

Magnetic and Polar Properties of some Geometrically Frustrated Transition Metal Oxides

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in Physics*

by

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Certificate

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Dr. Sunil Nair
(Thesis Supervisor)

Pune

Date: November 15, 2018

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*Dedicated to my parents
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Synopsis

Recently there has been a surge of research interest in the magnetoelectric multiferroics, where magnetic and polar orders co-exist. Intense study of magnetoelectric coupling in several materials has shed light on the different possible scenarios of combining magnetism and ferroelectricity in a single phase material. The discovery of type-II multiferroics, where the electric polarization is induced by a specific type of non-collinear magnetic ordering, has brought rapid growth in the research area of magnetoelectric multiferroic. The magnetic order in geometrically frustrated magnets are often nontrivial and has been a fertile playground for exploring magnetoelectric coupling. In this thesis, we aim to study geometrically frustrated transition metal oxides for designing new magnetoelectric multiferroic materials and to study their physical properties.

Chapter 1 gives a brief introduction and evolution of the research area of magnetoelectric multiferroics. The issues associated with the coexistence of magnetism and ferroelectricity are highlighted. Typically, multiferroics are broadly classified in two categories, namely type-I and type-II. In a type-I multiferroic, the magnetism and ferroelectricity occur from different origins and results in a weak coupling between the order parameters. On the other hand, for a type-II multiferroic various type of commensurate/incommensurate spin configurations break spatial inversion symmetry and provide a strong coupling between the order parameters. Possible mechanisms of inducing ferroelectricity and magnetism in both type-I and II multiferroics are described in details. Different theoretical models are qualitatively described and their experimental realization also is presented. Finally, technological applications of these materials are highlighted and the motivation and the scope of the thesis is presented.

Chapter 2 describes the following measurement facilities developed during the course of the this work:

- Dielectric and pyroelectric measurement setups : Sample holders for low-temperature dielectric and pyroelectric measurements in a closed cycle refrigerator (CCR) have been designed. Both the measurements were automated using LabVIEW program.
- Dielectric and pyroelectric measurements under magnetic field: Using a MPMS-XL Manual Insertion Utility Probe, low-temperature dielectric and pyroelectric measurements up to 7 Tesla magnetic field have been performed.

- Electric field dependent magnetic measurement: Using a MPMS-XL Manual Insertion Utility Probe, electric field dependent magnetic measurements have been performed successfully on a single crystal specimen of $\text{Mn}_4\text{Ta}_2\text{O}_9$, and the magnetoelectric coupling has been studied along different orientations of the crystal.

A description of experimental techniques/methods used during this work which include synthesis of polycrystalline and single crystal specimen, investigation of the nuclear and magnetic structure from powder X-Ray and Neutron diffraction and bulk physical properties measurement is also presented.

Chapter 3 describes the investigation of $\text{Dy}_{1-x}\text{Ca}_x\text{BaCo}_4\text{O}_7$ series ($x = 0$ to 1) using X-ray diffraction, magnetization and dielectric measurements. Systematic doping causes a lifting of the geometrical frustration through structural transition from a high symmetry trigonal $P31c$ to a low symmetry orthorhombic $Pbn2_1$ symmetry at the doping concentration of $x = 0.4$. For all the orthorhombic specimens, such a structural transition was also observed as a function of temperature. One of the distinguishing features of this structural transition is that the temperature at which this transition occurs in the RBaCo_4O_7 (R =Rare earth ions, Ca^{2+}) family is observed to scale linearly with the mean ionic radius of the R site ion. However, such a quasilinear relationship is violated for $R = \text{Ca}^{2+}$ comprising of an equal number of Co^{2+} and Co^{3+} , indicating that charge ordering could possibly influence the structural transition. The ZFC-FC magnetization exhibits a large paramagnetic background arising from Dy^{3+} ions that apparently masks the magnetic transition appearing from the cobalt sublattice. Using Thermo-remnant Magnetization (TRM) measurements, we have identified the magnetic ordering temperatures of the solid solution $\text{Dy}_{1-x}\text{Ca}_x\text{BaCo}_4\text{O}_7$. Finally, we chart out the phase diagram of the $\text{Dy}_{1-x}\text{Ca}_x\text{BaCo}_4\text{O}_7$ series. $\text{SrBaCo}_4\text{O}_7$, a new member of Swdenborgite family has been synthesized successfully by the solid state reaction route. We have solved the structure using DICVOL06 and LeBail profile refinement of powder X-ray diffraction data. It stabilizes in the orthorhombic $pbam$ space group. Detailed magnetic and thermodynamic study reveals multiple phase transitions as a function of temperature.

Chapter 4 of the thesis presents study of a new near room temperature ($\approx 280\text{K}$) magnetodielectric $\gamma - \text{Fe}_2\text{WO}_6$. The magnetic, thermodynamic and dielectric properties of the $\gamma - \text{Fe}_2\text{WO}_6$ system is discussed. Crystallizing in the centrosymmetric $Pbcn$ space group, this particular polymorph exhibits a number of different magnetic transitions, all of which are seen to exhibit a finite magneto-dielectric coupling. At the lowest measured temperatures, the magnetic ground state appears to be glass-like, as evidenced by the

waiting time dependence of the magnetic relaxation. Also reflected in the frequency dependent dielectric measurements, these signatures possibly arise as a consequence of the oxygen non-stoichiometry, which promotes an inhomogeneous magnetic and electronic ground state.

In **Chapter 5**, the study of a new type-II multiferroic specimen $\text{Fe}_4\text{Ta}_2\text{O}_9$ is presented. Combination of magnetic, dielectric, specific heat and pyroelectric measurements reveals a series of magnetic transitions, many of which are associated with the emergence of ferroelectric order. The anomaly observed in low field ZFC magnetic measurement as a function of decreasing temperature are also being identified in dielectric and pyroelectric measurements performed under zero field. The low temperature H - T phase diagram of $\text{Fe}_4\text{Ta}_2\text{O}_9$ is seen to exhibit a rich variety of coupled magnetic and ferroelectric phases, in similarity with that observed in the distorted Kagome systems. On cooling two distinct multiferroic states of $\text{Fe}_4\text{Ta}_2\text{O}_9$ labeled as AFM1 FE1, and AFM2 FE2, with onsets at $T_1 = 80\text{K}$ and $T_2 = 60\text{K}$ respectively are seen. On cooling further, and in the presence of magnetic fields in excess of 1 Tesla, we observe a field induced multiferroic state denoted as AFM3 FE3. Within this state, we also identify the presence of a metamagnetic (spin-flop) transition which appears to have no discernible influence on the polar state (SF-AFM3 FE3). We further observe the onset of possibly a different kind of antiferromagnetic order at temperatures of the order of 5K, (AFM4 FE3) as is evidenced by magnetic and dielectric measurements. We suggest that these properties arise due to an effective reduction in the dimensionality of the magnetic lattice, with the magnetically active Fe^{2+} ions preferentially occupying a quasi 2D buckled honeycomb structure.

Chapter 6 presents the crystal growth of magnetoelectric $\text{Mn}_4\text{Ta}_2\text{O}_9$ and temperature dependent magnetization and electric field dependent magnetic measurements along the different crystallographic axes of this hitherto unexplored single crystal. The magnetic structure solved from high-resolution T.O.F powder neutron diffraction data reveals that the magnetic structure comprises of antiferromagnetically coupled ferromagnetic chains of Mn^{2+} spins aligned along the trigonal c axis, in sharp contradiction to that reported in other isostructural members of this family. DC magnetic measurements performed with magnetic fields parallel and perpendicular to the crystallographic c axis of the crystal reveals anisotropic behavior with the presence of Dzyaloshinskii-Moriya driven weak FM phase, making the magnetic phase diagram of $\text{Mn}_4\text{Ta}_2\text{O}_9$ far richer than the other members of this family. More importantly, magnetic measurements performed under a period electric field indicate that the magnetoelectric response is also anisotropic, with

this coupling along the trigonal c axis and that perpendicular to it having different signs.

Chapter 7 summarizes the conclusions of the complete work presented in this thesis.

Also, possible methods and avenues for future work are listed

Appendix-I of the thesis presents a detailed description of solving the magnetic structure of $\text{Mn}_4\text{Ta}_2\text{O}_9$ from Neutron powder diffraction pattern using the Fullprof Suite. A step by step guide of using the K_Search Program for identifying k vector from the Neutron diffraction data is described. Use of the BasIreps program for representational analysis in solving magnetic structure is also discussed. Finally, construction of *.pcr (input control file for running the FULLPROF program) for incorporating the calculation of magnetic contribution and testing the different representations to find the correct magnetic model is highlighted.

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Chapter 1

Introduction

1.1 Basic Concepts

Magnetism was first discovered in the mineral called loadstone (Iron Oxide), having the ability to attract/repel other magnets. Classically, a magnetic moment was assumed to be an orbital motion of an electron/current loop. A magnetic material undergoes a phase transition from randomly oriented magnetic moments in the paramagnetic state to a long-range ordered ferromagnetic/antiferromagnetic state at a particular temperature, known as Curie (T_C) /Neel (T_N) temperature. Below this ordering temperature, a spontaneous magnetization (M) appears. One of the essential aspects of a ferromagnet is that the direction of the spontaneous magnetization can be switched by an external

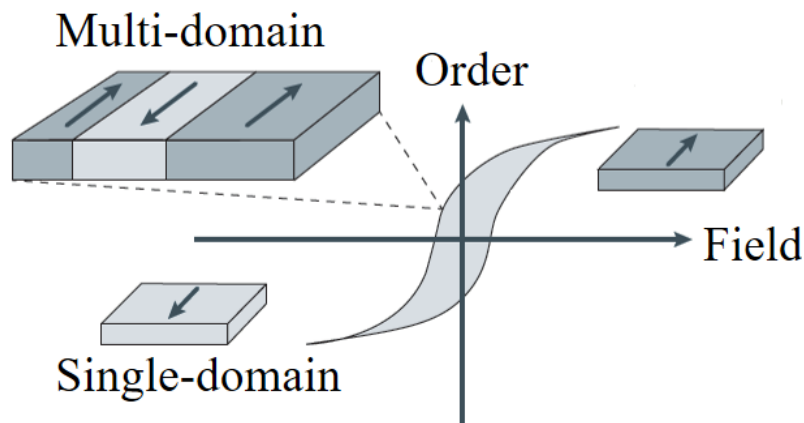


Figure 1.1: Schematic of the hysteresis loop of a ferroic material. Adapted with permission from Ref. [1], copyright (2006) by the Springer Nature.

magnetic field and these system exhibits a hysteresis loop due to multiple spontaneously magnetized magnetic clusters/domains, as shown in Fig.(1.1) [2, 3].

The famous Stern-Gerlach experiment revealed that electron has a spin degree of freedom with two possible states namely, spin up ($\uparrow$) and spin down ($\downarrow$) with respect to the applied magnetic field [4]. The development of quantum mechanics has revolutionized the understanding of magnetism in materials. The uncompensated/unpaired spin in a system causes it to be magnetic. The (direct/indirect) exchange interaction between the spins is responsible for the long-range ordered magnetic state. Above the magnetic ordering temperature, the thermal energy ($k_B T$) overcomes the exchange energy and causes a randomly ordered paramagnetic state. Needless to say, application of magnets as magnetic recording memory, loudspeakers, etc. have brought significant technological development in our society.

In addition to the electron spin degree of freedom, the electron has also charge $-e$, as measured by Robert A. Millikan in oil drop experiment [5]. Positive ($+e$) and negative charges ($-e$) separated in a specific distance makes an electric dipole. In a crystal, the structural units are tiny electric dipoles with each unit of the centres of positive and negative charge are slightly separated. Similar to ferromagnet, in certain materials (called ferroelectrics) these dipoles are ordered spontaneously below the Curie temperature (T_C) and gives rise to spontaneous electric polarization (P). Rochelle salt (sodium potassium tartrate tetrahydrate, $\text{NaKC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$) was the first discovered ferroelectric, prepared by Seignette in La Rochelle, France around 1665. Valasek (1920/21) measured the polarization hysteresis as a function of electric field and determined the Curie temperature (T_C) of this ferroelectric salt [6]. The direction of electric polarization ($+\vec{P}$ to $-\vec{P}$) can be switched by changing the direction of the applied electric field (E to $-E$). This observation was in many ways similar to the ferromagnetic properties of iron [7, 8].

1.1.1 History of the magnetoelectric effect

Despite so many commonalities between the properties of magnetic and ferroelectric materials, none of them was observed to exhibit the coexistence of magnetization and polarization in a single phase until the beginning of the twentieth century. In free space, electricity and magnetism are coupled inherently, as expressed by Maxwell's relations. However, in solid materials, this coupling is nontrivial due to the different symmetry requirements for ferroelectricity and magnetism. In 1894, Pierre Curie first discussed the symmetry requirement for inherent coupling between electric and magnetic properties in materials [9]. In 1926, P. Debye coined the term "Magnetoelectrics" to describe the

class of materials where magnetization can be induced by applying an electric field and polarization can be induced by applying a magnetic field [10]. In 1957, L.D.Landau and E.M.Lifshitz in the book titled "Electrodynamics of Continuous Media (Pergamon, Oxford, 1960)" [11] stated in the last paragraph of page number 119 :

"The other results from a linear relation between the magnetic and electric fields in a substance, which would cause, for example, a magnetization proportional to the electric field; Both these phenomena can occur for certain magnetic crystal symmetry classes."

Dzyaloshinskii in 1959 based on crystallographic symmetry, predicted that antiferromagnetic Cr_2O_3 [12] could host a linear magnetoelectric effect describing the cross-correlation as tabulated in Table. (1.1). Here the suffix $\parallel$ and $\perp$ are longitudinal and perpendicular

Table 1.1: The relations between induction and field strength proposed by I.E.Dzyaloshinskii [12] for Cr_2O_3

$\mathbf{D}_x = \epsilon_{\perp} \frac{Y_0}{c} \mathbf{E}_x + \alpha_{\perp} \frac{1}{c} \mathbf{H}_x$	$\mathbf{B}_x = \mu_{\perp} \frac{1}{Y_0 c} \mathbf{H}_x + \alpha_{\perp} \frac{1}{c} \mathbf{E}_x$
$\mathbf{D}_y = \epsilon_{\perp} \frac{Y_0}{c} \mathbf{E}_y + \alpha_{\perp} \frac{1}{c} \mathbf{H}_y$	$\mathbf{B}_y = \mu_{\perp} \frac{1}{Y_0 c} \mathbf{H}_y + \alpha_{\perp} \frac{1}{c} \mathbf{E}_y$
$\mathbf{D}_z = \epsilon_{\parallel} \frac{Y_0}{c} \mathbf{E}_z + \alpha_{\parallel} \frac{1}{c} \mathbf{H}_z$	$\mathbf{B}_z = \mu_{\parallel} \frac{1}{Y_0 c} \mathbf{H}_z + \alpha_{\parallel} \frac{1}{c} \mathbf{E}_z$

components and ϵ, μ, α are the dielectric constants, the magnetic susceptibility and the magneto-electric susceptibility respectively.

Soon after this prediction, this effect was experimentally verified by D.N.Astrov *et al.* (E dependent M effect)[13] and V.J.Follen *et al.* (H dependent P effect) [14] in a single crystal of Cr_2O_3 . In 1994, Hans Schmid coined the term multiferroics to categorize a particular class of materials with coexisting (ferro/anti-ferro) magnetic and (ferro) electric state [15]. Thermodynamically, the free energy of a magnetoelectric system can be expressed as [16]

$$F(E, H) = F_0 - P_i^s E_i - M_i^s H_i - \frac{1}{2} \epsilon_0 \epsilon_{ij} E_i E_j - \frac{1}{2} \mu_0 \mu_{ij} H_i H_j - \alpha_{ij} E_i H_j - \frac{1}{2} \beta_{ijk} E_i H_j H_k - \frac{1}{2} \gamma_{ijk} H_i E_j E_k - \dots, \quad (1.1)$$

F_0 refers to the ground state free energy and subscripts i, j, k represents three different components of spatial coordinates. α_{ij} is the component of linear magnetoelectric susceptibility tensor α , describing the cross coupling between the polarization P_i and magnetization M_i . β_{ijk} and γ_{ijk} are the third order tensor coefficients of quadratic coupling. ϵ_0, μ_0 are dielectric and magnetic susceptibilities of vacuum. The electric polarization is

given as

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

and the magnetization as

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

However, the magnitude of the linear magnetoelectric effect is limited by the relation

$$\alpha_{ij} \leq \epsilon_{ii} \mu_{jj} \quad (1.4)$$

1.1.2 Terminology

The different classes of materials (Fig.1.2) which exhibits coupling between the spin and charge degrees of freedom are categorized as following :

- **Multiferroics:** Coexisting spontaneous magnetic (including antiferromagnetic (AF), ferrimagnetic and helimagnetic) and ferroelectric orders [17, 1] .
- **Magnetoelectric:** This class consists of long-range magnetic order, but no electrical order. A magnetic field induces the electric polarization and vice versa [18].
- **Magneto – dielectric:** This class of material exhibits a dielectric anomaly at the magnetic transition. Neither magnetoelectric nor multiferroic [19].

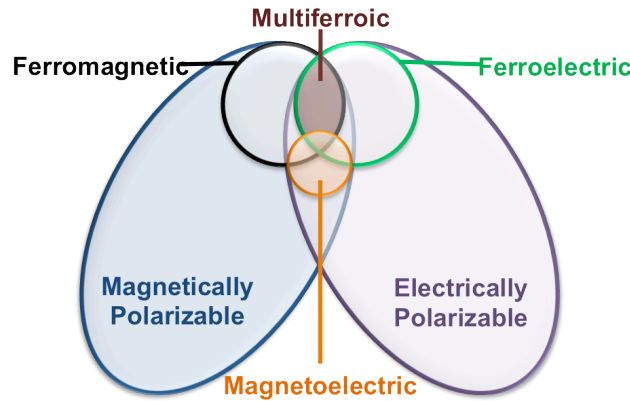


Figure 1.2: The relationship among the different classes of materials with coupling between the charge and spin degrees of freedom. Adapted with permission from Ref. [20], copyright (2008) by IOP Publishing.

1.2 Why are there only a few magnetic ferroelectrics?

The issues related to the coexistence of magnetism and ferroelectricity are listed as following:

1. **Symmetry requirement:** Landau theory of phase transitions suggested that each phase transition is associated with an order parameter and breaking of a particular symmetry. The occurrence of a ferroelectric state gives rise to spontaneous polarization, where electric dipoles order below the Curie temperature (T_C) through a phase transition from the paraelectric state to a ferroelectric state. For a ferroelectric state, polarization is the order parameter and space inversion symmetry is broken. Similarly, for a spontaneously magnetically ordered state, magnetization is the order parameter with broken time-reversal symmetry. Hence for a multiferroic, the space and time reversal symmetries have to be broken simultaneously [21]. Out of the 233 magnetic point group only 13 point groups namely, 1 , 2 , $2'$, m , m' , 3 , $3m'$, 4 , $4m'm'$, $m'm2'$, $m'm'2'$, 6 and $6m'm'$ are compatible for the coexistence of polarization and magnetization.

2. **d^0 vs d^n problem:** Typically, a conventional displacive type ferroelectric perovskite (ABO_3) oxide contains transition metal (TM) ions with a formal configuration d^0 (i.e., the TM ions with an empty d -shell), such as Ti^{4+} , Ta^{5+} and W^{6+} at B-sites. For instance,

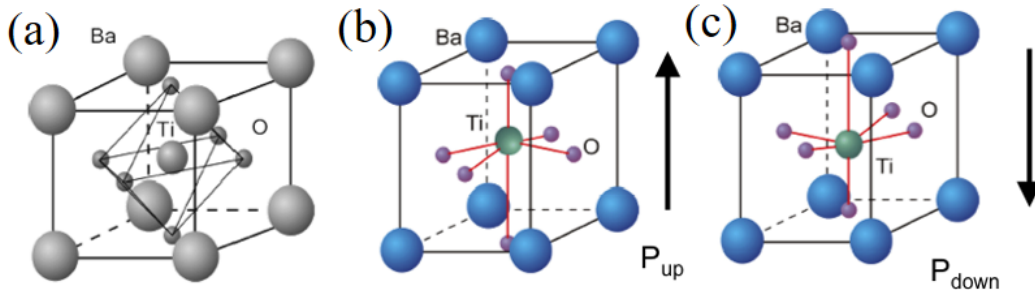


Figure 1.3: (a) Centrosymmetric unit cell of paraelectric BaTiO₃ (b) and (c) depicts the shift of the Ti^{4+} ion from the centre of O_6 octahedra towards one (or three) oxygen(s) to form a strong covalent bond at the expense of weakening the bonds with other oxygen ions. Such buckling breaks the space inversion symmetry and develops a electric polarization.

in the centrosymmetric paraelectric phase of BaTiO₃ (Fig.1.3(a)), the centre of gravity of positive and negative charge coincide with each other. Below T_C , the ion situated inside symmetrical octahedral oxygen cage shifts from the equilibrium position and generate a permanent dipole moment, as shown in Fig.1.3(b) and (c). The empty d -shell seems to assist in shifting the central ion by reducing the Coulomb repulsion and establishing a ferroelectric state. On the other hand, an unpaired electron in the d shell is a necessary

condition for magnetism. Hence an apparent contradiction occurs for the coexistence of these order parameters in a single phase material [21]. Irrespective of such incompatibility in coexisting ferroelectric and magnetic orders, to date there are hundreds of multiferroic materials.

1.3 Mechanism for the occurrence of multiferroicity

Following the above discussion where the coexistence of displacive type ferroelectricity and magnetic order is not possible, the search of non-displacive type ferroelectricity can give a possible way out. It has been found that lone pair electron cloud, geometrical effects, charge ordering of mixed valent cations and a special type of magnetic ordering are promising scenarios in establishing such a ferroelectric state.

