to our research

### 1.8.1 Griffiths phase

The “Griffiths phase (GP)” is an unusual strange magnetization where the system has neither long range magnetic ordering nor a pure paramagnet; rather it shows formation of magnetically correlated regions/clusters within the paramagnetic matrix just above magnetic transition temperature [100–104]. In this regime, the inverse DC magnetic susceptibility does not obey usual Curie-Weiss (CW) law and shows a downward deviation from the CW fitted line (i. e.  $\chi = C/(T - T_{CW})$ ) below a temperature  $T_G$  (Griffiths temperature) owing to emergence of short-range magnetic ordering. Hence, to probe the presence of GP one needs to measure the thermal variation of magnetization at different applied magnetic fields. The observed downturn in inverse magnetic susceptibility is dominant at lower applied fields and gets softened on increasing fields due to rising paramagnetic background. This helps us to differentiate the Griffiths phase from other clustered phases where inverse magnetic susceptibility upward deviation from the CW fitted line [101]. In Griffiths phase region inverse DC susceptibility follows the power-law (modified CW law) given by [105],

$$\chi^{-1}(T) = A[T - T_C^R/T_C^R]^{1-\lambda} \quad (1.8)$$

Where, A is a constant and  $T_C^R$  is the random critical temperature known as reduced temperature of randomly distributed clustered phase in paramagnetic region. The  $\lambda$  is a characterizing exponent of GP and it lies within 0 to 1 for  $T_C^R < T < T_{GP}$ . The value of  $T_C^R$  has been chosen in such way so that above equation yields value of  $\lambda$  almost equal to zero for  $T > T_{GP}$ . Thus, it can be understood that the value of  $T_C^R$  will be close to Curie-Weiss temperature.

## 1.8.2 Metamagnetic transition

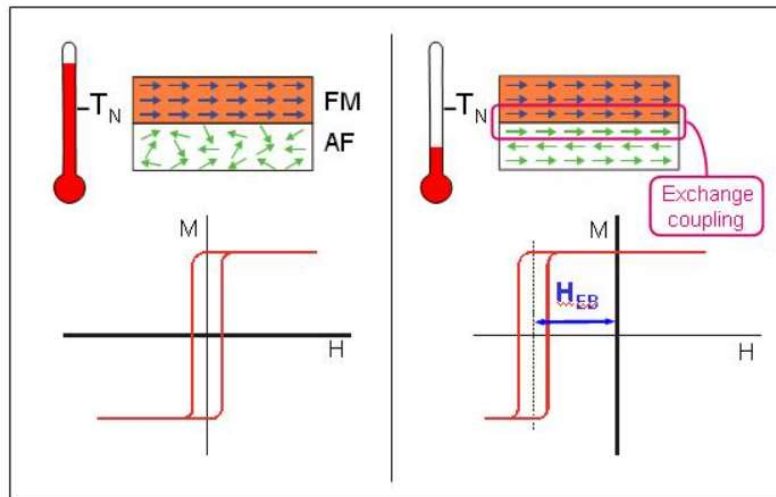
The “metamagnetic transition (MMT)” is the steps like (or sudden) discontinuous jumps in the magnetization, which is obtained by either change of temperature or magnetic fields. The steps appear due to first order magnetic transition between a low magnetization state and a high magnetization state with both states having low magnetic susceptibility. The MMT occurs owing to the spin’s reorientation along the direction of magnetic anisotropy and usually arises due to presence of strong anisotropy and different competing magnetic interactions [106]. Most relevant characteristic related to meta-magnetism is the presence of metastable magnetic plateaus (i.e., stairway to saturation). This type of discontinuity in magnetization can also originate owing to magnetic field induced lattice-distortion and spin flopping, which give rise to transition from an AFM to a FM state at certain critical values of the applied external magnetic field. However, in the case of the presence of dominating AFM ordering along with little FM clusters in the system under investigation, there is the possibility that FM phases are separated by an AFM anti-phase boundary (APB). For this case, the increase of the magnetic field will try to grow FM domains, however due to the presence of strong pinning forces there will be a very small change in the net magnetic moment. At a certain critical value of the magnetic field the energy of the external field is so high that it overcomes the energy related to the FM/AFM APB (magneto-striction energy), where some of the spins flop along the external field direction, thus leads to sudden increase in magnetization. In this process there is an increase in elastic energy whereas decrease in the magneto-static energy, thus the system enters another metastable state. Further increasing the external magnetic field, the magnetic strength field will reach another critical value where it

again flops a few spins and causes the second step in magnetization. In this way overall transitions are preceded by successive jumps from one meta-stable magnetic state to another [107,108].