1.3.1 Type-I multiferroics

In type-I multiferroics, the magnetism and ferroelectricity occur from different origins and results in a weak coupling between the order parameters. Often the electric ordering temperatures are higher than the magnetic ordering temperature. The different mechanisms that allows possible way of combining magnetization and polarization are as follows:

1.3.1.1 Lone pair Mechanism

For perovskite (ABO_3) ferroelectrics containing Bismuth (Bi) and Lead (Pb) in the A site, ferroelectricity occurs due to the $6s^2$ lone pair. Very often, this lobe like lone pair distorts the polyhedra and gives rise to ferroelectricity. These lone pairs which predominantly determine the structural/physical properties of a molecule are known as a *stereochemically active lone pair*. In 1959, L.E.Oregel [22] proposed that the lone pair cannot have purely s character when it is stereochemically active, and it must admix with the p orbital. In stereochemically lone pair active cations, off-centering towards a neighboring anion (or anions) is accompanied by a charge transfer into formally empty cation states (in this case Bi/Pb $6p$ orbitals), as depicted in Fig.1.4(a) and (b). The resulting covalent bond formation stabilizes the off-centering and produces a characteristic $6s^2$ lobe-shaped (instead of a spherical Fig.1.4 (c)) *lone pairs* around the cation [23]. BiMnO_3 and LaMnO_3 consisting trivalent Bi^{3+} , La^{3+} in the A site have very similar ionic radii e.g 1.24 and 1.22 respectively. But the Orthorhombic LaMnO_3 , which exhibits A-type Antiferro-

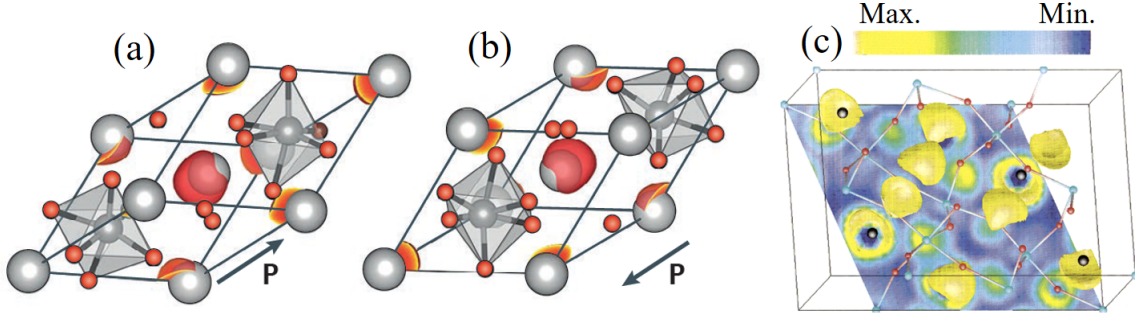


Figure 1.4: (a) and (b) represents shift of Bi lone pair along the FeO_6 octahedra generates polarization along the $[111]$ crystallographic axis. Figure adapted with permission from Ref. [1], copyright (2006) by the Springer Nature. (c) Isosurface of monoclinic BiMnO_3 calculated by DOS calculations, projected within a unit cell. The Black spheres corresponds to Bi atom and cyan spheres representing Mn bonded red O. Instead of a spherical lone pair, a lobe shape orbital is clearly visible which causes in stabilizing to a distorted structure. Figure adapted with permission from Ref. [23], copyright (2001) by the American Chemical Society.

magnetism and orbital ordering of manganese $d_{x^2-y^2}$ orbital do not show ferroelectricity, whereas the ferromagnetic insulator BiMnO_3 which stabilizes in a monoclinic phase [24] exhibits ferroelectricity. For BiMnO_3 , the origin of such lower symmetry structure has been explained by the stereochemical activity of the Bi^{3+} lone pair. This system exhibits a ferroelectric transition at $T_C = 800\text{K}$ and ferromagnetic ordering at $T_N = 110\text{ K}$ [25].

1.3.1.2 Geometrical Ferroelectricity

The perovskite manganites RMnO_3 (R =rare earth ions) stabilizes in a variety of structures depending on the radius of the R site ion. When the R site comprises of larger radii ion e.g. La, Nd and Pr, the cubic perovskite is distorted to orthorhombic $Pnma$ due to the Jahn-Teller distortion of the oxygen octahedral cage. When R site is occupied by smaller ions (e.g. $R = \text{Y, Dy, Ho, Er, Tm, Yb, Lu, or Sc}$) then the structure stabilizes in a hexagonal polar $P6_3cm$ at room temperature [26]. In hexagonal manganites, R ions are in the 7 fold coordination unlike cubic perovskites, and also Mn^{3+} is in the MnO_5 trigonal bipyramid instead of MnO_6 octahedra. This results in the crystal field splitting of Mn^{3+} into two doubly degenerate e_g orbitals and one single a_g orbital, different from cubic/orthorhombic RMnO_3 . This makes Mn^{3+} to be Jahn-Teller inactive.

Hexagonal YMnO_3 exhibits a ferroelectric transition at $T_c = 950\text{ K}$ (paraelectric $P6_3/mmc$ to ferroelectric $P6_3cm$ by tripling of c axis), and an A-type AFM ordering at $T_N = 77\text{K}$. It has been found that the ferroelectricity in YMnO_3 is driven by neither an off-center shift of Mn ions (displacive type) nor it has a lone pair which may cause

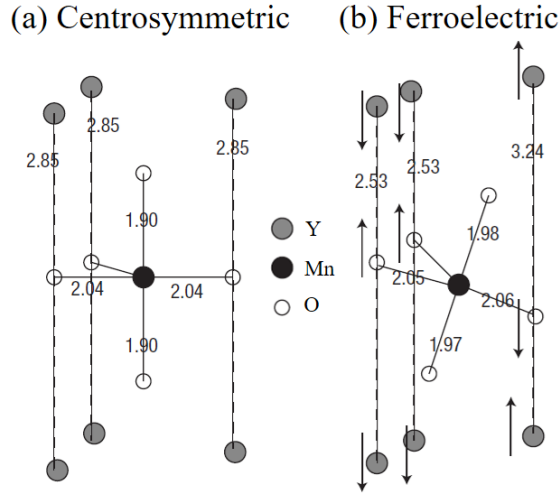


Figure 1.5: Schematic of the rotation of the MnO_5 polyhedra from para to ferroelectric phase. The digit implies the bond length in Å, whereas the arrow indicated the atomic displacement with respect to the centrosymmetric paraelectric phase. Figure adapted with permission from Ref. [27], copyright (2004) by the Springer Nature

noncentrosymmetric structure. For YMnO_3 a new route has been proposed to govern ferroelectricity where the rotation of MnO_5 polyhedra changes the Y-O bond along the hexagonal c axis, as depicted in Fig. 1.5. Such rotation makes the Y to be accentric with respect to its oxygen neighbors and breaks the inversion symmetry. In conventional ferroelectrics, the para to ferroelectric phase transition is governed by a change in chemical bonding and rehybridization. By DFT calculations it has been proposed that the Mn ions remain at the center of polyhedra cage and absence of interaction between Y and oxygen orbitals, ruling out the possibility of charge transfer and rehybridization like a proper ferroelectric [27]. The materials RFeO_3 ($\text{R} = \text{Lu}, \text{Yb}$), Ruddlesden-Popper series candidate $\text{R}_3\text{Mn}_2\text{O}_7$ ($\text{R} = \text{Ca}, \text{Ba}, \text{Sr}$), BaNiF_4 also belong to this class of multiferroics.

1.3.1.3 Ferroelectricity due to charge ordering

Since ferroelectricity is directly related with an electric charge, it is natural to expect ordering of charge to induce multiferroicity in a magnetic material. The occurrence of ferroelectricity by charge ordering can be explained schematically in 1D as depicted in Fig. 1.6. Let us consider a 1D array of neutral atoms. If there is charge ordering in this chain, i.e. one site has the charge $+e$ and the adjacent site $-e$, then the sites become inequivalent. In this case, the space inversion symmetry is not broken, as shown by two mirror plane with dotted red lines in Fig. 1.6(b). Again, if the same neutral chain forms a dimer then instead of charge, the bond becomes inequivalent with alternate

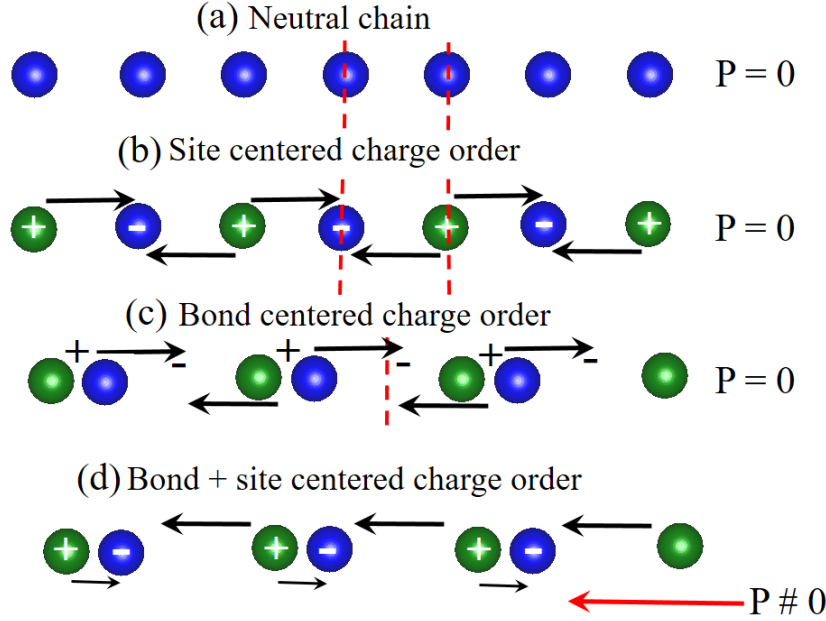


Figure 1.6: Schematic of the different scenario of charge ordering that give rise to the occurrence of polarization, where the arrow indicates the direction of polarization [28]. The dotted line indicates a mirror plane.

stronger and weaker bonds, called bond centered charge ordering. This configuration is also centrosymmetric and does not induce polarization. However when both site and bond centered charge ordering occurs simultaneously, then this configuration breaks space inversion symmetry and establishes a ferroelectric state [28]. Since the occurrence of ferroelectricity has no contribution from the spin of electron, the magnetic ordering and ferroelectricity are decoupled and can be categorized to be a Type-I multiferroic. Perovskite manganite $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ [29], magnetite Fe_3O_4 [30, 31], LuFe_2O_4 [32], LiFe_2F_6 [33] belong to this class.

1.3.2 Type-II Multiferroics

In a type-I multiferroic, ferroelectricity originates from the electronic, lattice, charge degree of freedom whereas magnetism occurs from the spin of the electron. As magnetism and ferroelectricity have different origins, the coupling between magnetization and polarization is very small. It has been found that various type of commensurate/incommensurate spin configurations are promising to break space inversion symmetry and provide a strong coupling between the order parameters. These systems are known as type-II multiferroics [34].

1.3.2.1 Spin driven multiferroics

A macroscopic polarization is generated from a non-collinear spin configuration. The origin of such polarization could be explained by three different models as follows:

1. Spin current model: According to KNB model, the superexchange interaction between two transition metal ions M1 and M2 mediated through the oxygen atom O with the non-collinear spin direction $\vec{e}_1$ and $\vec{e}_2$ will produce a spin current $\vec{J}_s$. The spin current $\vec{J}_s \propto \vec{e}_1 \times \vec{e}_2$ will induce an electric polarization $\vec{P}$ [35], as shown in Fig.1.7. The induced

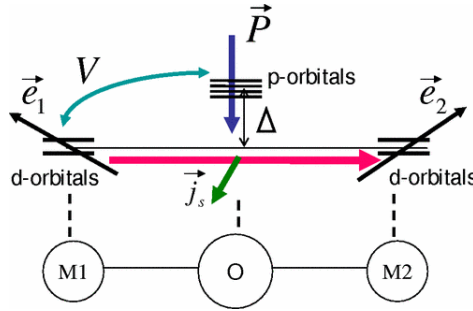


Figure 1.7: The superexchange interaction between two transition metal ions M1, M2 mediated through oxygen atom O between two nonparallel spins via oxygen ion. A spin current $\vec{J}_s \propto \vec{e}_1 \times \vec{e}_2$ is generated in this configuration. This spin current induces an electric polarization as proposed by KNB model [35]. Figure adapted with permission from Ref. [35], copyright (2004) by the American Physical Society

polarization is expressed as $\vec{P} = \lambda \sum_{\langle i,j \rangle} \vec{e}_{ij} \times (\vec{S}_i \times \vec{S}_j)$, where $\vec{e}_{ij}$ is the unit vector connecting the spins $\vec{S}_i$ and $\vec{S}_j$, λ is constant proportional to spin-orbit and spin-lattice coupling term. Hence the direction of polarization is determined by spin helicity/chirality $H = \vec{S}_i \times \vec{S}_j$.

2. Inverse Dzyaloshinskii-Moriya (DM) interaction: The DM interaction in a non centrosymmetric bond is expressed as $I_{DM} = \vec{D}_{ij} \cdot (\vec{S}_i \times \vec{S}_j)$, where $\vec{D}_{ij} \propto \vec{r}_i \times \vec{r}_j = \vec{r}_{ij} \times \vec{x}$. Hence $\vec{D}_{ij}$ will be zero if all the three ions are aligned linearly or the interacted spins are aligned parallel to each other. Often DM interaction drives weak ferromagnetism in such a non-collinear spin configuration [36]. A non-collinear spin configuration is set by competitive (FM/AFM) nearest neighbor magnetic interaction or by geometrical frustration. In order to minimize the energy, DM interaction tends to shift the oxygen ion from the center of the bond and leads to the generation of a macroscopic local polarization, as depicted in Fig.1.8.

3. Symmetry origin: The origin of polarization ($\vec{P}$) in a spiral magnet could also be explained based on space and time reversal symmetry argument. The space inversion operation $\vec{r} \rightarrow -\vec{r}$ transforms polarization $\vec{P} \rightarrow -\vec{P}$ and leaves magnetization $\vec{M}$ invariant

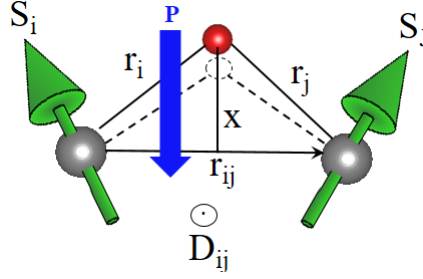


Figure 1.8: Dzyloshinskii-Moriya antisymmetric exchange interaction in non-collinear spin configuration. The dotted line represents the shift of oxygen ion due to the DM interaction and the blue arrow indicates the direction of induced polarization

whereas the time reversal operation $t \rightarrow -t$ transforms $\mathbf{M} \rightarrow -\mathbf{M}$ leaves P invariant. Considering magneto electric coupling to be invariant under time reversal operation $t \rightarrow -t$, requires that the lowest order of coupling should be quadratic in M . The same for space inversion requires a linear term in $\mathbf{P}$ (Homogeneous polarization) and a ∇M i.e a spatial variation of magnetization established by spiral spin order [37]. Hence, the Landau free energy for simple cubic lattice can be written as

$$\phi_{em}(P, M) = \gamma P \cdot [M(\nabla \cdot M) - (M \cdot \nabla)M]$$

Considering quadratic part of the thermodynamic potential $\phi_e = \frac{P^2}{2\chi_e}$, where χ_e is the dielectric susceptibility without magnetic ordering. Minimizing $\phi_e + \phi_{em}$ w.r.t P one obtains,

$$P = \gamma \chi_e [(M \cdot \nabla)M - M(\nabla \cdot M)]$$

Considering now a SDW with wave vector Q , $M = M_1 e_1 \cos Q \cdot x + M_2 e_2 \sin Q \cdot x + M_3 e_3$ where e_1 , e_2 and e_3 are the orthogonal basis. The average polarization is

$$P = \frac{1}{V} \int d^3x P = \gamma \chi_e M_1 M_2 [e_3 \times Q].$$

Hence the polarization is orthogonal to the spin rotation axis e_3 and the wave vector Q . The direction of the induced polarization for several spiral spin configurations are described in Fig.1.9. For a non zero value of M_1 or M_2 , the SDW describe to a sinusoidal spin configuration with $e_3 \parallel$ to Q and the resultant polarization is zero. While M_1 and $M_2 \neq 0$ causes a helical spin structure with e_3 as spin rotation axis. If simultaneously M_1 , M_2 and $M_3 \neq 0$ then the spin configuration is conical, as depicted in Fig.1.9(d) and results in a finite value of polarization. Since spin helicity ($H = e_3 \times Q$) results in ferroelectricity as

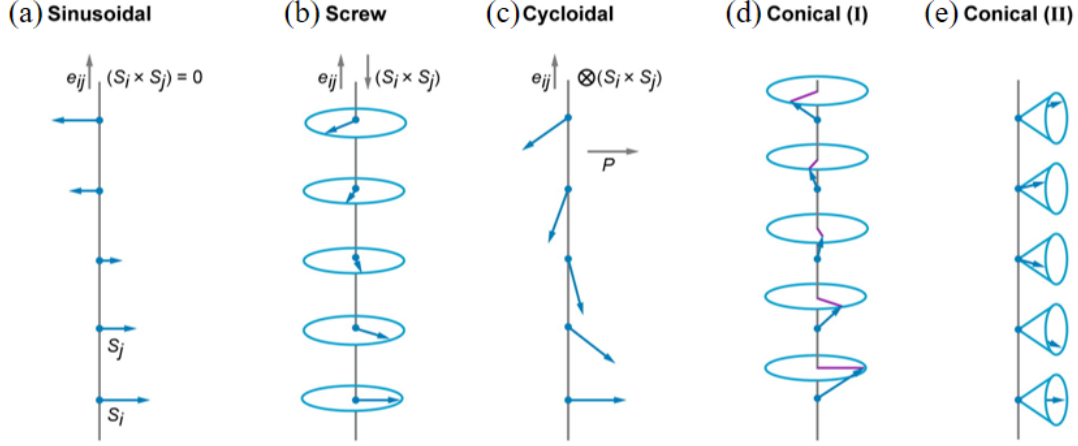


Figure 1.9: Schematic of the direction of spin propagation (e_{ij}), spin helicity/ vector spin chirality ($S_i \times S_j$) and polarization (P) for different magnetic structures, illustrating the spiral spin order induced polarization [34]. Figure adapted with permission from Ref. [34], copyright (2007) by the Annual Reviews.

a secondary order parameter, there is strong coupling between the order parameters. It is possible to control the direction of helicity/vector chirality $\sum_i S_i \times S_{i+1}$ by an electric field and thereby flip the direction of polarization.

Spin-polarized neutron scattering has verified direct experimental evidence of breaking space inversion symmetry by spiral spin order and establishing a ferroelectric state. The helicity of a noncollinear magnetic structure could be determined by spin-polarized neutron diffraction intensity study of magnetic satellite reflections. The L scan of magnetic satellite reflections $(4, +q, 1)$ and $(4, -q, 1)$ with $q \approx 0.27$ were measured for a TbMnO_3 single crystal [38]. The polarization of the incident neutron beam (S_n) could be aligned parallel/ antiparallel with respect to the scattering vector (Q_s) by a spin flipper, as shown in Fig.(1.10 (a) and (b)). When S_n is anti-parallel to Q_s the scattering intensity $I_\downarrow$ is 9 times higher than the intensity $I_\uparrow$ for $(4, +q, 1)$ satellite reflection and the resultant polarization is positive ($P_c > 0$). Such behavior is typical for a spiral magnet with single helicity. By poling the crystal in the negative electric field, the polarization is flipped i.e $P_c < 0$. Interestingly, the polarized neutron intensity ratio also flipped i.e $I_\uparrow > I_\downarrow$ clarifying that the opposite helicity domain is being now more populated Fig.(1.10 (c) and (d)). This clearly proved that the helicity of spiral magnet could be controlled by an electric field. It is to be noted that the difference between $I_\uparrow$, $I_\downarrow$ emerges only in the ferroelectric state. It has also been proved that the polarization measured from pyroelectric measurement follow $(I_\downarrow - I_\uparrow)$ which is proportional to $m_b m_c$, and provides a direct verification of the discussed theoretical model.

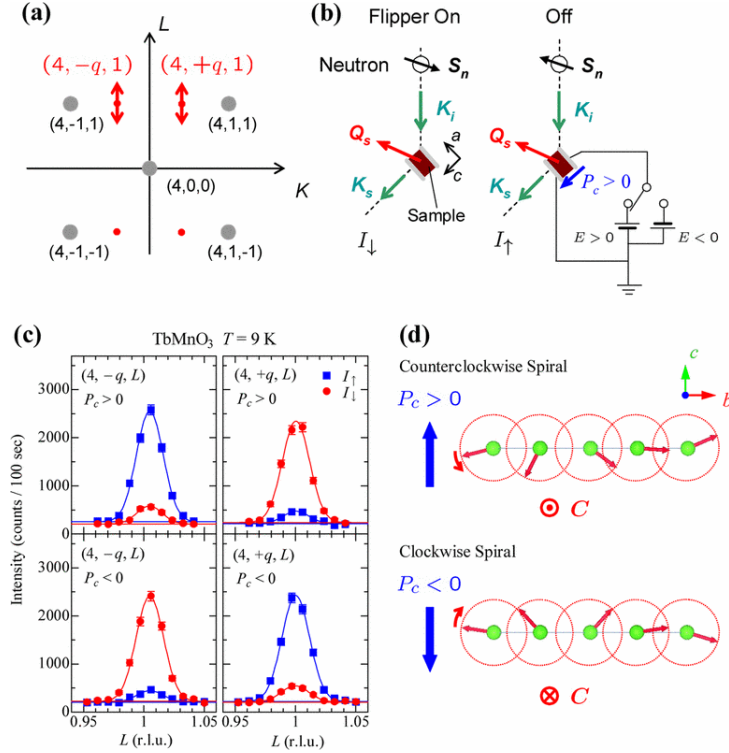


Figure 1.10: (a) The magnetic satellite reflections in the reciprocal (K, L) plane corresponded to the L scan in spin polarized-neutron-diffraction measurements (b) The schematic illustration of the apparatus explaining the control of the spin of incident neutron beam S_n , parallel (when the flipper was off) or antiparallel (on) to the scattering vector Q_s . (c) Electric polarization dependence of the intensity of magnetic satellites $(4, \pm q, 1)$ at 9 K. L-scan profiles of magnetic satellites $(4, \pm q, 1)$ with $P_c > 0$ and $P_c < 0$. (d) The relation between the spin helicity and the electric polarization in TbMnO_3 as proposed by KNB model [38]. Figure adapted with permission from Ref. [34], copyright (2007) by the American Physical Society.