## 1.8.3 Exchange bias

Exchange bias (EB) phenomenon is the horizontal (i.e., along the magnetic field axis) shifting of the hysteresis loop. The EB arises due to strong pinning force at the different magnetic interfaces (like FM/AFM, FM/Ferrimagnet, FM/Spin glass, hard/soft FM phase, etc.) and rise of non-switchable unidirectional anisotropy which provides additional remanence [109,110]. For example, a system having both FM and AFM phases is cooled under some external magnetic field. When temperature is down to FM ordering temperature ( $T_C$ ) but above the AFM ordering temperature ( $T_N$ ), then the AFM spins will be randomly orientated like a paramagnetic state but the FM spins will try to align in the field direction. Furthermore, when temperature reaches down to  $T < T_N$ , the first monolayer of AFM spins and FM spins are coupled across the interface due to exchange interaction. During isothermal magnetization process some magnetic field energy goes in doing work due to coupling of spins at interface and this cost of energy appears as shifting of hysteresis loop, which eventually exchange bias effect. When exchange bias appears after cooling the system under application of magnetic field, known as conventional EB, however when it is seen without cooling the sample in external magnetic field, known as spontaneous EB. In the Fig 1.9, a typical exchange bias has been demonstrated. In this figure, left panel is showing M-H loop above the antiferromagnetic transition temperature (i.e., Neel temperature,  $T_N$ ) where AFM spins are disordered. Left panel is showing M-H loop below antiferromagnetic transition temperature where both FM and AFM

spins are ordered and the exchange coupling at the interface of FM and AFM domains spins cause shifting of the hysteresis loop.



**Figure 1.9:** Demonstrating exchange bias in a typical FM/AFM material. (Taken from <https://ischuller.ucsd.edu/research/exchange-bias/>).

### 1.8.4 Spin-glass

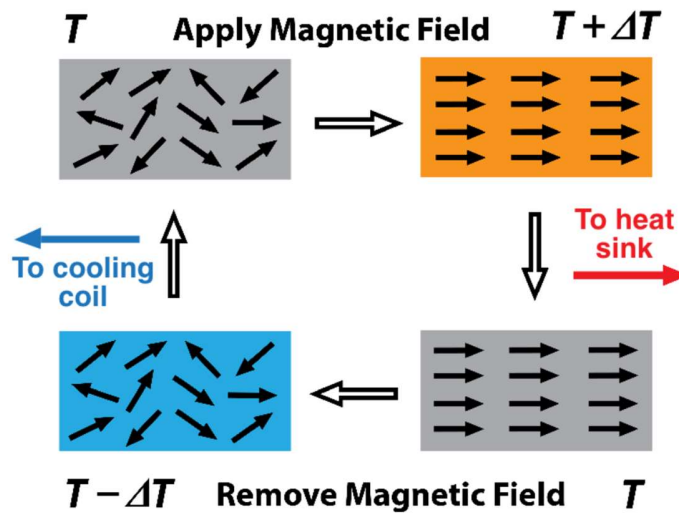
In normal crystallography, “glass” is a state where atoms/molecules/ions are randomly distributed in the materials without any long-range ordering. Glassy state arises when a liquid is cooled down to a temperature (known as glass transition temperature) from a high temperature with a relatively high cooling rate, the atoms/molecules/ions lose their mobility and get frozen randomly in 3D space. Similar to normal glass, the spin-glass is a magnetic state of material where the spin moments are frozen in random direction at some lower temperatures rather than forming ordered spin configuration [111–114]. In fact, the magnetic frustration originating from the competition among the FM and AFM exchange interactions or owing to the structural disorder or geometrical spin frustration leads to multiple degenerate ground states which

originate the spin glass state at lower temperatures [111,114,115]. In a magnetically ordered system, the magnetic domain evolves to minimize energy and attain an equilibrium state. However, the presence of disorder in the system inhibits the system to acquire an equilibrium and thus leading to a spin glassy dynamic which can be realized through non-exponential decay of magnetization, slow spin-relaxations, memory/aging effects, thermomagnetic irreversibility, etc. Consequently, the disorder plays a main role in originating the spin-glass states in any system. Moreover, in some systems where one of the competing exchange interactions (AFM/FM) is weaker than other, the glassy states are localized in small regions or clusters and thus known as cluster-spin-glass [112,113,116]. Moreover, when a system has long range magnetic ordering at higher temperature but it shows a glassy state at lower temperature, it is known as re-entrant spin/cluster glass. The re-entrant glassy state was well described by Sherrington- Kirkpatrick using the mean-field model for Ising spin system and by Gabay and Toulouse for Heisenberg spin system [117,118].