1.3.2.2 Exchange striction driven multiferroics

Multiferroicity originating from exchange striction does not require relativistic spin-orbit coupling or helical/ spiral magnetic structure. Magnetically inequivalent lattice ($\uparrow\uparrow\downarrow\downarrow$) along with different charges (different TM ions/ same TM ions with different valence states) breaks the space inversion symmetry due to the exchange striction. Magnetostriction drives selective distortion of ferro and antiferro bonds and makes the bond inequivalent. Hence, both the site and bond become inequivalent and breaks the space inversion symmetry, as shown in Fig. 1.11(a). This can be understood by considering a simple Ising model with nearest neighbor (J_1) and next nearest neighbor (J_2) interactions expressed as $H = J_1 \sum_i S_i^z S_{i+1}^z + J_2 \sum_i S_i^z S_{i+2}^z$. If the interaction J_2 is antiferromagnetic ($J_2 < 0$) and the interaction strength is larger than J_1 ($J_2 > \frac{1}{2|J_1|}$), will give rise to (up-up-down-down) $\uparrow\uparrow\downarrow\downarrow$ type magnetic ordering [28]. If $J_1 < 0$ then bond with parallel spin and $J_1 > 0$

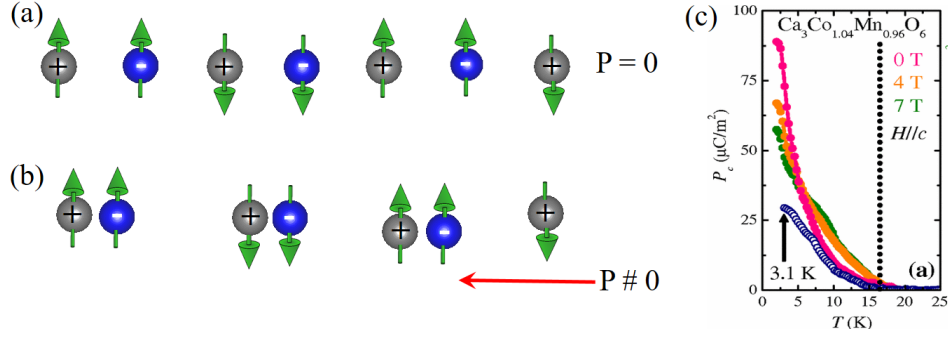


Figure 1.11: (a) Charge ordering in an up-up-down-down spin chain (b) The magnetostriction between the ferro and antiferro bond makes the bond inequivalent and produce a polarization as indicated by the red arrow. (c) Polarization induced in an Ising up-up-down-down spin chain with charge ordering of Co^{2+} and Mn^{4+} . Electric polarization of single crystal $\text{Ca}_3\text{Co}_{1-x}\text{Mn}_x\text{O}_6$ ($x=0.96$) along the chain direction ($P \parallel c$), taken upon warming. The samples were poled upon cooling from 40 K to 2 K (filled circles), and to 3.1 K (open circles) before the measurement [39]. Figure adapted with permission from Ref. [39], copyright (2008) by the American Physical Society.

then the bond with anti-parallel spin will be shortened in order to increase the gain of magnetic energy of that particular bond and consequences in a macroscopic polarization along the direction of the bond.

$\text{Ca}_3\text{Co}_{2-x}\text{Mn}_x\text{O}_6$ contains low spin Co^{2+} and high spin Mn^{4+} with $\uparrow\uparrow\downarrow\downarrow$ type of magnetic order along the c axis. A charge ordering of Co^{2+} and Mn^{4+} ions occupying the trigonal prismatic and octahedral sites respectively in this spin chain breaks the space inversion symmetry due to magnetostriction. Below the magnetic transition ($T_N \approx 16.5$ K), polarization emerges along the c axis due to exchange striction, as is depicted in Fig. 1.11(b)[39].

In the present case, polarization is generated parallel to the bond/ spin chain. However, exchange striction also can generate polarization perpendicular to the $\uparrow\uparrow\downarrow\downarrow$ spin chain, when the bond angle (TM-O-TM) is manipulated instead of the bond length. Transition metal cations with intervening oxygen anions (O^{2-}) could play a similar role as described in the previous case of TM ions with different valences. According to Goodenough-Kanamori rule of super exchange, the strength of ferromagnetic/AFM exchange will increases by decreasing/increasing the angle of TM-O-TM i.e. by moving the oxygen ion downwards. This results in shifting the oxygen ion perpendicular to the spin chain for ferro and antiferro bonds in the same direction and gives rise to polarization, as illustrated in Fig. 1.12. The orthorhombic perovskite HoMnO_3 is highly distorted with Mn-O-Mn bond ($\approx 144^\circ$) because of the smaller size of A site ion. Here in a collinear antiferromagnetic-E (AFM-E) spin configuration, the ferromagnetic zigzag spin chains of

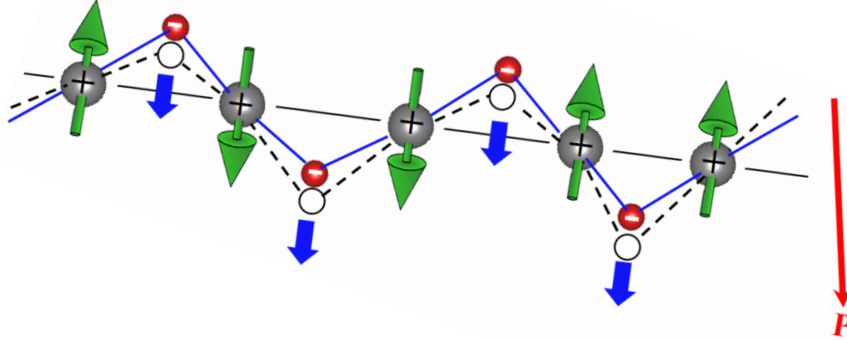


Figure 1.12: Schematic illustration of the distortion of the Mn-O-Mn angle by Goodenough-Kanamori superexchange interaction. The dotted line shows the resultant displacement of the oxygen ion due to such exchange striction. The red arrow indicates the direction of resultant polarization.

the MnO_2 planes are antiferro-magnetically coupled with respect to both the adjacent in-plane chains and gives rise to a similar scenario as depicted in Fig.1.12. The exchange striction results in a shift in the intervening oxygen ions by distorting the bond angle and generate a macroscopic polarization perpendicular to the spin chain [40].

1.3.2.3 d-p hybridization

The covalency between a magnetic d orbital and oxygen p orbital can be modulated depending on the alignment of the magnetic spin via the spin-orbit coupling [41]. This causes generation of polarization along the bond direction. Unlike the exchange striction and spin current/ IDM mechanisms, where spin correlation plays an important role, this mechanism requires a single magnetic atom with a ligand. Multiferroicity in a class of noncentrosymmetric systems Ba_2MXO_7 ($\text{M} = \text{Co}, \text{Mn}, \text{Cu}$; $\text{X} = \text{Ge}, \text{Si}$) [42, 43] are governed by this mechanism. For spin dependent d-p hybridization induced multiferroicity, the system does not need complex helical magnetic ordering, provided the underlying crystal lattice is noncentrosymmetric. The akermanite $\text{Ba}_2\text{CoGe}_2\text{O}_7$ stabilizes in the space group $P\bar{4}2_1m$ with two non-equivalent Co tetrahedra. When the Co^{2+} moment is aligned parallel to the upper-lying oxygen bond i.e the direction of $\text{O}_1\text{-O}_2$, polarization is generated along the [001] direction. The polarization is reversed when Co spin is

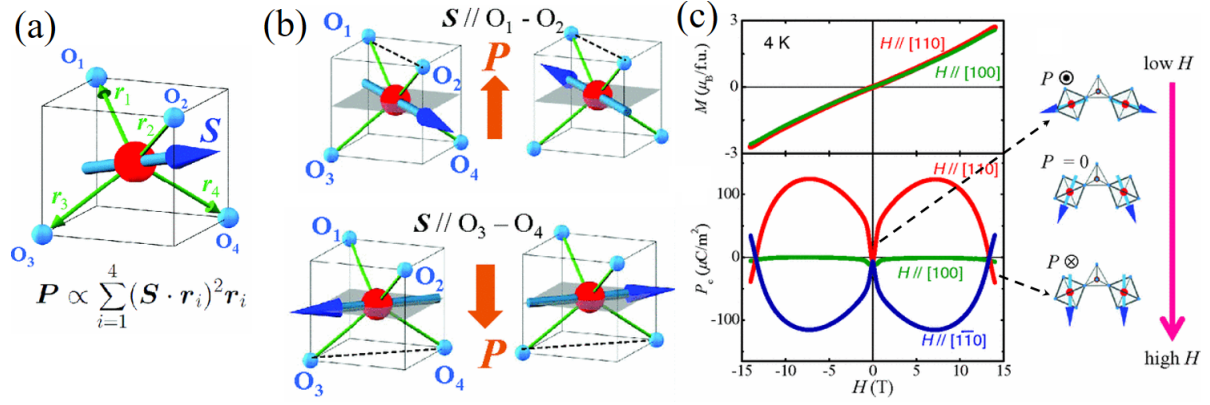


Figure 1.13: (a) The spin moment in tetrahedral coordination of Akermanite structure. (b) The direction of the polarization depending on the orientation of the spin along upper/lower lying oxygen bonds. (c) Variations of magnetization and out of-plane component of the electric polarization (P_c) of $\text{Ba}_2\text{CoGe}_2\text{O}_7$ in H along several directions in the (001) plane at 4 K. The magnetic moments are almost perpendicular to the H direction in low H , while they are aligned along the H direction in high H . The polarization shows a sign change in the course of the spin structural change [42, 43]. Figure adapted with permission from Ref. [42], copyright (2012) by the American Physical Society.

aligned along the $\text{O}_3\text{-O}_4$ bond (Fig.1.13(a) and (b)). Such spin directional variation of polarization because of the manipulation of d-p hybridization can be expressed as $P \propto \sum_i (\mathbf{S}_i \cdot \mathbf{r}_i)^2 \mathbf{r}_i$. According to this mechanism for $\text{Ba}_2\text{CoGe}_2\text{O}_7$ the polarization $\mathbf{P} = (P_a, P_b, P_c)$ is expressed as $\mathbf{P} \propto (0, 0, \sin 2\phi_H)$, where ϕ_H is the angle between the $[100]$ axis and the applied magnetic field (H) direction in the (001) plane, as shown in Fig.1.13(c). A similar response has been also observed for other akermanite members and noncentrosymmetric B_2CuO_4 [44]

1.3.2.4 Ferroaxial Multiferroics

Electric polarization can emerge by coupling structural axiality with the underlying magnetic structure, known as ferroaxial coupling. A crystal structure can be considered axial if there exists a structural distortion that is unchanged by inversion and makes the two senses of rotation (clockwise or counterclockwise) about an axial vector $\mathbf{A}$ distinguishable. It is to be noted that polarization is a polar vector whereas ferroaxial distortion possess an axial vector symmetry.

If σ is the spin helicity then phenomenologically the trilinear coupling term $\sigma \mathbf{A} \cdot \mathbf{P}$ is invariant both under time and space inversion and is a promising scenario for inducing multiferroicity. Multiferroicity in $\text{RbFe}(\text{MoO}_4)_2$ [45], $\text{Cu}_3\text{Nb}_2\text{O}_8$ [46], $\text{CaMn}_7\text{O}_{12}$ [47] belong to the ferroaxial class. Let us consider the case of $\text{RbFe}(\text{MoO}_4)_2$ (RFMO), where

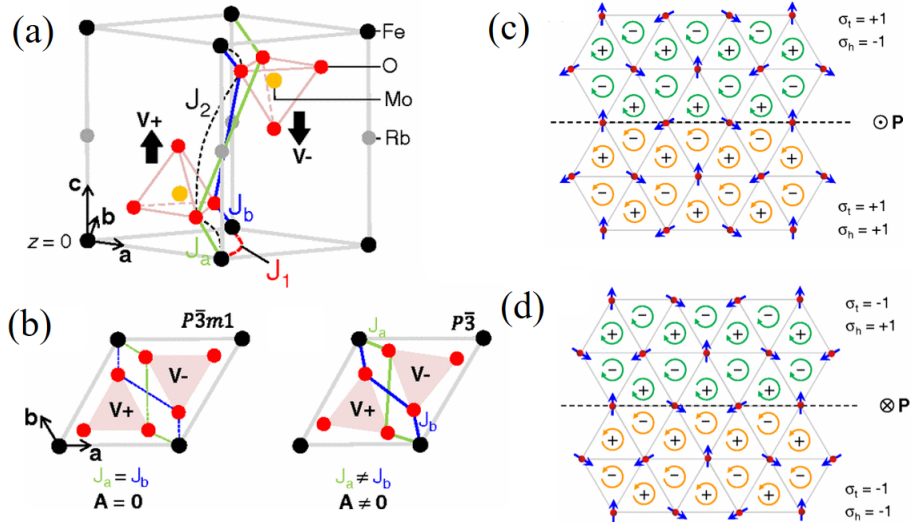


Figure 1.14: (a) Possible exchange interaction in $\text{RbFe}(\text{MoO}_4)_2$ structure. Where J_1 and J_2 are in plane and vertical exchange path. J_a and J_b are supersuper exchange path along the diagonal. (b) and (c) The rotation of MoO_4 tetrahedra (v_+ and v_-) due to structural transition and the effect of ferroaxial distortion on exchange path. The direction of polarization and magnetic structure upon (c) positive and (d) negative field cooling. The arrow indicates the axial rotation of MoO_4 tetrahedra. [45]. Figure adapted with permission from Ref. [45], copyright (2012) by the American Physical Society.

previously the origin of multiferroicity was mistaken as spin-dependent d-p hybridization with 120° screw spiral magnetic ordering. RFMO stabilizes in the $P\bar{3}m1$ symmetry where the superexchange J_a and J_b have the same strength. A structural transition occurs at 190K by rotating MoO_4 tetrahedra from the symmetry $P\bar{3}m1$ to $P\bar{3}$ (point $\bar{3}$ belongs to ferroaxial class) and results in $J_a \neq J_b$. The difference $J_a - J_b$ is determined by the strength and sign of the ferroaxial distortion, as is illustrated in Fig. 1.14(a) and (b)

The rotation of the magnetic layer and creation of ferroaxial domains could be understood by defining a staggered triangular chirality σ_t and magnetic helicity σ_h , where $\sigma_t = (\mathbf{S}_1 \times \mathbf{S}_2 + \mathbf{S}_2 \times \mathbf{S}_3 + \mathbf{S}_3 \times \mathbf{S}_1) \cdot \mathbf{v} / S^2$ and $\sigma_h = (\mathbf{S}_{z=0} \times \mathbf{S}_{z=1}) \cdot \hat{\mathbf{r}}_{01} / S^2$. v^+ and v^- are unit vectors, when MoO_4 tetrahedra is aligned to the positive and negative direction of c^* respectively. $\sigma_t = +1$ if the Fe spins rotate counterclockwise with v^+ tetrahedra at its centre, otherwise it is -1. σ_h has ± 1 value for right/left handed screw spiral.

The symmetric exchange energy for each Fe ion can be expressed as $E \propto E_0 + \sigma_h \sigma_t (J_a - J_b)$ where E_0 is the contribution without magnetic chirality. The second term will lower the energy for $J_b > J_a$ and the states $\sigma_t, \sigma_h = (+, +); (-, -)$ have lower energy than $(+, -); (-, +)$ and vice versa for $J_a > J_b$. This gives rise to two possible axial domains with different propagation vector. By neutron spherical polarimetry, the configuration of σ_t, σ_h under positive (Fig. 1.14(c)) and negative (Fig. 1.14(d)) electric field and the direction of polar-

ization have been found explicitly. The electric polarization $= (0,0,P_z)$ can be expressed as $S^2P_z(c_1\sigma_t+c_2A\sigma_h)$ where c_1, c_2 are coupling constants and axial vector $A=(0, 0, A)$. By reversing the direction of electric field, it is possible to switch both σ_t and σ_h [48].

1.4 Technological application of Multiferroics

Multiferroic materials have been widely studied with an eye on potential applications in the form of magnetic sensors, spintronics etc [49, 50, 51]. Out of several applications, the most promising use of multiferroic is a Four state memory device. Till date, most popular nonvolatile random access memory (RAM) are ferroelectric RAM (FRAM) and magnetoresistive RAM (MRAM). In a FRAM, ferroelectric capacitor architecture is used for storage. Unfortunately, FRAM has the disadvantage of destructive read and reset operation. On the other hand, MRAM uses spin-dependent high and low resistance for binary bit 0 and 1. However, writing in a MRAM involves a magnetic field generated by electric current and larger power consumption. A multiferroic random access memory will solve the disadvantage of FRAM/MRAM by writing the data electrically and reading magnetically. Moreover, a single phase multiferroic provides an opportunity to encode information both in electric polarization and magnetization, to obtain a four state logic with two remanent polarization (+P,-P) and remanent magnetization(+M,-M). Experimentally, using thin films of multiferroic $\text{La}_{0.1}\text{Bi}_{0.9}\text{MnO}_3$ in a magnetic tunnel junction Gajek et al. has demonstrated a four bit memory operation [52].

Multiferroics have been proposed to show giant solid state cooling combining the heat absorption of electrical dipole and magnetic spins, called multicaloric effect [53, 54]. The thermodynamic relations of multicaloric effect induced by electric and magnetic field are expressed as:

$$\Delta T_e = -\frac{T}{C} \cdot \int_{E_f}^{E_i} \left[\frac{\alpha_e}{\mu_0 \chi^m} \cdot \left(\frac{\partial M}{\partial T} \right)_{H,E} + \left(\frac{\partial P}{\partial T} \right)_{H,E} \right] \cdot dE$$

$$\Delta T_m = -\frac{T}{C} \cdot \int_{H_f}^{H_i} \left[\frac{\alpha_m}{\epsilon_0 \chi^e} \cdot \left(\frac{\partial P}{\partial T} \right)_{H,E} + \left(\frac{\partial M}{\partial T} \right)_{H,E} \right] \cdot dH$$

Where T is temperature, C is heat capacity, μ_0 and ϵ_0 are magnetic permeability and electric permittivity of vacuum, χ_m and χ_e are magnetic and dielectric susceptibilities, α_m and α_e are magnetic and electrically induced magnetoelectric susceptibilities, M is magnetization and P is polarization. Unlike electro/magnetocaloric effect, during adiabatic

demagnetization/depolarization, in a multiferroic both the electric dipoles and magnetic moments absorb heat simultaneously during the relaxation process and could lead to an enhancement in the caloric effect [53].

1.5 Motivation of work

This thesis aims to explore magnetoelectric coupling in geometrically frustrated transition metal oxides. Geometrical frustration refers to the phenomena where the magnetic interaction among the spins is incompatible with the underlying lattice. Antiferromagnetically interacting spins residing in face/corner shared triangle give rise to a situation where one of the magnetic interactions is frustrated out of three (1.15 (a) and (b)). A

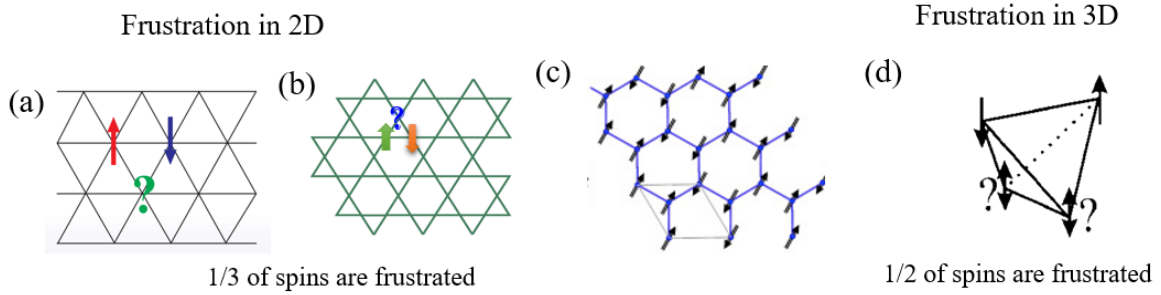


Figure 1.15: Antiferromagnetically interacted spins in (a) Face (b) corner sharing triangle (c) a honeycomb network represents geometrically frustrated magnetic lattice in 2D and (d) a tetrahedra in 3D.

similar situation arises in a honeycomb and tetrahedral configurations (1.15 (c) and (d)). Experimentally, an empirical measure of frustration is determined by the frustration parameter $f = \theta_{CW}/T_N$ where θ_{CW} is the Curie-Weiss temperature (usually set by coupling strength), and T_N is the magnetic ordering temperature [55]. Typically, $f > 5-10$ indicates a strong suppression of long-range magnetic ordering, as a result of frustration [56]. Often such frustrated systems manifest in a highly degenerate ground state instead of a single stable ground state. Geometrical frustration often leads to competitive magnetic interaction and consequences in a complex magnetic ordering.

For a type-II multiferroic, the electric polarization (P) is induced by a specific type of non-collinear magnetic order, and it is expressed as $P \propto (M \cdot \partial) M - M(\partial \cdot M)$ [57]. Hence the spatial variation of magnetization is a promising scenario for inducing a polarization. The magnetic order set by geometrical frustration often gives rise to an unconventional magnetic ground state with a spatial variation of magnetization which inherently breaks the spatial inversion symmetry and induces ferroelectricity, as shown in Fig. 1.16.