## 1.9.5 Magnetocaloric effect

The “magnetocaloric effect (MCE)” is a phenomenon of change of temperature (i. e. heating/cooling) of a material with change of an external magnetic field applied on that system. The change of applied external magnetic field on any system leads to change in magnetic entropy. And according to thermodynamics the change in entropy of any system is proportional to the change in energy of the system and change of energy of the system will leads to change in internal energy and hence temperature of the system. In the Fig. 1.10 the working cycle of magnetocaloric materials for cooling purpose is demonstrated. The initial cycle (top row) cause cooling of the material with application of a magnetic field which aligns the magnetic domains in field direction and hence decreases its magnetic entropy. To recompense reduced entropy

the material heats up an amount  $\Delta T$ . This extra heat has been removed to a fluid (sink) to lower the temperature of the material (lower right). Now, the applied field is removed and the magnetic domains again become randomly oriented, and hence increases its magnetic entropy. To recompense increased entropy the material cools down by an amount  $\Delta T$  (lower left). Finally, the cold material warms up as it is connected to a heat-exchange fluid for cooling, which is flowing through the coils of a refrigerating system. The change in magnetic entropy



**Figure 1.10:** Demonstrating the working cycle of a magnetocaloric material at temperature  $T$ . [<https://physics.aps.org/articles/v13/21>].

( $\Delta S_M$ ) of any system can be estimated using the magnetization measurement at different temperature and different external field using the Maxwell relations of classical thermodynamics [49,119]. From there, we have relation for the change of in magnetic entropy,

$$\Delta S_M(T, H) = \int_0^H \left[ \frac{\delta M(T, H)}{\delta T} \right]_H dH \quad (1.9)$$

If the isothermal magnetization is measured at very small intervals of magnetic fields, then the integration can be replaced by summation and thus the above relation can be re-written as

$$\Delta S_M(T, H) = \sum_i \left[ \frac{M_{i+1}(T_{i+1}, H) - M_i(T_i, H)}{T_{i+1} - T_i} \right] \Delta H \quad (1.10)$$

## 1.9 Motivations of the thesis

The recent progress on materials for different technology attract people towards a new class of multifunctional materials. In this regards, double perovskite oxides (described earlier) are very interesting owing to their room temperature magnetic ordering, multiferroicity, different types of coupling (like spin-phonon, magnetoresistance, magnetodielectric, etc.) and many more extraordinary magnetic and electrical properties exhibited by these materials motivated us to further elaborate double perovskites.

Various study on many DPs of  $R_2CoMnO_6$  family shows that  $R_2CoMnO_6$  with R-site having non-magnetic ions (like La, Y, Lu, Eu) has drawn extensive attention. In such system the magnetic interaction originates only owing to the exchange interaction of Co/Mn ions whereas R-site cations plays role only in the formation of lattice. These systems exhibit multiple exciting magnetic phenomena including meta-magnetic-transition [5,120–122]. Among these systems,  $Eu_2CoMnO_6$  is an interesting member [122], and there is more possibilities to further explore its electrical and magnetic properties. Further, it can be more interesting to elaborate this system via doping of some magnetic ions (Like Tb, Pr, Gd etc.) on Eu site with different ionic radii.

Moreover, the previous report on titanate pyrochlore  $Eu_2Ti_2O_7$  (ETO) shows different interesting magnetic ground states owing to local spin frustration and crystal field anisotropy [12]. Further, the substitution of Fe3d ions on Eu4f site induced f-d and d-d interactions along with f-f interaction and thus additional interesting magnetic states has been observed [123].

However, the X-ray absorption spectroscopy (XAS) study on  $\text{Eu}_2\text{Ti}_2\text{O}_7$  also revealed that the Ti ions occupy a distorted octahedral site (Oh) owing to the presence of an interstitial anionic site (8a) adjacent to the  $\text{TiO}_6$  octahedra. The existence of a local disorder of O-anions/local cationic ordering may lead to subtle modification of cubical symmetry in pyrochlore system. It is expected that such modification of local cubical symmetry or octahedral distortion may lead to the generation of electric dipoles and thus the ferroelectricity. Thus, we are interested to elaborate dielectric property of this system.