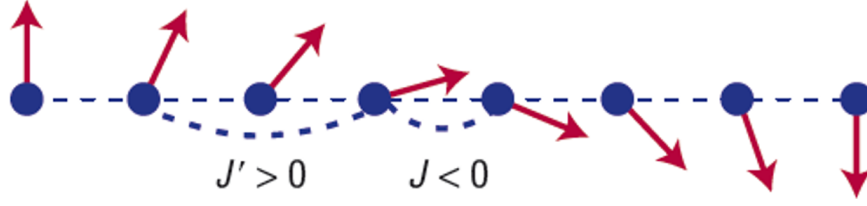


Figure 1.16: A competitive magnetic interaction between (nearest neighbour J and next nearest neighbour J') causes to establish a non-collinear magnetic order. This magnetic ordering is a promising scenario in inducing a electric polarization [57]. Figure adapted with permission from Ref. [57], copyright (2007) by the Springer Nature.

1.6 Scope of the thesis

The discovery of type-II multiferroics has brought rapid growth in the research area of magnetoelectric multiferroic. Intense study of magnetoelectric coupling in several materials has shed light on the different possible scenario of combining magnetism and ferroelectricity in single phase material. In this thesis, we aim to design new magnetoelectric multiferroic materials and study their physical properties. A number of measurement facilities were also setup during the course of this thesis. This includes developing the following experimental tools:

- Dielectric and pyroelectric measurement setups : Sample holder for low-temperature dielectric and pyroelectric measurements in a closed cycle refrigerator (CCR) have been designed. Both the measurements were automated using LabVIEW program.
- Dielectric and pyroelectric measurement under magnetic field: Using MPMS-XL Manual Insertion Utility Probe, low-temperature dielectric and pyroelectric measurements up to 7 Tesla magnetic field have been performed.
- Electric field dependent magnetic measurement: Using MPMS-XL Manual Insertion Utility Probe, electric field dependent magnetic measurements have been performed successfully on single crystal specimen, and the magnetoelectric susceptibility has been measured along different orientations of the crystal.

This thesis presents:

- A new type -II multiferroic $\text{Fe}_4\text{Ta}_2\text{O}_9$ - the only genuine multiferroic in its material class. We suggest that the observed properties arise as a consequence of an effective reduction in the dimensionality of the magnetic lattice, with the magnetically active Fe ions preferentially occupying a quasi-2D buckled honeycomb structure.

- The observation of anisotropic linear magnetoelectric coupling along different crystallographic orientations of single crystalline $\text{Mn}_4\text{Ta}_2\text{O}_9$. We also reveal the magnetic structure of this system using powder neutron diffraction measurements.
- A near room temperature magneto-dielectric Fe_2WO_6 characterized by inhomogeneous magnetic and electric ground states.
- The Swedenborgite series $\text{Dy}_{1-x}\text{Ca}_x\text{BaCo}_4\text{O}_7$ where geometrical frustration is lifted through a structural transition associated with the buckling of the Kagome layer. This transition also occurs as a function of temperature, and this temperature scales linearly with the mean ionic radius of the Dy/Ca site ion. However, multiferroic $\text{CaBaCo}_4\text{O}_7$ clearly violates this quasilinear relationship. We also report on a new member of this material class - $\text{SrBaCo}_4\text{O}_7$.
- A step by step guide of solving magnetic structure from Neutron powder diffraction data using FullProf Suite.

Chapter 2

Instrumentation and Experimental techniques

2.1 Introduction

Experimentally, the onset of magnetic ordering in a material is typically identified by the observation of an anomaly in a temperature dependent magnetic measurement. The magnetic susceptibility diverges at the phase transition from the paramagnetic state to a magnetically ordered state. Similarly, the onset of an electrical (dipole) ordering in materials is characterized by performing a temperature dependent dielectric measurement. However, an anomaly in dielectric measurement alone does not necessarily imply a long-range ordering of permanent electric dipoles or the appearance of a ferroelectric state. Often relaxation of charges or changes in electrical conductivity causes a similar feature in temperature-dependent dielectric measurement. Further confirmation of the occurrence of the ferroelectric state is typically obtained by performing a pyroelectric measurement across an observed dielectric anomaly. A type-II multiferroic is identified by the concurrence of the onset of ferroelectric ordering temperature (T_C) with the magnetic ordering temperature (T_N). The study of the coupling between magnetic and polar is further explored by the manipulation of dielectric constant (ϵ)/polarization (P) under an applied magnetic field (H) and by estimating the magnetoelectric susceptibility $\alpha = \left(\frac{\partial P}{\partial M} \right)_E$. The other approach is to measure magnetization (M) in the presence of an electric field (E) and exploiting the electrical control of magnetization i.e. $\alpha = \left(\frac{\partial M}{\partial E} \right)_H$. In this chapter details of the instrumentation work performed during the course of the thesis is presented. Development of low temperature dielectric and pyroelectric measure-

ment setups under zero magnetic field (in a Close Cycle Refrigerator) and in the presence of magnetic field (using manual insertion utility probe of MPMS-XL SQUID) are discussed. Demonstration of the design of electric field dependent magnetic measurement performed in MPMS is presented. Also, a detailed description of the sample preparation and several experimental techniques used for characterization of the materials studied during the course of this work are described.

2.2 Accessing Low temperatures by Close Cycle Refrigerator

For performing a low temperature experiment, the specimens are typically cooled by using a cryoliquid. Most commonly used cryoliquids are liquid Nitrogen (N_2) and Helium (He) stored using a Dewar flask, which is a double sidewall vacuum container for prohibiting heat conduction, convection and radiation from surrounding to the cryoliquid. However, a Close Cycle Refrigerator (CCR) provides cryogenic cooling without the use of cryogenic liquids and requires minor maintenance [58]. In a closed cycle refrigerator (CCR), low

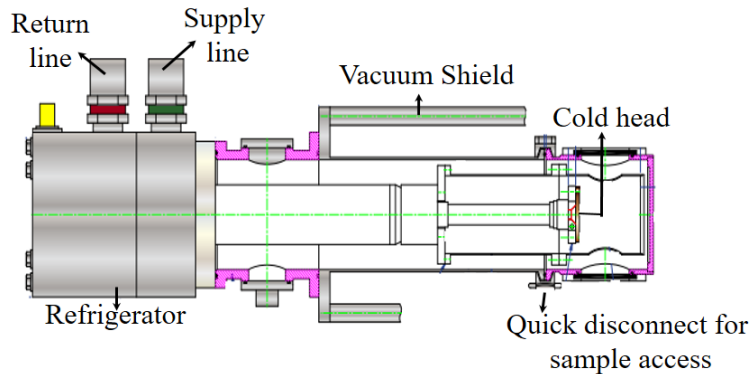


Figure 2.1: A schematic of the Closed Cycle Refrigerator (CCR) for accessing low temperature without a constant supply of cryoliquids. The continuous compressor pumping on Helium gas causes to achieve low temperature following Gifford McMahon refrigeration cycle [59]. A CCR provides a low-temperature platform for performing temperature dependent experiments down to liquid Helium temperature.

temperature is achieved by performing thermodynamic refrigeration cycle by expansion and compression of gas (e.g. Gifford McMahon (GM) cycles [59]), as schematically shown in Fig. 2.1. High-pressure helium gas is supplied to the refrigerator through the supply line and low-pressure helium gas returns from the refrigerator through the return line. A CCR lab system is accompanied with several support systems e.g. chiller for cooling the compressor, and a vacuum pump for the sample space etc. We have used a CCR from

Cryo Industries of America, Inc (Model-204-N) for our experiments. Our CCR setup provides a low temperature platform down to 9.5 K.

2.3 Principle of dielectric measurements

A capacitor is an assembly of two electrodes separated by a dielectric, typically used for storing charge. If C is the capacitance of a dielectric and C_0 is the capacitance of an identical capacitor in vacuum, the dielectric constant/permittivity depicted by the Greek letter ϵ , is expressed as $\epsilon = \frac{C}{C_0}$. Dielectric permittivity is represented by a number without dimension/unit and for any material, it is always greater than 1 (its value for vacuum).

The sample is mounted in between two parallel electrodes forming a sample capacitor

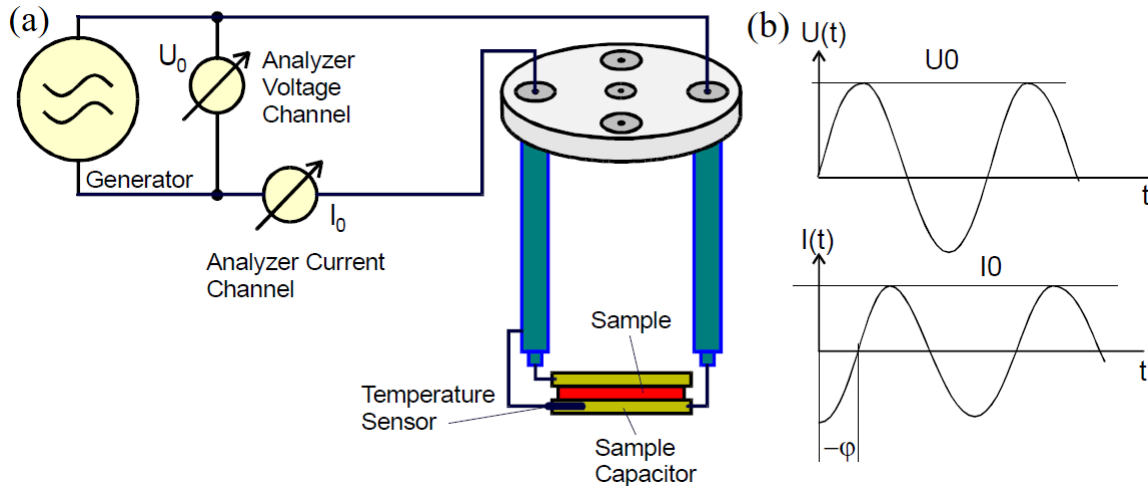


Figure 2.2: (a) Circuit diagram of phase sensitive impedance measurement by Alpha mainframe analyzer in parallel plate configuration as function of frequency and temperature. By measuring impedance, the dielectric permittivity of the sample is calculated from the equation (2.1) for a given frequency (b) An AC voltage of magnitude U_0 and frequency f is applied on the specimen via the parallel plate capacitor and this causes a current I_0 at the same frequency with phase ϕ [60].

as depicted in Fig. 2.2(a). A voltage of magnitude U_0 with frequency $f = \omega/2\pi$ is applied. This causes a current through the sample I_0 at the same frequency with phase ϕ , Fig. 2.2(b). The phase angle (ϕ) depends on the electrical properties of the dielectric e.g. conductivity, permittivity etc.. The voltage and current through the parallel plate capacitor can be expressed as:

$$U(t) = U_0 \cos(\omega t) = \text{Re}(U^* \exp(i\omega t)) \quad ^1$$

$$I(t) = I_0 \cos(\omega t + \phi) = \text{Re}(I^* \exp(i\omega t))$$

With $U^* = U_0$, $I^* = I' + iI''$, $I^* = \sqrt{(I')^2 + (I'')^2}$ and $\tan(\phi) = \frac{I''}{I'}$. Assuming a sample with linear electromagnetic response, the impedance measured in the parallel plate configuration for a given frequency ω can be expressed as

$$Z(\omega) = Z' + iZ'' = \frac{U^*}{I^*}$$

This impedance is related to the dielectric constant as

$$\epsilon(\omega) = \epsilon' + i\epsilon'' = \frac{-i}{\omega \cdot Z(\omega)} \cdot \frac{1}{C_0} \quad (2.1)$$

Where C_0 is the capacitance measured in the empty cell configuration. Hence by measuring the impedance for different frequency, the dielectric constant can be obtained using equation 2.1.

2.3.1 The Alpha Analyzer

The Alpha-A high performance frequency analyzer from Novocontrol Technologies used during this work measures the complex dielectric, conductivity and impedance function of materials for several frequencies at a given AC voltage [60]. The measurement ranges of the analyzer is tabulated in Table.2.1. The Alpha analyzer is a combination of one

Table 2.1: Specification of Alpha-A mainframe impedance analyzer [60]

Ranges	Frequency	1mHz to 20 MhZ
	Impedance	0.01Ω to $10^{14}\Omega$
	Capacity	1fF to 1F
	loss factor $\tan(\delta)$	10^{-5} to 10^4
	AC Voltage	100 μ V to 3V rms

base unit called *Alpha analyzer mainframe* and *test interfaces* (as depicted in Fig.2.3), which can be connected to the mainframe. The mainframe contains a frequency response

¹For easy calculation and representation of the formulas, it is convenient to use complex notation

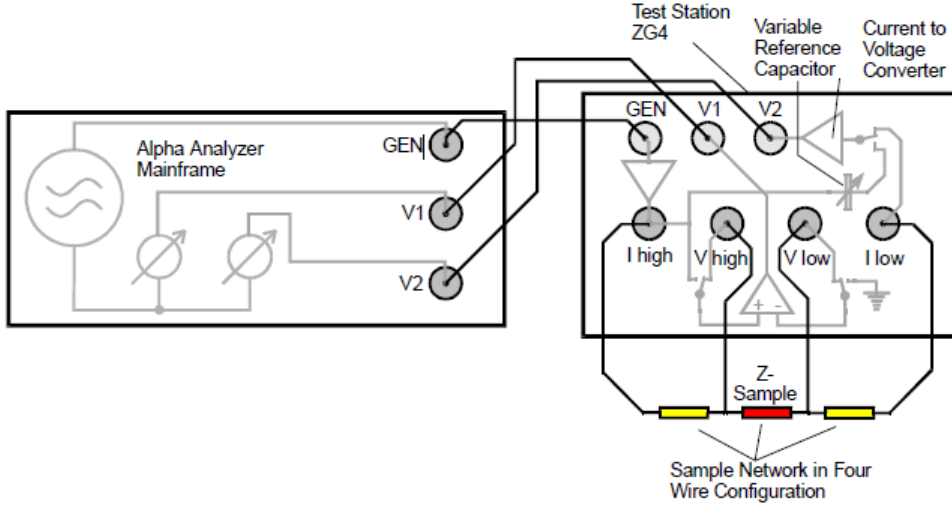


Figure 2.3: The circuit diagram for dielectric measurement in 4-wire configuration using Alpha main frame analyzer and test interface from Novocontrol Technologies [60].

analyzer with a sine wave and dc-bias generator and two ac voltage input channels. The analyzer measures the amplitude and phase angle of the harmonic base wave component while suppressing other signal components. It is also possible to measure higher harmonics using the analyzer. The measurement can be performed in the 2-, 3- or 4-wire mode. Most of the dielectric measurement in the thesis has been performed in the 4-Wire configuration with the circuit connection as is illustrated in Fig. 2.3. Before performing any measurement, calibration of the circuit is necessary. This was done by a load short (shorting both the electrodes) and 100Ω standard resistance following the protocol by User's manual from Novocontrol Technologies [60]. Before calibration, the electrodes should be cleaned, polished and the electric cables are properly tightened. The calibration is typically done in intervals of 4 weeks and after calibration, the external wires are preferably kept fixed in their respective positions.

2.4 Dielectric measurements in CCR

Temperature dependent dielectric measurements were performed by mounting the sample in CCR low temperature platform and connecting the electrode wires with the test interface of the Alpha-A analyzer. By using a programmable heater, the temperature of the cold head and the temperature at the sample position can be controlled. A sample holder for dielectric measurements under parallel plate configuration has been designed, which is compatible with CCR cold head attachment, as shown in Fig. 2.4.

2.4.1 Design considerations for the sample holder

For the design of the sample holder compatible with CCR, following necessary care has to be taken:

1) Unlike a gas cooling system, in a CCR the sample temperature is controlled by the heat flow via thermal conduction from the cold head to sample position through the electrodes. For dielectric measurements, an electric signal is applied to the electrodes. This leads to an electrical short between the CCR cold head and electrodes. To avoid such a short, electrical insulation between the electrode and cold head is necessary. Moreover, the heat has to flow enough through this insulation so that sample is cooled to the lowest possible temperature of the CCR. In our set up, a thin layer of Teflon has been used.

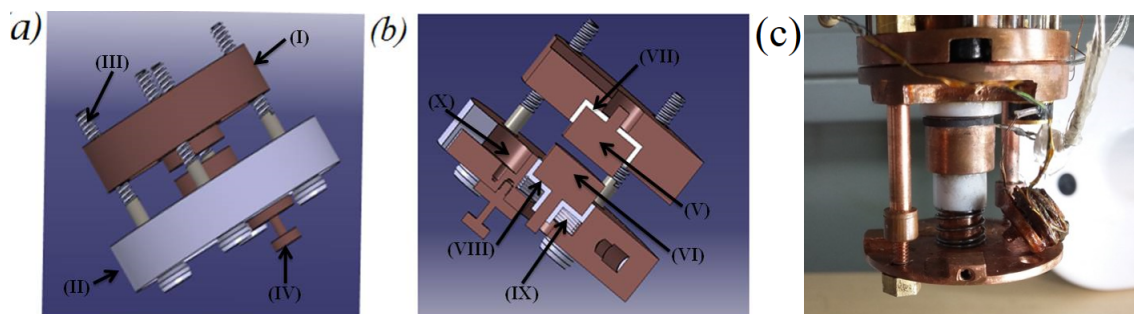


Figure 2.4: 3D drawing of the sample holder for dielectric measurement using CATIA V.4. The essential components of the sample holder indicating with an arrow and roman numbers are described in the text. (a) Side view of the sample holder. (b) Cross section of the sample holder (c) Picture of the sample holder attached to the cold head of CCR in our dielectric measurement setup

2) The total weight of the sample holder has to be optimized so that the heat load is minimized and the lowest possible temperature is attained at the sample position.

3) The refrigerator of the CCR is continuously pumping to maintain the lowest temperature at the cold head position. This pumping generates severe mechanical vibration in the measurement assembly. Often such vibration leads to the generation of both random and systematic noise during the measurement. Necessary measures need to be taken to minimise such vibrations at the sample positions.

The conceptual design of sample holder's 3D drawing was performed using *CATIA V.4* (Computer aided three dimensional interactive application). The different components of the sample holder as is depicted in Fig.2.4 are the following:

- (I) Upper electrode housing: it remains in contact with the cold head and is tightened through a screw.
- (II) Lower electrode housing: this helps the sample to be sandwiched between both the

electrodes during a measurement.

(III) Stud: this holds both the electrodes together, aligning them vertically and keeping whole assembly tightened with the cold head of the CCR.

(IV) Post for wrapping of the temperature sensor extra wire in order to maintain a uniform temperature and avoiding thermo e.m.f generation.

(V), (VI) Upper and the lower electrode, with a cylindrical shape and a narrow notch end where the electrode wires were soldered.

(VII), (VIII) Thin Teflon to electrically insulate from the both upper (I) and lower (II) electrode body.

(IX) A cylindrical hole where the temperature sensor is mounted.

(X) Spring to push the lower electrode upwards and take care of the mechanical vibration generated from the pumping of the CCR.

2.4.2 Dielectric measurements with the designed sample holder

The sample holder is made of Copper (Cu), an excellent electrical and thermal conductor over the temperature range 5K-300K. A preliminary design of the sample holder weighed 180 gm and only a minimum temperature of 32K could be achieved at the sample position. Later the design was changed with a major decrement of the upper and lower electrode body parts and final weight was ≈ 90 gm. With this design, a minimum temperature of 11K at the sample position was achieved with the cold head temperature being at 9.5K. A snapshot of the sample holder assembly is depicted in Fig.2.4(c)

2.4.2.1 Automation of the measurement

The Alpha main frame impedance analyzer is a compact instrument with no control knobs for manual operation. The measurement operations were performed by WinDETA software. However, a temperature dependent dielectric measurement requires temperature stability at the sample position during a temperature scan of each measurement. Dielectric measurement automation was performed using the LabVIEW program [61, 62]. The flowchart for the automation is as depicted in Fig.2.5. The GPIB of Novocontrol impedance analyzer (Novo GPIB from Novocontrol) and the temperature controller from Lakeshore (GPIB from National Instruments) are incompatible with each other and do not respond in the logic flow of the automation. This issue was resolved by creating extra *.dll and header files. The snapshot of the dielectric measurement automation user

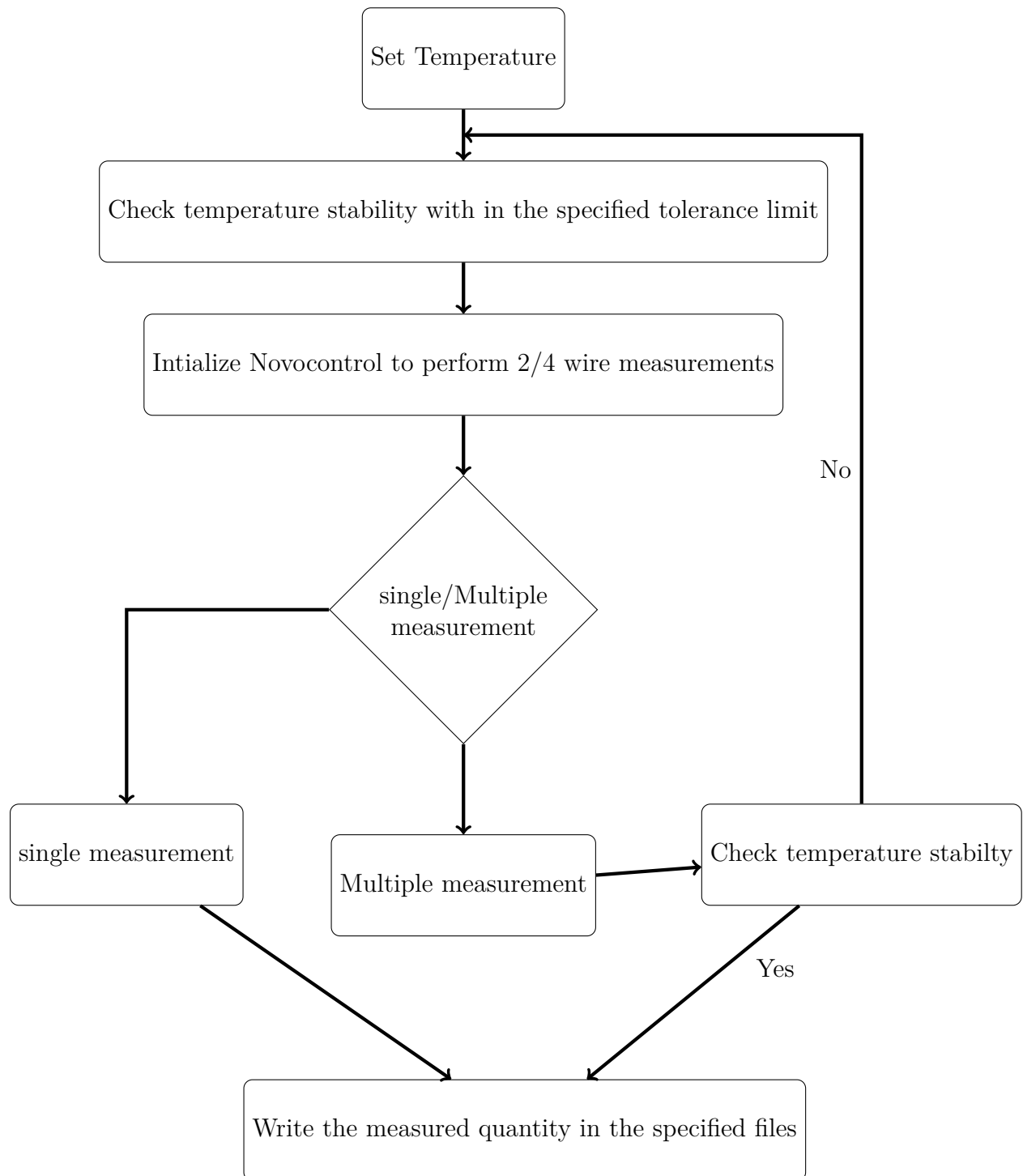


Figure 2.5: Flowchart depicting the steps involved in an automated dielectric measurements

interface is shown in Fig.2.6.

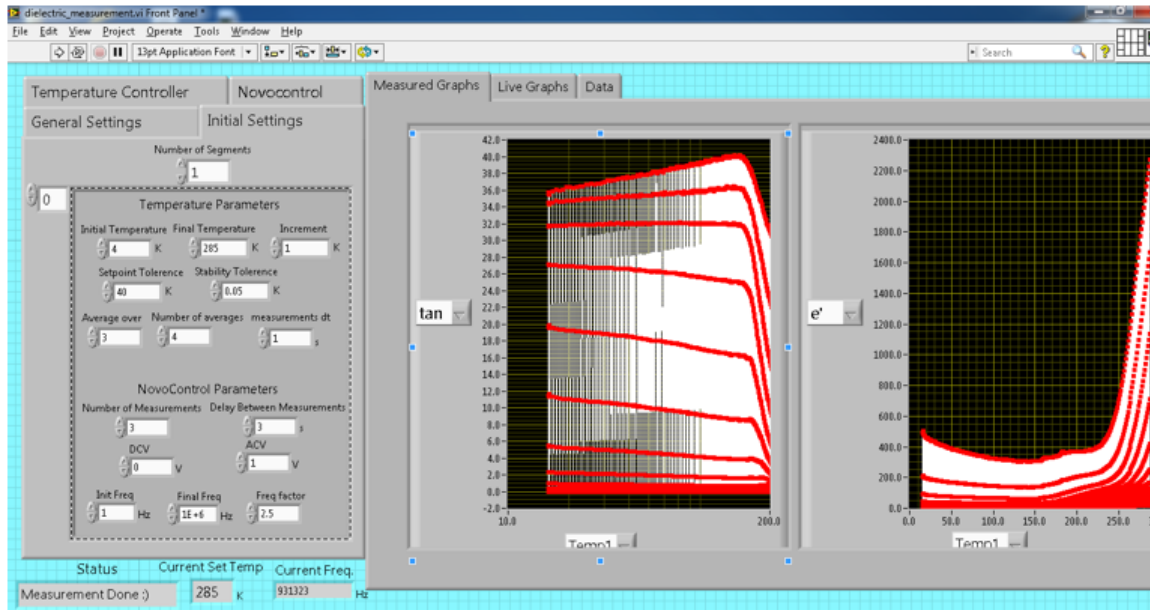


Figure 2.6: The user interface of the dielectric measurement automation developed using LabVIEW.

2.4.2.2 Eliminating noise

Dielectric measurements involve an AC insulation and cause the measurement signal to be coupled with several noise sources. However, better electrical soldering of cables/wires in the circuit always minimize the chances of occurrence of the random noise in the measurement. For instance, electrical soldering with a shiny curved surface instead of any sharp spike is advisable, as often the spike acts as an antenna and gives rise to noise. Most common source of noises are listed below:

1. **Capacitive coupling:** In an analog circuit, the capacitive coupling is used to transfer an AC signal while blocking the DC part. However, a parasitic capacitive coupling between two cables close to each other may occur and causes interference with the measured signal. Such an effect can be avoided by using metal shielding in the measured cable/ experimental assembly.
2. **Inductive coupling:** Two conductors are referred to be as inductively coupled, when the change in current through one conductor induces a voltage to the other one via electromagnetic induction. Such inductive coupling is often a source of noise, especially during an AC measurement. One way to get rid of such noise is by twisting the cable/wires instead leaving them lying parallel to each other. Such

twist creates a number of loops which tend to cancel each other instead of one large loop.

3. **Resistive Coupling (Ground loop):** A ground loop occurs when two different grounds of the circuit have developed a potential in between them. Often ground loops are the major causes of noise in any measurement setup. For instance, we

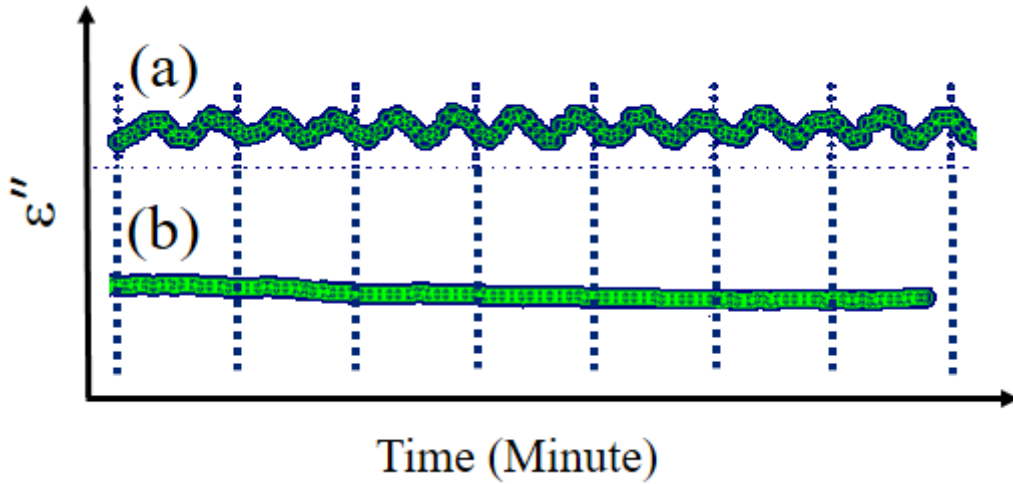


Figure 2.7: The appearance of sequential noise in the dielectric measurement. (a) An oscillation in the imaginary part of the dielectric constant is observed as a function time when the air conditioner is ON during the measurement. (b) The oscillation vanishes when the air conditioner is switched OFF.

observe an oscillation in the imaginary part of dielectric constant ϵ'' as a function of time when the lab air conditioner was on, as depicted in Fig. 2.7. The oscillation disappears when the air conditioner is switched off. Such oscillation is a typical example of resistive coupling between the equipments/instruments. However, this parasitic effect can be removed by creating a star ground configuration. Also by improving the ground quality of primary power source of the instrument.

2.4.2.3 Calibration using KH_2PO_4

Polycrystalline KH_2PO_4 (Potassium dihydrogen phosphate) powder from Sigma Aldrich of $\geq 99.0\%$ purity was adequately ground, cold pressed in pellet form and then sintered at 150°C ². KH_2PO_4 is known to undergo a phase transition at 123K from a paraelectric to a ferroelectric state. The phase transition reported in the literature (powder obtained by crushing single crystal) [63] (Fig. 2.8(a)) are reproduced in our measurement setup. Temperature dependent dielectric measurement performed in our setup at 100 kHz with

²The melting point of KH_2PO_4 is $\approx 252^\circ\text{C}$.

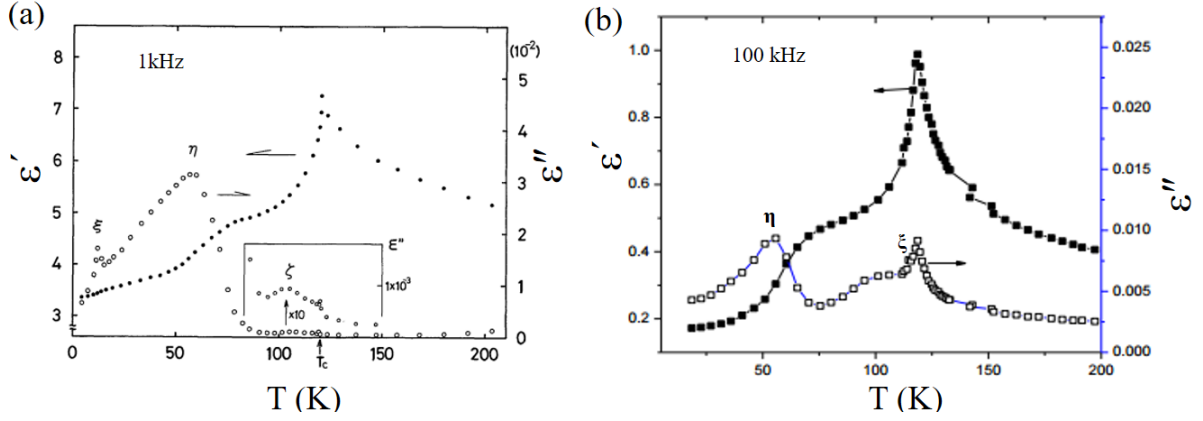


Figure 2.8: Temperature dependent dielectric measurement of Potassium dihydrogen phosphate (KH₂PO₄). (a) Dielectric measurement as is reported in the literature [63] (b) Dielectric measurement performed on our setup. The anomalies in both the real and imaginary part of dielectric constant are reproduced, as is observed in the literature report.

the KH₂PO₄ pellet is shown in Fig.2.8(b). The differences in the respective magnitude of dielectric constants might be due to the particle size (decrease in dielectric constant with decreasing particle size) [64]. Thus the developed setups with the designed sample holder is ready for further measurements.

2.5 Principle of pyroelectric measurements

Pyroelectric effect refers to the ability of specific materials (which have polar point group symmetry) to generate a current as a result of heating. The steps involved in performing pyroelectric measurement is schematically illustrated in Fig.2.9. The domains of pyroelectric/ferroelectric material are randomly oriented in the paraelectric state. A single domain is prepared after applying an electric field and cooling the sample across the ferroelectric transition/ Curie temperature (T_C), called poling (1→2). At lowest temperature, the poling field is removed, and the sample is shorted to remove stray surface charges built during poling (2→3). During heating, the pyrocurrent is measured across the Curie temperature (3→4). A sharp peak appears in the recorded pyrocurrent at the ferroelectric to paraelectric transition [65]. For a specimen with area A , warming rate $\frac{dT}{dt}$, the measured pyrocurrent can be written as

$$I = p(T)A \frac{\partial T}{\partial t} \quad (2.2)$$

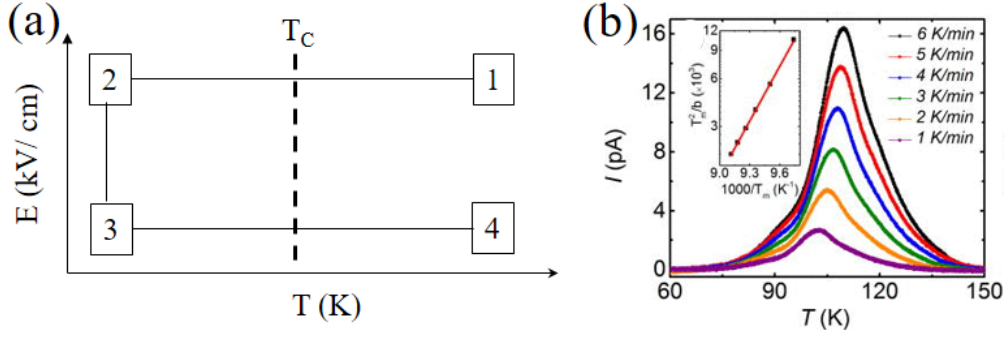


Figure 2.9: (a) Schematic of the protocol of pyroelectric measurement (1→2→3→4) with an electric field (E) and temperature (T) (b) An experimental artifact in pyroelectric measurement arising due to thermally stimulated charge carrier (TSC). A rate dependent measurement exhibits shifting of the observed pyrocurrent peak temperature T_m towards high temperature for TbMnO_3 powder. The inset shows the least square fit with the equation 2.5[66]. Figure adapted with permission from Ref. [66], copyright (2014) by the AIP Publishing.

where $p(T)$ is pyroelectric coefficient for a particular temperature T , is defined as the rate of change of spontaneous polarization with temperature.

$$p(T) = \frac{\partial P_s}{\partial T} \quad (2.3)$$

Combining the equations 2.2 and 2.3 we obtain,

$$P_s = \int \frac{I}{A} dt \quad (2.4)$$

Hence by measuring pyrocurrent (I) and integrating the pyrocurrent density ($\frac{I}{A}$) with respect to time, the spontaneous polarization (P_s) can be calculated. At the onset of the ferroelectric transition, depolarization current is maximum and exhibits a peak.

However during poling, if ions are trapped (localized energy levels) then the pyrocurrent measurement often results in a similar peak as observed in ferroelectric to para electric transition, called thermally stimulated current (TSC) [66, 67, 68]. To check whether a peak is appearing due to an experimental artifact, one typically performs a measurement with different warming rate ($b = \frac{dT}{dt}$). A peak corresponds to trapped charge will shift due to its relaxation behavior, whereas a peak occurring in FE-PE transition (T_m) remains robust and independent of warming ramp rate (b). Following formula gives the dependence of peak with the warming rate in the case of TSC:

$$\ln \frac{T_m^2}{b} = \frac{E_a}{K_B T_m} + \ln \frac{\tau_0}{K_B E} \quad (2.5)$$

where k_B denotes the Boltzmann constant, E_a is the activation energy, and τ_0 represents Debye relaxation time at a high-temperature limit. The activation energy E_a could be determined through the least-square fit of the above equation. For instance in polycrystalline TbMnO_3 , a pyrocurrent peak appear at 107K and shifts towards higher temperature with warming, as depicted in Fig.2.9(b) [66].

2.6 Pyroelectric measurements in CCR

Pyroelectric measurement performed with sample loaded in the dielectric measurement configuration as discussed in the section 2.4.2 was not successful due to the high value of background current. A schematic of the pyroelectric measurement assembly is depicted in Fig.2.10. Individual components of the sample holder assembly are the following:

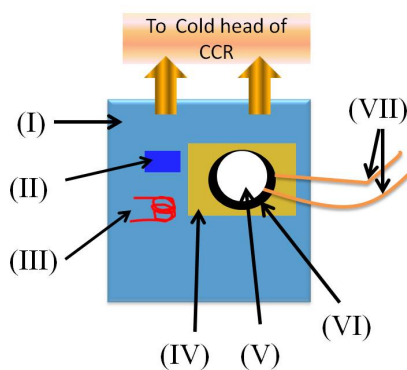


Figure 2.10: Schematic of the Pyrocurrent measurement setup in CCR

- (I) Rectangular thick Cu plate: It is attached with the cold head of the CCR and provides the low temperature to the mounted sample.
- (II) Temperature sensor to record the sample position temperature.
- (III) A heater to heat the sample.
- (IV) Cigarette paper, to exchange heat from the Cu base to the sample and maintain electrical isolation between the sample and Cu plate.
- (V) Adhesive silver epoxy.
- (VI) The sample in pellet form.
- (VII) Thin Cu/Au wire.

2.6.1 Pyroelectric measurements with the designed sample holder

The specimen in a compact and hard pellet form with specific geometry (rectangular/ circular) were used ³for the measurement. Cu/Au wires were mounted on both sides of the sample through adhesive silver epoxy as a parallel electrode. It was then stuck on the Cu block on top of a cigarette paper with GE varnish ensuring electrical insulation from the CCR. A temperature sensor was also mounted for measuring the temperature of the sample. The Cu block with the sample mounted on it were tightened with the cold head of the CCR for temperature dependent measurement. Since a high DC voltage was applied during the poling process of pyroelectric measurement, it is necessary to perform a thorough electrical insulation check between the Cu body and the sample electrode. The individual step for performing pyroelectric measurement in this configuration is as follows:

The sample temperature was stabilized (called initial poling temperature (T_{pi}) 5K-10K above the ferroelectric transition/ Curie temperature (T_C). A sufficiently high dc voltage was applied (polarity of the applied voltage has to be taken care since the sign of the pyrocurrent depends on the polarity of the poling voltage). The sample was cooled down across T_C to a temperature called the final poling temperature (T_{pf}). At this temperature, the poling voltage was removed, and the two electrode wires were shorted together. Typically the magnitude of measured pyrocurrent is in the picoampere range and is often coupled with noise. This has to be optimized by avoiding ground loop (star ground), taking care of better soldering of junction wires and using a Triaxial cable for measurement. Before starting the pyrocurrent measurement, it is necessary to minimize the noise level in the measured current and also decrease the background current (1-5 pA in this setup). If this background current was seen to decay with time, then the electrode wires were shorted for a longer period allowing the stray charge to decay. Once the background current was noise (random/periodic) free, the sample temperature was increased with a fixed ramp rate, and the discharge current was measured. We used Keithley sourcemeter (Model 2612B) and a Picoammeter (Model 6482) for the measurement. The measurement was automated by LabView program with tabulating the time, temperature of the sample position and pyrocurrent response. Since the direction of polarization can be flipped by changing the direction of the electric field, It is necessary to measure the pyrocurrent after changing the polarity of poling electric field. This will result in a pyrocurrent with opposite polarity and hence confirming the reversal of the sign of the electric polarization.

³This is necessary to calculate the area for estimating the exact value of polarization

2.6.1.1 Calibration using BaTiO₃

BaTiO₃ undergoes a first-order ferroelectric phase transition at $\approx 200\text{K}$ (T_C) accompanied with a structural transition from orthorhombic to rhombohedral structure [69]. The sample was loaded in the similar configuration as discussed in section 2.6. At 250K (T_{pi}) a positive voltage of 150V was applied and the specimen was cooled down to 20 K (T_{pf}). At this temperature, the electric field was removed and the sample was shorted. At T_{pf} ,

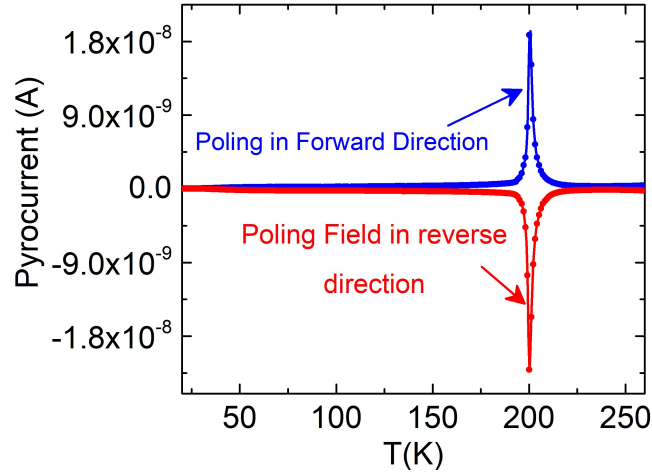


Figure 2.11: Pyroelectric measurement performed on the BaTiO₃ pellet. Poling with a positive electric field exhibits a pyrocurrent peak at the ferroelectric transition. The direction of pyrocurrent can be changed by poling with a negative electric field.

the current across the sample was $\approx 1\text{pA}$ (background of pyrocurrent measurement) . The sample was heated with a constant ramp rate of 10 K/min and the response current was measured, as depicted in Fig.2.11. A sharp peak was observed across the ferroelectric to paraelectric phase transition (T_C). Performing a similar measurement after reversing the direction of the electric field resulted in changing the polarity of the measured pyrocurrent, which implies switching of the sign of electric polarization. Observation of a sharp pyrocurrent peak at the ferroelectric to paraelectric verified that the designed configuration was ready for further measurements.

2.7 Dielectric and pyroelectric measurements in the presence of a magnetic field

Dielectric and pyroelectric measurements in the presence of a magnetic field is an indispensable probe to study the magnetoelectric and magneto-dielectric coupling in materials.

The measurement performed in Closed Cycle Refrigerator (CCR) as described in the sections 2.4 and 2.5 do not provide access to a magnetic field. Hence, the measurements under magnetic field was performed by using a Manual Insertion Utility Probe (MIUP) of MPMS (Magnetic Property Measurement System)-XL magnetometer. MPMS provides magnetic field up to ± 7 Tesla and temperature down to 1.8 K. Unlike the CCR, in a MPMS the sample is cooled through Helium gas and do not require specially designed sample holders for measurement.

2.7.1 Sample loading in MIUP

MIUP is a multifunction sample loading platform mounted with ten electrical wires and at the very end of MIUP, a thick Copper plate is attached for loading the sample. For loading single crystals, the copper plate was replaced with a flexible gold sheet (which was bent in L shape) to align the crystal with respect to the applied magnetic field, as shown in Fig.2.12. The smaller bore radius of the MPMS sample chamber restricts

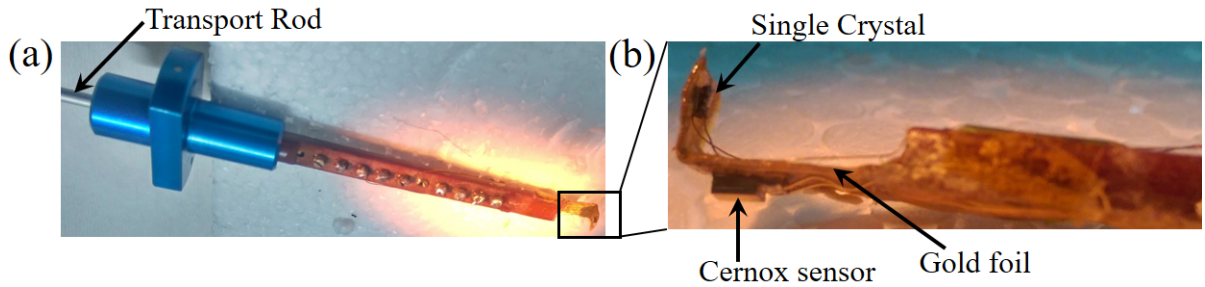


Figure 2.12: (a) The Manual Insertion Utility Probe of MPMS-XL. At the end of transport rod gold foil sheet has been used for sample loading platform. (b) An enlarged view of the sample and temperature sensor stuck in the gold foil with GE varnish on top of the cigarette paper.

the dimension of the sample for measurement. Rectangular shaped pellet sample was loaded at MIUP in the similar configuration as the sample was loaded in CCR for pyroelectric measurement (described in section 2.6). Both the dielectric and pyroelectric measurements were performed with the sample mounted in a similar configuration. The dielectric measurements were performed in a 4-wire configuration whereas the pyroelectric measurements were done in 2-wire configuration. The sample temperature can be measured either from the MPMS or by installing a separate temperature sensor in MIUP. Temperature-dependent dielectric measurements were performed in a stable temperature mode and the temperature sensor mounted with MPMS has been used to record the sample position temperature. Pyroelectric measurements were performed by heating the

sample at a fixed ramp rate and it was necessary to track the sample temperature over the measurement period. For this purpose, a temperature sensor (Cernox) was mounted on the sample platform, as shown in Fig.2.12(b).

2.7.2 Dielectric measurements in MIUP

A calibration (with load short and 100 ohm as described in section 2.3.1) of the dielectric measurement setup with MIUP was necessary for excluding the contribution from the measurement wires and contacts. Short check among the contacts of MIUP were mandatory before installing the transport rod in the MPMS sample space. Because of the extended length of unshielded wire in MIUP, it was not possible to measure very low frequency (< 100 Hz) and high-frequency measurement (> 0.1 MHz). Dielectric measurements performed in MIUP on BaTiO₃ pellet is depicted on Fig.2.13. A dielectric anomaly was observed at ≈ 200 K (as reported in the literature) and convinced us that the designed configuration in MIUP was ready for further measurements.

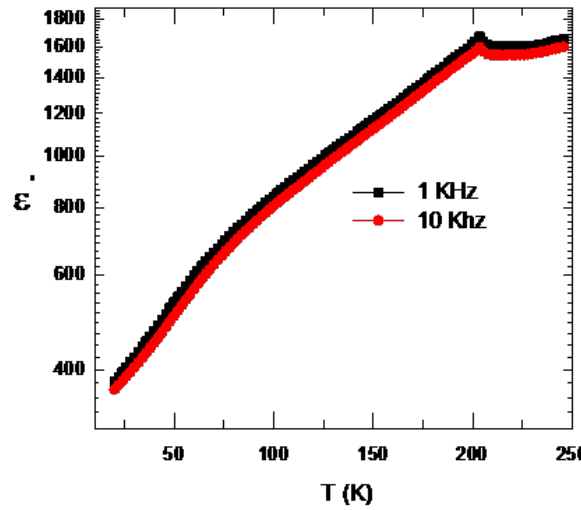


Figure 2.13: Temperature-dependent dielectric measurements performed on BaTiO₃ pellet in MPMS-XL with Manual Insertion Utility Probe (MIUP). A sharp anomaly was observed at the ferroelectric to paraelectric phase transition.

2.7.3 Pyroelectric measurements in MIUP

After poling, during the measurement of the background current a periodic sawtooth signal ($\approx$ nA) was observed. A similar sequential noise pattern was also observed, when the current was recorded after keeping the MIUP outside the MPMS sample chamber.

Interestingly, such sequential noise pattern vanished after disconnecting the temperature controller wire from MIUP, as is illustrated in Fig. 2.14(a). Typically in a temperature

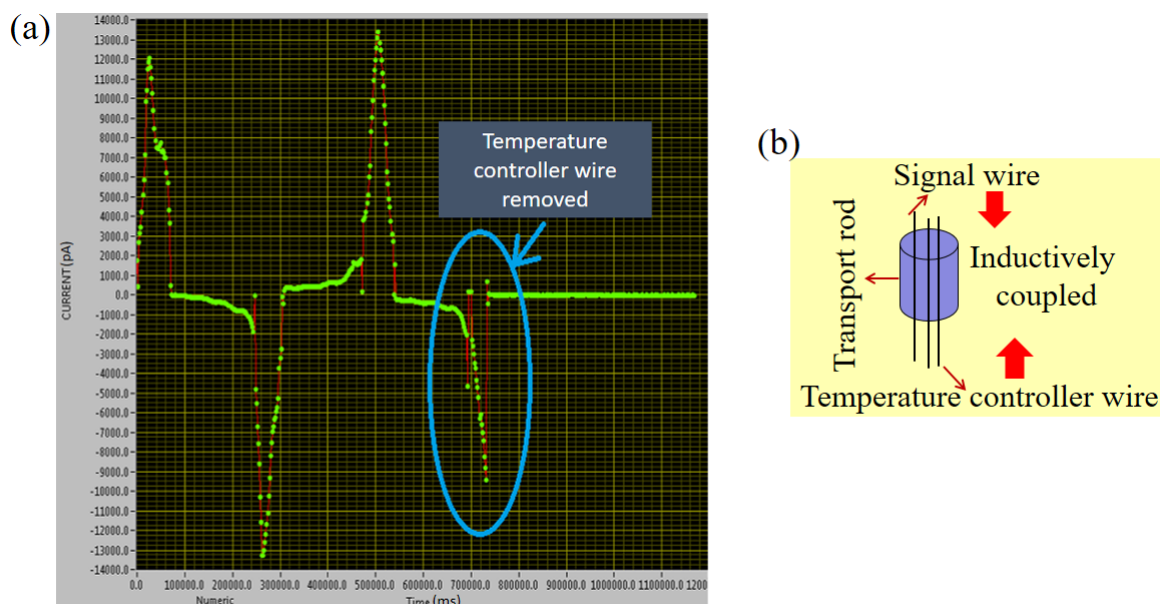


Figure 2.14: (a) Observation of a sawtooth wave like signal during measuring current as a function of time keeping the sample temperature fixed while sample is loaded in Manual Insertion Utility Probe (MIUP). Such oscillation vanishes after disconnecting the temperature controller (b) Schematically describes the sources of sequential noise pattern in the measurement with MIUP. The signal wire for measuring current across the sample and temperature controller wire for measuring sample temperature were inductively coupled within the MIUP transport rod .

sensor (2-lead/4-lead) temperature were determined by measuring the resistance using a temperature controller. From the calibration table of resistance (R)-temperature (T) curve provided in the temperature controller, the corresponding temperature is calculated [70]. In MIUP, the wire for measuring current across the sample and temperature sensor wires were anchored together. The temperature controller signal possibly induces the observed periodic oscillation in the measured current across the sample due to inductive coupling, as schematically described in Fig.2.14(b).

Thus a simultaneous measurement of current and temperature was not possible. It restricted our pyrocurrent measurements to be performed in two steps. In the first step, the temperature was measured as a function of time for a given ramp rate ($b = \frac{dT}{dt}$). In the second step, the pyrocurrent was measured (keeping the temperature controller wire open) as a function of time under same ramp rate. Now combining both this measurements, where time was the same for given ramp rate, it was possible to calculate the electric polarization. Such a measurement strategy was appropriate due to the fixed allocation of temperature with time for a given ramp rate in different measurement runs. The

pyroelectric measurement performed on the BaTiO₃ pellet mounted in MIUP is shown in Fig.2.15. Observation of a sharp pyrocurrent peak at the ferroelectric to paraelectric transition verified that the designed configuration was ready for further measurements.

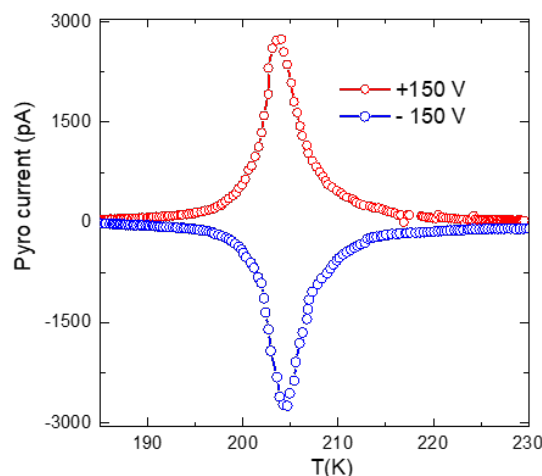


Figure 2.15: Pyrocurrent measurement performed on the BaTiO₃ pellet after poling the specimen under positive and negative electric field. The measurement was performed in a MPMS with the sample loaded in MIUP.

2.8 Synthesis of materials

There are several forms in which a solid can adapt, e.g., Polycrystalline, Single-crystalline, amorphous and thin film. In the course of this thesis work, the materials studied are in single/polycrystalline form. There are many available routes for preparing powder/polycrystalline samples, e.g. solid state reaction, sol-gel, combustion, hydrothermal synthesis etc. Whereas a single crystal can be grown using Four mirror zone, flux growth, Bridgman and Czochralski methods etc.

2.8.1 Synthesis of the polycrystalline specimens

For synthesizing oxide materials, solid state reaction is one of the most convenient routes. The non-volatile precursor oxides were mixed according to stoichiometric ratio and ground thoroughly using a mortar and pestle or by using a ball mill. This resulted in a homogeneous and fine powder of the precursors. The homogeneous mixture (either in powder/pellet form) was heated in an alumina crucible using a PID controlled programmable high-temperature furnace. In a typical heat treatment, the reaction temperature was

reached with a specific ramp rate (e.g 150°C to 200 °C per hour) and waited there for a particular time, e.g. 12 hrs to several days/ weeks. The sample was cooled with specific ramp rate or quenched in different media (e.g., Liquid N₂, (Dry) Ice, Air). If a reaction was incomplete, the same procedure was repeated. Depending on the nature of the reaction (an oxidation/ reduction reaction), the precursor mixture was heated in a different environment e.g. Oxygen (O₂), Argon(Ar), Nitrogen (N₂), Carbon di /mono oxide (CO₂/CO), Argon + Hydrogen (Ar+H₂) mixture inside a tube furnace. In case the reactants were volatile/ air sensitive/ sensitive to moisture, then the reactants were loaded inside an evacuated quartz tube.

The high temperature reaction happens through diffusion of ions following Fick's law $J = -D \frac{\partial \phi}{\partial x}$, where J is the diffusion flux, $\frac{\partial \phi}{\partial x}$ is the concentration gradient, D is the diffusion coefficient depending on the reaction temperature with a typical value 10^{-12} cm²/s [71, 72]. The rate of reaction depends on the area of contacts among the reacting solids, the rate of diffusion and the rate of nucleation of product phase. Making a pellet often increases the contact between the crystallite and enhances the rate of reaction.

Details of the synthesis procedure carried out during this work are described explicitly in respective chapters.

2.8.2 Single crystal growth

Single crystal growth was performed in a Four mirror optical floating zone furnace from Crystal System Corporation [73]. The floating zone technique involves optical heating by focusing the light emitted from halogen lamps and reflected by ellipsoid mirrors. A pair of high-density polycrystalline rods of a pure phase material, called feed and seed rods are loaded inside a transparent quartz sample chamber. The rods are made by filling the powders inside a rubber tube (Diameter $\approx$ 7 mm, length $\approx$ 120mm) and compressed under hydrostatic pressure $\approx$ 600 bar. The furnace consists of four halogen lamps (with wattage 150W, 500W, 1000W), each placed at the center of ellipsoidal mirrors. The radiation from the lamp is focused at the point where feed rod (hang from top) and seed rods (support from bottom) meet each other. By controlling the lamp intensity, it is possible to melt both the rods with temperature more than several thousands of degree ($\approx$ 1000 °C to 3000 °C). A small part of the homogeneous rotating (10-15 rpm) feed rod is melted uniformly by the highly focused halogen light. For creating a uniform molten zone, the feed and seed rods are rotated in the opposite direction, as depicted in Fig.2.16. This molten part is solidified slowly on top of the seed rod to grow a single crystal. The

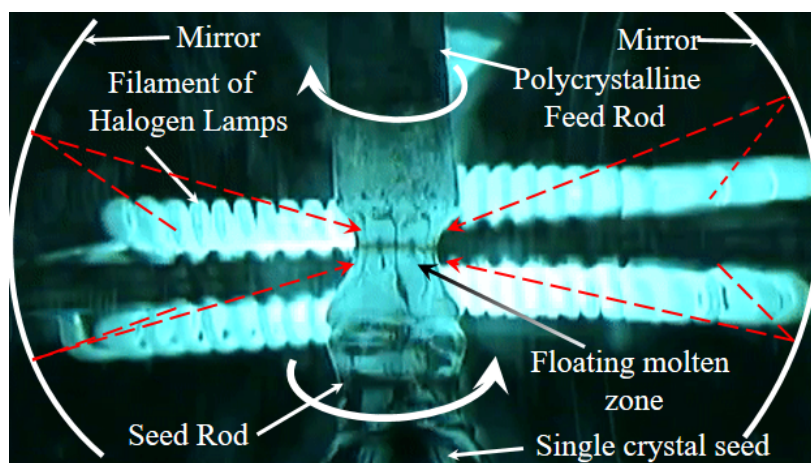


Figure 2.16: Single crystal growth using four mirrors floating zone furnace. The feed and seed rods were melted by focusing highly intense halogen light with four ellipsoidal mirrors. The feed and seed rods were rotated in the opposite direction to maintain a homogeneous mixture at the molten zone. The crystal was grown on top of the seed rod

feed rod was moved downwards with a certain speed (0.5 to 10 mm/h) and determined the growth speed top of the seed rod. The growth happens inside the sealed quartz tube and could be filled up with the required gas for oxidation/reduction process or applying a high pressure. One major advantage of Optical Floating Zone (OFZ) method is the absence of possible contamination from a crucible, and growing a larger size of single crystal is possible. However, the stability of the growth condition should be optimized for a stable growth depending on the congruent/ incongruent melting of the specimen.

2.9 Powder X-Ray diffraction

X-Ray diffraction (XRD) is a nondestructive tool in elucidating the distribution of atoms of crystalline solid in three dimensions. X-Ray of a specific wavelength (e.g $\text{CuK}_\alpha = 1.542 \text{ \AA}$) when diffracted constructively from the parallel crystallographic plane of a crystallite (small and fine grain of powder) follows Bragg's law, as illustrated in Fig.2.17. The condition for constructive diffraction as given by Bragg's law is [74],

$$2d \sin \theta = n\lambda \quad (2.6)$$

Where d is inter planar spacing, λ is the wavelength of the incident X-Ray beam, θ is the angle between the incident beam and the diffracting plane, n is an integer. Since a specific material possesses a unique crystallographic structure (e.g unit cell, space group etc), the diffraction of X-ray from a material is a unique chemical fingerprint. X-Ray

diffraction has been used extensively in chemical phase identification (including details of the crystal structure), grain size, strain, disorder, thermal expansion and in many more aspects. The X-Ray powder diffraction measurements in this work were performed in a

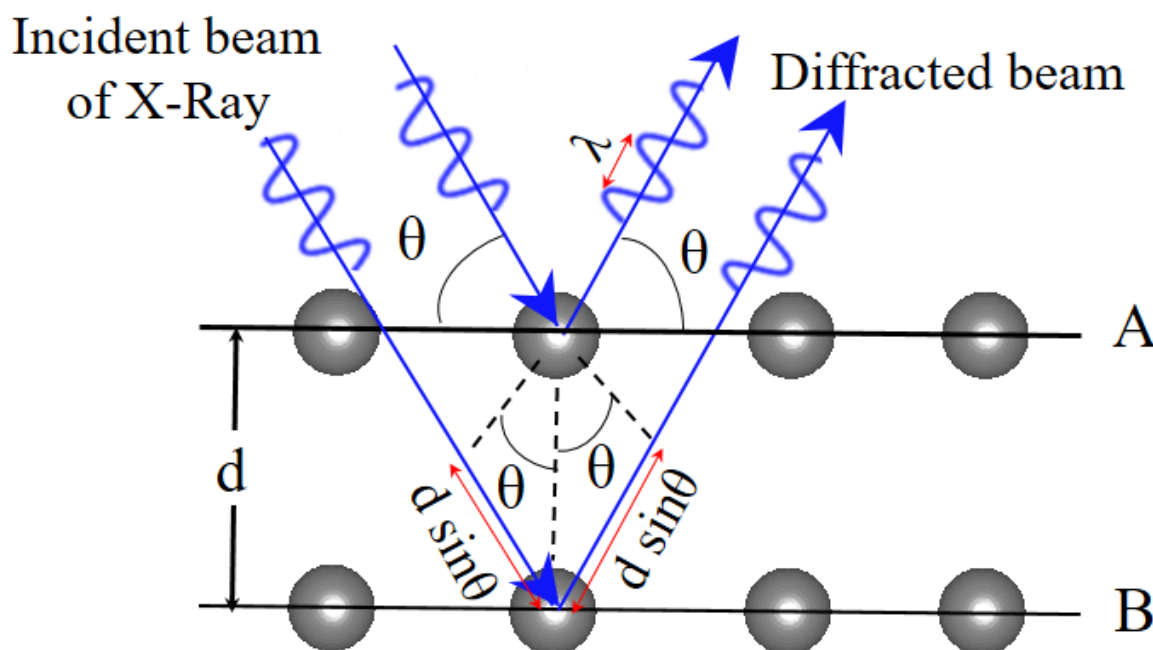


Figure 2.17: X-Ray diffracted from two-dimensional crystal with inter planner spacing d , according to the Bragg's law of diffraction. An X-ray incident at an angle θ on the crystal exhibits constructive interference when the path difference of the scattering $2d\sin\theta$ is integral (n) multiple of the wavelength (λ)

diffractometer from Bruker, Germany with a solid state linear detector and $\text{CuK}\alpha$ source. Measurements were performed in a Bragg-Brentano (parafocusing) θ - 2θ geometry where the sample was kept fixed whereas the incident X-Ray beam and detector were moved. The X-ray scanning started from a user-specified angle (θ_1) and set the detector for a specified time (counting time) to collect the scattered X-ray photons from the sample. After that, the source was set to the next angle $\theta_1 + \delta\theta$ (where $\delta\theta$ is the scanning increment) and the process was repeated until the user specified stop angle (θ_2) was reached. In our work, most of the diffraction patterns were collected with $\theta_1 = 15^\circ$, $\theta_2 = 85^\circ$, $\delta\theta = 0.02^\circ$, and counting time = 1s values respectively. However, if a material contains elements near to Copper in the periodic table e.g Fe, Cr etc. gave rise to inelastic contribution to the diffraction profile and leads to less signal to noise ratio. Using a different X-Ray source e.g. Molybdenum or high-intensity synchrotron X-ray beam can provide a better signal to noise ratio.

Our X-ray facility also provided measurement above room temperature up to 1000°C . The sample was loaded in a Pt plate, and the temperature dependent measurement was

executed by heating the sample through PID controlled heater in a vacuum environment. In the diffraction pattern, the Pt Bragg peaks have to be excluded carefully before analyzing the collected data.

2.10 Rietveld refinement of X-Ray diffraction data

Rietveld refinement is a widely used computer based technique for complete structural analysis of experimentally measured X-ray diffraction profile. It is a least square refinement of observed pattern and simulated/calculated pattern[75, 76]. The simulated pattern model is based on detailed parameters of crystal structure, experimental factors, Bragg peak profile, background etc. In the least square refinement, the residual (S) is minimized where,

$$S_i = \sum_i w_i (y_i^{obs} - y_i^{cal})^2 \quad (2.7)$$

$$w_i = \frac{1}{y_i}$$

y_i^{obs} = observed intensity at the i th step

y_i^{cal} = calculated intensity at the i th step

In the refinement model y_i^{cal} of miller indices h,k,l Bragg reflection is expressed as

$$y_i^{cal} = s \sum_K L_K |F_K|^2 \phi(2\theta_i - 2\theta_K) P_K A + y_i^{bac} \quad (2.8)$$

s is the scale factor

L_K is the Lorentz polarization correction and multiplicity factor.

ϕ is the reflection profile fitting function e.g Gaussian, Lorentzian, Pseudo-Voigt.

P_K is the preferred orientation function.

A is the absorption factor,

F_K is the structure factor for the K th Bragg reflection,

y_i^{bac} is the background intensity for the ith step. It can be expressed as a "n" order polynomial as

$$y_i^{bac} = \sum_0^n B_n [(2\theta_i / B_{start}) - 1]^n \quad (2.9)$$

The mathematical parameters that are often used to determine the quality of a fit for the K^{th} Bragg reflection with intensity I_K at the end of the refinement cycle are the following

$$R_F = \frac{\sum |\sqrt{I_K^{obs}} - \sqrt{I_K^{cal}}|}{\sum \sqrt{I_K^{obs}}} \quad (2.10)$$

$$R_B = \frac{\sum |I_K^{obs} - I_K^{cal}|}{\sum I_K^{obs}} \quad (2.11)$$

$$R_p = \frac{\sum |y_i^{obs} - y_i^{cal}|}{\sum y_i^{obs}} \quad (2.12)$$

$$R_{wp} = \sqrt{\frac{\sum w_i (y_i^{obs} - y_i^{cal})^2}{\sum w_i (y_i^{obs})^2}} \quad (2.13)$$

$$R_{Expected} = \sqrt{(N - P) \sum w_i (y_i^{obs})^2} \quad (2.14)$$

The most commonly used parameter to estimate the quality of the refinement is the goodness of fit factor $G = \frac{R_{wp}}{R_e}$

The least square refinement was achieved by finding a global minima. However, sometimes a good fit could also be obtained with a false minima. A careful observation of the value (physical meaning) of each parameter and intuition can often avoid such issues. The phase purity and structural details in this thesis work were obtained by the Rietveld refinement of X-Ray diffraction profile using FullProf [77]. The structure was visualized using VESTA [78].

The structural refinement in FullProf were performed by providing *.pcr and *.dat files. The *.dat file contains experimentally recorded data in a specific format, whereas the *.pcr file comprises the structural (lattice constant, space group, atomic position etc.), instrumental and profile parameters. For a reported structure, the structural parameters were obtained from the Inorganic Crystal Structure Database (ICSD). Whereas for an unknown structure, the structural parameters were obtained using Dicvol06 of FullProf package [79]. The instrumental parameter includes mainly background and peak profile of the pattern. The Background can be selected manually or modeled with a polynomial function as

$$y_{ib} = \sum_n a_n (2\theta_i)^n \quad (2.15)$$

By refining the coefficient a_n , the background can be matched for a diffraction pattern. Ideally, the Bragg peaks should be a sharp peak (δ function form), since a monochromatic X-Ray beam ($\lambda = \text{constant}$) diffracted at lattice planes with an exactly defined d-spacing would fulfill Bragg's law only for an precisely defined angle. However, due to the error occurring from the experimental setup and defect in sample (crystallite size, strain, dislocation of the plane), the Bragg peaks are broadened. The width of a peak profile is designated by Full Width Half Maxima (FWHM), which describes the width of the peak at half of its height. The Psuedo-Voigt(pV) peak shape functions were used for

structural refinement. The pV function is a linear combination of Gaussian (G) and Lorentzian function(L)

$$pV = \eta L + (1 - \eta) G; \text{ where } 0 \leq \eta \leq 1 \quad (2.16)$$

The FWHM (H_k) for Gaussian and Lorentzian peak function are

$$(H_k)_G = \left(U \tan^2 \theta + V \tan \theta - W \right)^{\frac{1}{2}} \quad (2.17)$$

$$(H_k)_L = X \tan \theta + \frac{Y}{\cos \theta} \quad (2.18)$$

During the refinement, the parameters U,V,W, X and Y were refined for pattern matching. Simultaneous refinement of too many parameters causes a divergence. The refinement was started by refining only the scale parameter and then the background. Next, the zero shift and lattice parameters were refined for taking care of the peak positions. To match the peak profile, U,V and W (FWHM parameters) and shape parameters were refined later. The refinement progress was tracked by decreasing the standard deviation (χ^2) for each refinement cycle. A false minima in the refinement can be judged by lower value of χ^2 where the refined parameters have unphysical values. Finally, patience and expertise has a significant influence on the refinement progress.

2.11 Powder neutron diffraction

Unlike a X-ray photon, neutron is charge less which allows the neutron beam to penetrate into the bulk of the sample. Also, neutron has an intrinsic magnetic moment which can interact with the unpaired spins of a lattice, hence directly probing the magnetic structure. In analogy with the nuclear Bragg peaks (section 2.9) of X-Ray diffraction, elastic neutron diffraction gives rise to magnetic Bragg peaks. One of the significant advantage of neutron diffraction measurement is that it contains both the nuclear and magnetic reflections of a specimen. However, If the magnetic and crystallographic unit cell are of the same dimension then the magnetic reflection superposes with the nuclear reflection. Collimated neutron beam is produced either in a nuclear reactor (by nuclear fission reaction) or in a spallation source(by proton pulses produced in a synchrotron fired into a heavy metal target) and this results in the emission of pulses of neutrons. The diffraction data were collected as a function of scattering angle 2θ / Energy (E) /

Time of flight (T.O.F).

Temperature dependent powder neutron diffraction (ND) measurements presented in this thesis were carried out using time-of-flight (TOF) WISH diffractometer at ISIS facility. The time of flight involves measuring the diffracted intensity/kinetic energy by measuring the time required to travel between two known fixed points. If the scattered neutron of wavelength λ travel with different velocities (v), reaches at the detector with a TOF t then according to wave-particle duality [80]

$$t = \frac{h}{mv} = \frac{ht}{mL} = 2d \sin \theta \quad (2.19)$$

Hence the TOF t is directly related with the inter planer spacing d of the crystal lattice. Once the start time of neutron is fixed then by measuring the arrival time of the scattered neutron at the detector, it is possible to obtain the diffraction profile of a given material. A high- resolution T.O.F measurement makes possible to probe very small to larger d (inter planer spacing) with multiple detectors fixed at different angles.

2.12 Solving magnetic structure from neutron diffraction data

The distribution of magnetic moments in a magnetic unit cell is described by its position and orientation with a specific symmetry. The crystallographic symmetry alone does not work for a magnetic structure, as the magnetic moment is an axial vector and requires a time reversal operation. A complete description of the magnetic structure is based on the nuclear unit cell, a propagation vector k and a basis vector Ψ . The propagation vector k describes the relationship among moment orientations of equivalent magnetic atoms in the different nuclear unit cells. The basis vector Ψ describes the projection of the moment along the crystallographic axes. The magnetic moment m_j of the j th atom in magnetic structure is described as

$$m_j = \sum_k \Psi_j^k \exp^{-2\pi i k \cdot t} \quad (2.20)$$

Where Ψ_j is projection of moment along crystallographic axis, called the basis vector and t is translation vector. Let us consider, a 1D AFM chain along c axis with the magnetic moment aligned along b axis, as depicted in Fig.2.18. The magnetic structure of this configuration can be described following equation 2.20 with the propagation vector

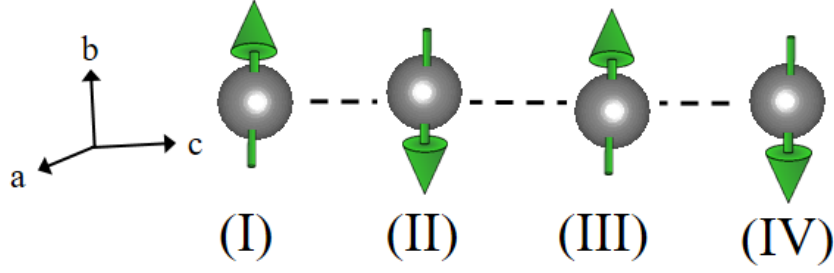


Figure 2.18: A 1D chain of antiferromagnetically interacted spins along c axis, where the moments are aligned along b axis. Such spin configuration can be described by a propagation vector $\mathbf{k} = (0, 0, 0.5)$ and basis vector $\Psi = (0, 1, 0)$ following the equation 2.20.

$\vec{k} = \begin{pmatrix} 0 \\ 0 \\ 0.5 \end{pmatrix}$, and basis vector $\Psi = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}$ and translation vector t . The different cases as

represented in Fig. 2.18 are illustrated below. For the case (I) of Fig. 2.18

$$m_{(I)} = \vec{\Psi} \exp^{-2\pi i \mathbf{k} \cdot \mathbf{t}} = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \exp \left[-2\pi i \begin{pmatrix} 0 \\ 0 \\ 0.5 \end{pmatrix} \cdot \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix} \right] = (010) \quad (2.21)$$

For case (II)

$$m_{(II)} = \vec{\Psi} \exp^{-2\pi i \mathbf{k} \cdot \mathbf{t}} = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \exp \left[-2\pi i \begin{pmatrix} 0 \\ 0 \\ 0.5 \end{pmatrix} \cdot \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \right] = (0 - 10) \quad (2.22)$$

For case (III)

$$m_{(III)} = \vec{\Psi} \exp^{-2\pi i \mathbf{k} \cdot \mathbf{t}} = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \exp \left[-2\pi i \begin{pmatrix} 0 \\ 0 \\ 0.5 \end{pmatrix} \cdot \begin{pmatrix} 0 \\ 0 \\ 2 \end{pmatrix} \right] = (010) \quad (2.23)$$

For case (IV)

$$m_{(IV)} = \vec{\Psi} \exp^{-2\pi i \mathbf{k} \cdot \mathbf{t}} = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \exp \left[-2\pi i \begin{pmatrix} 0 \\ 0 \\ 0.5 \end{pmatrix} \cdot \begin{pmatrix} 0 \\ 0 \\ 3 \end{pmatrix} \right] = (0 - 10) \quad (2.24)$$

Possible $\mathbf{k}$ vector basis vectors for a case study was determined by K_Search program in

FullProf tool bar [77].

Let us consider, a space group G_0 describing the three-dimensional symmetry with several symmetry operations e.g translation (screw axes and glide planes) and rotation of a crystal structure. The symmetry operations of G_0 that leaves the k vector invariant, is called little group G_k . However, only the rotation part of the symmetry operation changes the propagation vector k . The operation of all symmetry elements of the little group G_k on all the atomic positions (Γ_{perm}) and all the axial vectors (Γ_{axial}) can be described by a matrix called magnetic representation Γ_{mag} , which is expressed as:

$$\Gamma_{mag} = \Gamma_{perm} \otimes \Gamma_{axial} \quad (2.25)$$

Where, Γ_{perm} represents the way all the symmetry operations permute all equivalent atoms and Γ_{axial} describes how different symmetry operations change the components of a moment vector. The representation of Γ_{mag} can be written in terms of the different irreducible representation of the little group G_k .

$$\Gamma_{mag} = \sum_n n_\nu \Gamma_n \quad (2.26)$$

Where n_ν is the number of times the irreducible representation Γ_n appears in the representation of Γ_{mag} . Such decomposition into the irreducible representations of the little group G_k gives the number of basis vectors contributing to Γ_{mag} . For a given k vector, the basis vectors were determined by representational analysis using *BasIreps* toolbar of FullProf package and SARAh [81] program.. Any linear combination of basis vectors of a particular irreducible representation is necessarily a symmetry-allowed basis vector. The basis vector is the summation of several components

$$m_j = \sum_\nu C_\nu \psi_\nu \quad (2.27)$$

Where, ψ_ν is the ν^{th} component of the basis vector and C_ν is the mixing coefficient of the basis vector. By refining the mixing coefficients of the basis vector within the irreducible representation, the magnitude and orientation of the moment were examined. By incorporating each Irreps one has to find the best fit and hence correct description of the magnetic structure. The refinement was performed with FullProof and the magnetic structure was visualized using VESTA [78]. The successive steps of solving the magnetic structure of $Mn_4Ta_2O_9$ is described in the chapter APPENDIX- I of the thesis.

2.13 Single crystal Laue diffraction

Laue diffraction involves scattering of the polychromatic X-Ray beam from a stationary single crystal. The diffraction measurement is performed either in transmission or backscattered mode to orient a single crystal. We have used a backscattered Laue setup from Photonic Science Laue diffractometer with Tungsten source and provides X-Ray in the wavelength range 0.35Å to 2.5Å. In a backscattered setup, the detector is placed in between the sample and a detector (a CCD camera/ Imaging plate), as depicted in Fig.2.19. The sample was placed on a Goniometer and facilitates the rotation of the crystal in all possible directions for alignment of the crystal.

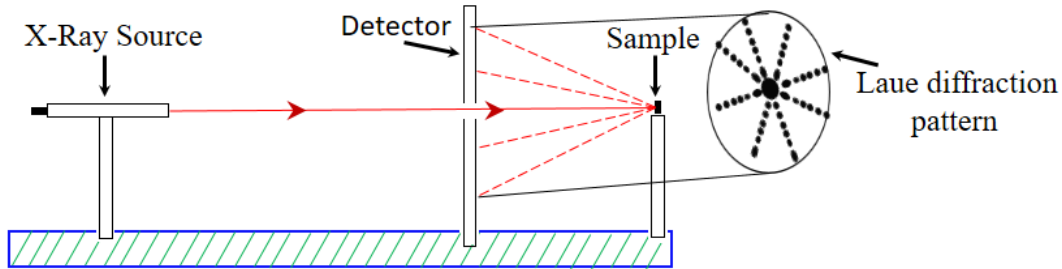


Figure 2.19: Back scattering Laue diffraction of X-ray from single crystal. The CCD detector is placed in between the sample and the X-ray source. The polychromatic incident X-ray beam produce a Laue pattern which is characteristic of specific crystallographic symmetry following the equation 2.28

- Principle of Laue diffraction: Let us consider a crystalline plane with Miller indices $[h,k,l]$ and $\vec{a}_1, \vec{a}_2, \vec{a}_3$ are the primitive lattice vectors. If $\vec{k}_i, \vec{k}_r$ are incident and scattered wave vectors then the condition for Laue diffraction is [82]

$$\vec{a}_1 \cdot \vec{\Delta k} = 2\pi h; \vec{a}_2 \cdot \vec{\Delta k} = 2\pi k; \vec{a}_3 \cdot \vec{\Delta k} = 2\pi l \quad (2.28)$$

where $\vec{\Delta k} = \vec{k}_i - \vec{k}_r$

Hence the scattering vector must be oriented within a particular direction in relation to the primitive vectors of the crystal lattice for constructive interference. The diffraction pattern produces symmetric dots corresponding to a stereographic projection of the crystal. For a given crystallographic symmetry and unit cell specifications the Laue pattern can be simulated using Orient Express software [83]. Comparing both the experimental Laue diffraction pattern and simulated pattern for a crystal, one can assign the crystallographic axis in the crystal.

2.14 Energy dispersive X-Ray analysis

Energy dispersive X-Ray analysis (EDAX/EDS/EDX) is an analytical method for determining the elemental composition of materials. It employs an incident electron beam to stimulate the emission of characteristic X-Ray from a specimen which is dependent on atomic number and characteristic of every materials. An EDX is conventionally equipped with Scanning Electron Microscope (SEM), used for mapping the sample morphology. We have used a SEM from ZEISS Ultraplus for EDX study. It is possible to characterize the type of elements and weight/atomic percentage of each elements present in a particular specimen. Typically an EDX spectrum consists of sharp peaks corresponding to several elements. In our study, the EDX data has been used to quantify the cation ratio of a specific material.

2.15 Physical property measurements

2.15.1 DC magnetization

The magnetic measurements were performed in a MPMS (Magnetic property measurement system)-XL SQUID (Superconducting Quantum Interference Device) from Quantum Design, USA. The measurement principle is based on Faraday's law of induction [84]. When a magnet moves through a closed circuit, an electric voltage is induced in that circuit. Mathematically, the magnetic flux (ϕ) through a coil with "n" turn, area A is $\phi=AB$ and the induced electric voltage is

$$V = -n \frac{d\phi}{dt} = -nA \frac{dB}{dt} \quad (2.29)$$

Where B is the magnetic induction. Measurement was performed by moving the sample through a second-order gradiometer superconducting detection coil placed at the center of a superconducting magnet. This produces a change in the persistent current in the circuit which is inductively coupled to a SQUID, as depicted in Fig.2.20(a). A SQUID consists of a closed superconducting loop including one or two Josephson junctions in the loop's current path. The magnetic field inside SQUID is quantized in the unit of flux quanta

$$\phi_0 = \frac{2\pi\hbar}{2e} \cong 2.0678 \times 10^{-12} Tesla \quad (2.30)$$

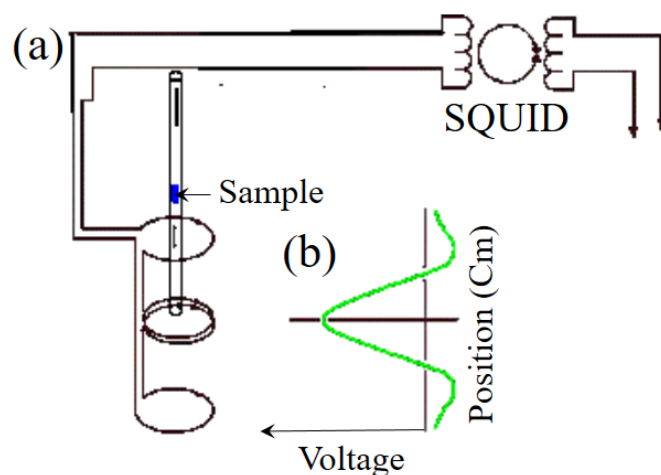


Figure 2.20: (a) The second order gradiometer superconducting detection coil of a MPMS. The movement of a magnet through the pickup coil produces a voltage according to Faraday's law of induction. This voltage is coupled with the SQUID for measuring the magnetic moment. (b) The voltage profile as function of position due to the movement of magnetic specimen through the pickup coil.

Hence any minute change as small as a flux quanta can be detected by measuring the voltage. This makes SQUID a sensitive device for measuring magnetic fields. In MPMS, sample was loaded inside a gelatine capsule incorporated in a plastic straw. The straw was fixed to the end of a transport rod. This transport rod was attached with a stepper motor controlled platform that moves the sample through the detection coils in discrete steps. Before performing a measurement, it was necessary to put the sample in the center of the detection coil, which corresponds to maximum voltage response in the scan, as is shown in Fig.2.20(b)

Conventionally, temperature dependent magnetic measurements were performed during heating the sample after cooling the specimen either in the Zero Field Cooled (ZFC) or the Field Cooled (FC) protocols.

2.15.2 High temperature DC magnetization

In a MPMS, magnetic measurement at high temperature was measured with sample space oven option from 300K-800K [85]. The oven is equipped with a nonmagnetic and noninductive heater and a specially constructed platinum thermometer mounted on an isothermal sleeve in the bottom of the oven assembly, which is kept in vacuum insulation (10^{-7} torr). The smaller bore size of the oven restricts the measured sample diameter to less than 3.3 mm. For loading sample, a sample holder made of brass was designed as depicted in Fig2.21(a). High temperature magnetization of Ni wire was performed up to

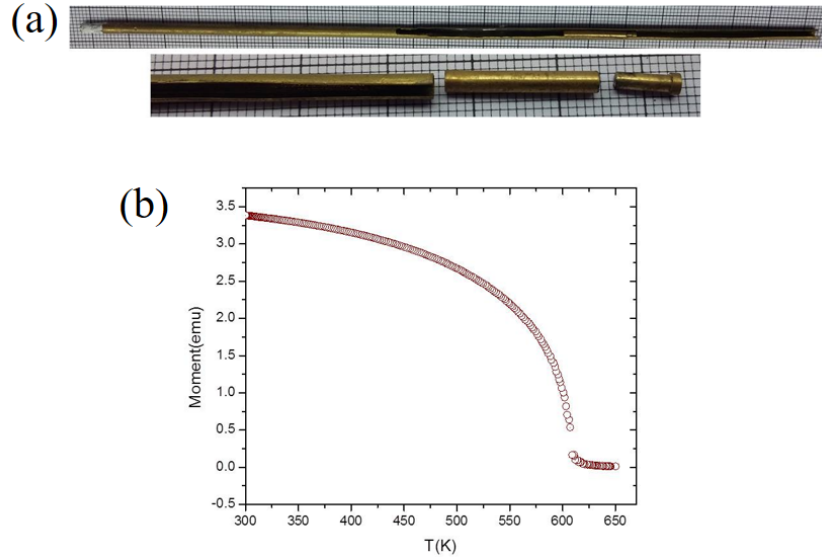


Figure 2.21: (a) Sample holder designed for high temperature magnetic measurement in MPMS. The designed assembly is made of brass and compatible with oven attachment of MPMS-XL. Sample with magnetic moment more than 10^{-4} emu can be measured till 700K. (b) Magnetic measurement performed on Nickel wire mounted in the designed sample holder with oven attachment

650 K in oven with the designed sample holder. The high temperature magnetic transition is clearly discernible in our measurement, as depicted in Fig.2.21(b). Since brass has magnetic moment $\approx 10^{-4}$ emu, only samples with moments more than this value was measurable.

2.15.3 Electric field dependent magnetic measurements

One of the significant application of multiferroics is the manipulation of magnetization by applying an electric field. Using MIUP, it was possible to measure magnetization in MPMS XL while an electrical bias was applied to the sample. Since MPMS-XL is very sensitive to measure magnetization, it is advantageous to study the change in magnetization with the applied electric field and study the electromagnetic susceptibility $\left(\alpha_{dc} = \frac{\partial M}{\partial E}\right)$.

The sample loading configuration as described for dielectric and pyroelectric measurements (section 2.7.1) using MIUP was not effectively useful for electric field dependent magnetic measurement. Since the soldering wire used for applying electric bias were close to the sample position and contributed to a magnetic moment in the measurement. Also, the sampling loading platform was made of Cu/Au which itself contributed in the

magnetic moment $\approx 10^{-4}$ emu.

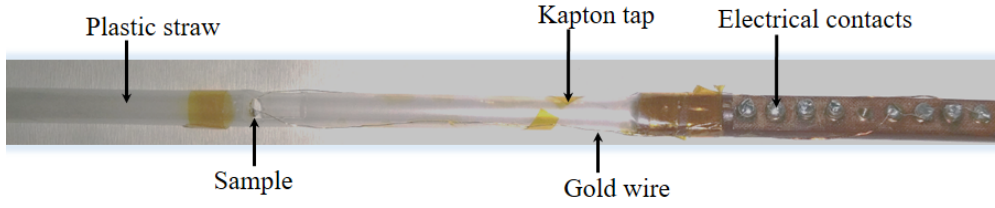


Figure 2.22: The sample loading configuration for electric field dependent magnetic measurement using a plastic straw.

The sample was loaded inside a plastic straw and gold wires were anchored on this straw for applying an electric field, as schematically shown in Fig.2.22. This allows for the sample to be positioned far away from the soldering point. Straw was cut as per requirement to align the sample with respect to the magnetic field.

2.15.4 Specific heat

Heat capacity (C) of a specimen is the amount of heat required to increase the temperature (of unit mass) by unit amount. In this thesis work, heat capacity has been measured using a PPMS from Quantum Design. The instrument measures heat capacity at constant pressure

$$C_p = \left(\frac{dQ}{dT} \right)_P \quad (2.31)$$

In PPMS, a known amount of heat is passed for a given period of time and resulting

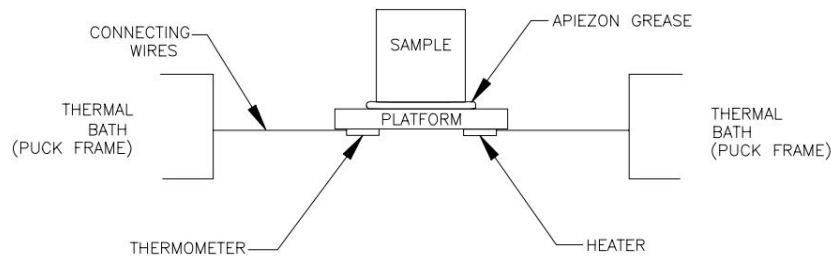


Figure 2.23: Schematic of heat capacity measurement performed in PPMS

change in temperature is monitored, and after heating the same is followed by a cooling period for same time [86]. The sample is thermally coupled as well as fixed in the sample platform by apiezon grease, as illustrated in Fig.2.23. In a standard measurement protocol, first the the heat capacity of apiezon grease, called addenda was measured. Next, the sample was stuck using apiezon grease and heat capacity was measured both under zero and in presence of magnetic field. The contribution to sample heat capacity was obtained

by subtracting addenda heat capacity from the sample plus grease contribution. Typically, the heat capacity of a specimen exhibits a peak at the long-range magnetic ordering/structural transition, if the change in entropy across the phase transition is large. The total heat capacity is

$$\begin{aligned} C_p^{Total} &= C_p^{Phonon} + C_p^{electron} + C_p^{magnetic} \\ &= \beta T^3 + \gamma T + C_p^{magnetic} \end{aligned} \quad (2.32)$$

Where, $\beta = \frac{12}{5} \frac{\pi^4 \cdot n \cdot R}{\Theta_D^3}$, n is the number of atom per formula unit, Θ_D is Debye temperature, Universal gas constant $R = 8.310 \text{ J/mol-K}$. The coefficient of electronic specific heat $\gamma = \gamma_0 \frac{m^*}{m}$.

For a magnetic material, the contribution of magnetic specific heat ($C_p^{magnetic}$) was calculated by subtracting the lattice contribution of heat capacity. The lattice contribution to the specific heat was obtained by measuring the heat capacity of isostructural nonmagnetic specimen or by fitting the high temperature heat capacity data with the Einstein-Debye Model. The change of magnetic entropy from a magnetically ordered state to disorder state is calculated as [87, 88]:

$$\Delta S^{magnetic} = \int_{T_1}^{T_2} \frac{C_p^{magnetic}}{T} \quad (2.33)$$

The magnetic entropy for a spin system in S state is

$$S^{magnetic} = R \ln(2S + 1) \text{ per mole} \quad (2.34)$$

Where, S is the spin state of the magnetic ion. Hence the spin state of a magnetic specimen can be calculated from the magnetic heat capacity, using equations 2.33 and 2.34

2.15.5 Resistivity

The temperature dependent resistivity measurements were performed in a PPMS from Quantum Design in the temperature range 2K-300K using four probe method. Four point contacts were made on compact, hard bar shaped pellet (length $\approx 5\text{-}8\text{mm}$). Four equispaced contacts were made with Cu/Au wires using silver paint in a single line array on the sample. Then the sample was mounted on PPMS puck platform by sticking

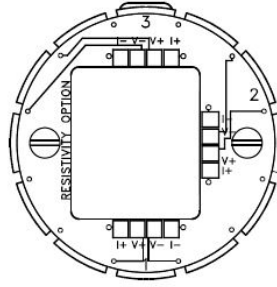


Figure 2.24: Sample platform for Resistivity measurement in PPMS. Three individual sample could be mounted simultaneously.

it with GE Varnish, as depicted in Fig.2.24 [89]. The four wires were soldered on the specified notch on the Puck (I^+ , I^- , V^+ and V^-) for driving current and measuring voltage. The four probe measurement reduces the contact and lead resistance contribution in the measurement. A constant current was applied through two wires and corresponding voltage was measured in the other wires. The resistivity is calculated by Ohm's law. Before performing measurement careful short check among the contacts is necessary.

Chapter 3

Study of the Swedenborgites

$\text{Dy}_{1-x}\text{Ca}_x\text{BaCo}_4\text{O}_7$ ($x=0$ to 1) and the $\text{SrBaCo}_4\text{O}_7$ system

3.1 Summary

In this chapter, investigation of the geometrically frustrated antiferromagnet $\text{DyBaCo}_4\text{O}_7$ through a combination of x-ray diffraction, magnetization and dielectric measurements is discussed. Systematic doping in the $\text{Dy}_{1-x}\text{Ca}_x\text{BaCo}_4\text{O}_7$ series causes a lifting of the geometrical frustration resulting in a structural transition from a high symmetry trigonal $P31c$ to a low symmetry orthorhombic $Pbn2_1$ symmetry at the doping concentration $x = 0.4$. For all the orthorhombic specimens, such a structural transition was also observed as a function of temperature. One of the distinguishing features of this structural transition is that the temperature at which this structural transition occurs in the RBaCo_4O_7 ($\text{R}=\text{Rare earth ions, Ca}^{2+}$) family is observed to scale linearly with the mean ionic radius of the R site ion. However, such a quasilinear relationship is violated for $\text{R}=\text{Ca}^{2+}$ comprising an equal number of Co^{2+} and Co^{3+} , indicating that charge ordering could possibly influence the structural transition. The ZFC-FC magnetization exhibits a large paramagnetic background arising from Dy^{3+} ions that apparently masks the magnetic transition appearing from the cobalt sublattice. Using Thermo-remanent Magnetization (TRM) measurements, we have identified the magnetic ordering temperatures of the solid solution of the series $\text{Dy}_{1-x}\text{Ca}_x\text{BaCo}_4\text{O}_7$. $\text{CaBaCo}_4\text{O}_7$ is known as a ferrimagnetic pyroelectric. The observation of a dielectric anomaly at the onset of magnetic transition

further reconfirms the presence of a magnetoelectric coupling in $\text{CaBaCo}_4\text{O}_7$. However, substitution of Dy^{3+} in the Ca^{2+} site leads to the disappearance of the dielectric anomaly. Finally, we chart out the phase diagram of the $\text{Dy}_{1-x}\text{Ca}_x\text{BaCo}_4\text{O}_7$ series.

$\text{SrBaCo}_4\text{O}_7$, a new member of Swedenborgite family has been synthesized successfully by the solid state reaction route. We have solved the structure using DICVOL06 and LeBail profile refinement of powder X-ray diffraction data. It stabilizes in the orthorhombic *pbam* space group. Detailed magnetic and thermodynamic study reveals multiple phase transitions as function of temperature.

3.2 Introduction

The mineral $\text{SbNaBe}_4\text{O}_7$ was discovered in 1924 by Gregori Aminoff [90] in the mines of Lngban (Vrmland, Sweden). It is the first member of Swedenborgite family crystallizing in hexagonal $P6_3mc$, named after the Swedish philosopher *Emanuel Swedenborg*. The crystal structure was solved by Pauling *et.al* in 1935 [91], demonstrating that the structure is made up of star like Be_4O_{13} clusters. However, over time several new compounds have been synthesized due to the incredible chemical flexibility of the Swedenborgite structure. For instance, the octahedrally coordinated Sb site can be substituted by rare earth ions (R^{3+}) or Ca^{2+} and the tetrahedrally coordinated Be site can hold nonmagnetic Al, Zn or magnetic Fe, Co etc. A plethora of specimens with the formula ABaM_4O_7 have been explored recently with exceptional electrical and magnetic properties [92, 93, 94, 95, 96]. This has generated wide experimental and theoretical interest owing to its geometrically frustrated structural motifs and a polar noncentrosymmetric structure. The mixed valence state of the M site depends on the charge state of the R site ion. When a divalent cation occupies the R site e.g. Ca^{2+} , Sr^{2+} etc. then $\text{M}^{3+}:\text{M}^{2+}=1:1$ and the same ratio becomes 1:3 when $\text{R}=\text{Ln}^{3+}$. The underlying lattice provides a unique exchange topology with such mixed valency to this class of materials. The magnetic ions reside in a tetrahedral configuration within a geometrically frustrated triangular lattice exhibiting a rich diversity in their magnetic ground states with varying valency and ionic radii of the R site ion. For instance, most members of the $\text{R}^{3+}\text{BaCo}_4\text{O}_7$ series exhibit low temperature anti-ferromagnetic order [96, 94], whereas for $\text{R}=\text{Y}^{3+}$, In^{3+} the stabilization of a glassy state along with short range magnetic correlations in both the triangular and Kagome sublattices have been suggested [97, 98]. Ca^{2+} is reported to be the only divalent cation that can completely replace R^{3+} ions ($\text{CaBaCo}_4\text{O}_7$), where an orthorhombic distortion results in lifting of the geometric frustration and is reported to stabilize to a ferrimagnetic pyroelectric state with a significant magneto-elastic coupling [99, 100]. The Co^{2+} ion has been thought to reside in the kagome network with spin only value $S=3/2$ whereas the Co^{3+} occupies the triangular network [101].

One of the defining features of the Swedenborgite family is a first-order structural transition from high symmetry trigonal ($P31c$)/hexagonal ($P6_3mc$) (Fig. 3.1(a)) to low symmetry orthorhombic structure (typically $Pbn2_1$ or Cmc_21) as a function of temperature due to the buckling of kagome layer (Fig.3.1(b)). The crystallographic relation between the two structures is $a_o \approx a_H$, $b_o \approx \sqrt{3}b_H$ and $c_o \approx c_H$, where the subscript

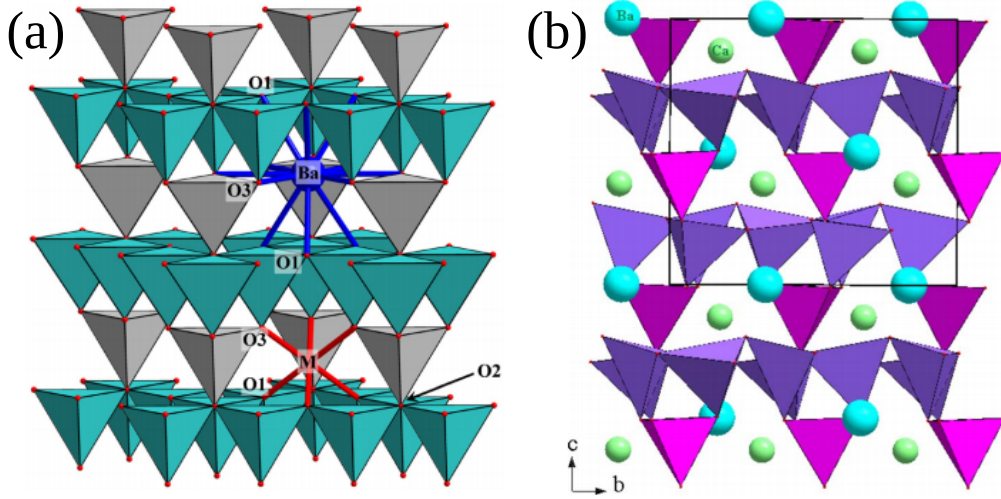


Figure 3.1: (a) Undistorted CoO_4 tetrahedra in trigonal/hexagonal structure and [102]. Figure adapted with permission from Ref. [102], copyright (2010) by the Elsevier. (b) Buckled kagome layer of orthorhombic RBaCo_4O_7 [103]. Figure adapted with permission from Ref. [103], copyright (2010) by the American Physical Society.

"o" and "h" stands for orthorhombic and hexagonal structures respectively. However, the origin of this structural transition has been controversial and an issue of debate. In some members, the charge redistribution/charge ordering of $\text{Co}^{2+}/\text{Co}^{3+}$ in the tetrahedral network has been assigned as the driving factor of this structural transition [104]. Whereas in some materials, the underbonding of the $\text{Ba}^{2+}\text{-O}_{12}$ network has been attributed as the cause of this structural transition [101].

3.2.1 Existing structural variants of the Swedenborgite family

The Swedenborgite structure consists of corner shared MO_4 tetrahedra distributed in Kagome (K) and Triangular layers (T) similar to the Spinel structure. However, in a Spinel structure the magnetic ions (M) resides in an Octahedra [105, 106]. There are three different structural variants available in the Swedenborgite family, as listed below:

- **The Hexagonal $P6_3mc$ or Trigonal $P31c$** : The well known geometrically frustrated Spinel structure have "ABCABC" close packing of " O_4 " layers, as depicted in Fig.3.2(a). In "114" Swedenborgite, one of the " O_4 " layer is substituted by BaO_3 layer in the packing of Spinel structure and results in "ABCB" close packing , as is shown in Fig.3.2(b). The magnetic atoms (M) are distributed in two distinct crystallographic sites [107].
- **Orthorhombic $Pbn2_1$** : The orthorhombic structure at room temperature is

stabilized by the buckling of the Kagome layer while the triangular layer remains flat. Such buckling removes the geometrical frustration and results in a long range magnetic ordering. The magnetic atoms (M) are distributed in four distinct crystallographic sites [107].

- **Cubic ferrite:** The Swedenborgite ferrite member (when the M site is occupied by iron (Fe)) stabilizes in a cubic structure [108]. The ferrite members are different in terms of crystal chemistry relative to cobaltites. Comparable to hexagonal structure, one of the BaO_3 layer is shifted by $\frac{a}{2}$ along $\langle 111 \rangle$ direction in the triangular layer and stabilizes in a cubic structure. The stacking sequence is ABC as similar to the Spinel.

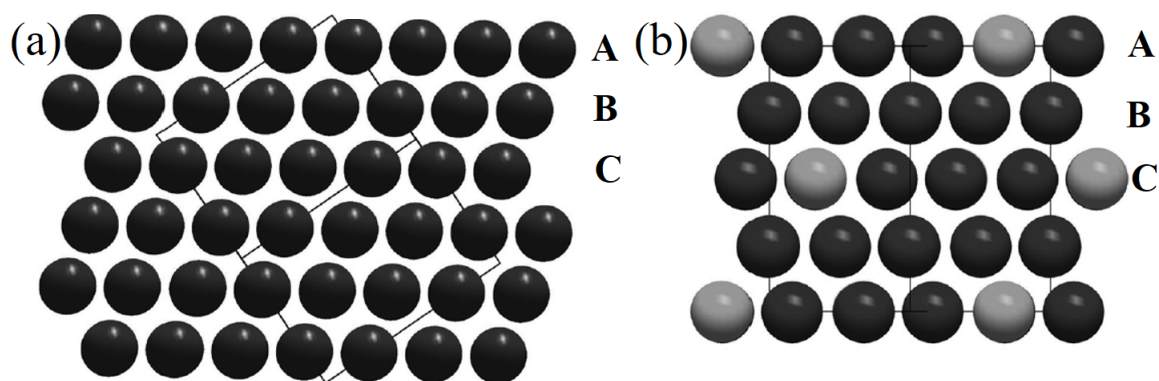


Figure 3.2: (a) Close packing of O_4 layer in spinel structure (b) Packing of BaO_3 and O_4 layer in hexagonal Swedenborgite [107]. Figure adapted with permission from Ref. [107], copyright (2011) John Wiley and Sons.

3.3 Results and Discussions

3.3.1 Synthesis of the $\text{Dy}_{1-x}\text{Ca}_x\text{BaCo}_4\text{O}_7$ series

The solid solution of the series $\text{Dy}_{1-x}\text{Ca}_x\text{BaCo}_4\text{O}_7$ ($x=0$ to 1) were synthesized in polycrystalline form by the standard solid state reaction technique. High purity Dy_2O_3 , CaCO_3 , BaCO_3 and Co_3O_4 precursors were mixed in stoichiometric amounts and thoroughly ground using a mortar and pestle. The fine homogeneous powder was then calcined in air at 900°C for 24 hrs for decarbonation and followed by a heat treatment at 1000°C for 48 hrs. The resulting powders were then cold pressed and heat treated in air for 12 hrs at temperatures varying from 1100°C to 1050°C . Slow cooling causes the appearance

of secondary brownmillerite phase $\text{BaCoO}_{2.6}$, and hence all samples were quenched in air to the room temperature.

3.3.2 Structural investigations

X-ray diffraction patterns of the polycrystalline specimens of the solid solution $\text{Dy}_{1-x}\text{Ca}_x\text{BaCo}_4\text{O}_7$ ($x=0$ to 1) recorded at room temperature are shown in Fig.3.3. Rietveld refinement of all these diffraction patterns were performed with the goodness of

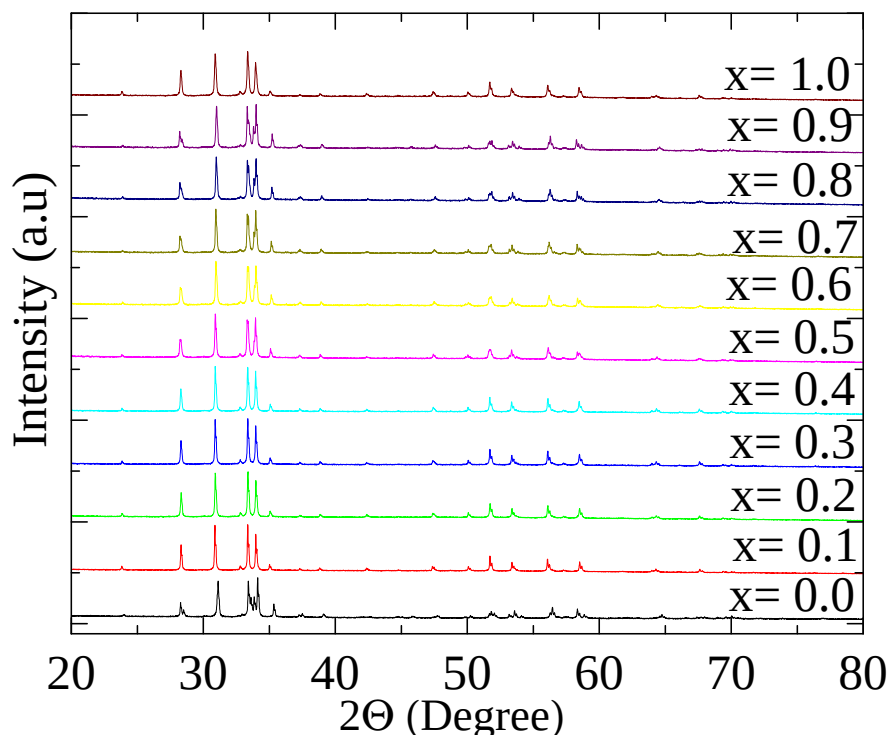


Figure 3.3: The room temperature x-ray diffraction patterns for all members of the $\text{Dy}_{1-x}\text{Ca}_x\text{BaCo}_4\text{O}_7$ series ($x=0$ to 1).

fit (R_{wp}/R_e) being < 1.6 . Refinement of $\text{DyBaCo}_4\text{O}_7$ (DBCO) with the Trigonal $P31C$ is shown in Fig.3.4(a). This observation is similar to the earlier reports of the other members of the $R\text{BaCo}_4\text{O}_7$ series (with $R = \text{Ho, Er, Tm, Yb and Lu}$) [109]. The details of structural parameters as obtained from room temperature Rietveld refinement for DBCO is tabulated in Table.3.1. On the other hand, the Rietveld refinement of $\text{CaBaCo}_4\text{O}_7$ (CBCO) as (performed with orthogonal $Pbn2_1$ space group) depicted in Fig.3.4(b) [103]. The structural parameters of CBCO as obtained from Rietveld refinement is tabulated in Table.3.2.

Table 3.1: Structural parameters of $\text{DyBaCo}_4\text{O}_7$ (DBCO) as obtained from Rietveld refinement of room temperature X-Ray diffraction data

Space Group : $P\bar{3}1c$, Crystal System: Trigonal				
$a = b = 6.311(65) \text{ \AA}$, $c = 10.241(48) \text{ \AA}$; $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$				
Atom	Wyckoff	x/a	y/b	z/c
Dy	2b	0.66670	0.33330	0.33330
Ba	2b	0.666 70	0.33330	0.50000
Co1	2a	0.00000	0.00000	0.444(81)
Co2	6c	0.157(50)	0.815 00	0.685(90)
O1	6c	0.512(31)	0.505(31)	0.752(66)
O2	2a	0.00000	0.00000	0.244(40)
O3	6c	0.117(03)	0.788(40)	0.500(50)

3.3.2.1 Crystal Structure

A view of the structure along the crystallographic c axis for high symmetry DBCO and low symmetry CBCO are depicted in Fig.3.5 where the basic structural units are CoO_4 tetrahedra . The buckling of the kagome layer in the low symmetry CBCO could be clearly seen in the Fig.3.5(b). The magnetic Cobalt (Co) ion of DBCO comprises two in-equivalent sites, with one of them residing in the Kagome sublattice, and the other one constituting the intervening triangular layers. The ratio of the tetrahedra in the triangular and Kagome layers is 3 : 1. It has been speculated that the Co^{2+} occupies the Kagome sublattice whereas the Co^{3+} making up the triangular lattice. CBCO stabilizes in orthorhombically distorted structure, having four in-equivalent Co sites. The Kagome layer is now made up of three corrugated tetrahedra Co2, Co3 and Co4 and all of them occupies the same Wyckoff position 4a as tabulated in Table 3.2. Such buckling of the kagome layer relieves the geometrical frustration, and is also thought to be responsible for the stabilization of a long-range ordered ferrimagnetic ground state in CBCO.

3.3.2.2 Structural transition due to chemical doping

Following the above discussion, where the one end member (DBCO) of $\text{Dy}_{1-x}\text{Ca}_x\text{BaCo}_4\text{O}_7$ series stabilizes in high symmetry $P\bar{3}1c$ and other end member (CBCO) stabilizes in the low symmetry $Pbn2_1$ phase, it is natural to expect a structural transition ($P\bar{3}1c \rightarrow Pbn2_1$) transition in the $\text{Dy}_{1-x}\text{Ca}_x\text{BaCo}_4\text{O}_7$ series as a function of doping. The X-ray diffraction patterns indicate that such transition occurs at $x > 0.4$ as is shown in Fig. 3.6(a) This structural transition could be clearly identified by splitting of Bragg peaks (112) and (201) in the trigonal phase into the peaks (132), (202), (041) and (221) in the

Table 3.2: Structural parameters of $\text{CaBaCo}_4\text{O}_7$ (CBCO) as obtained from Rietveld refinement of room temperature X-Ray diffraction data

Space Group : $Pbn2_1$, Crystal System: Orthorhombic				
$a = 6.281(55) \text{ \AA}$, $b = 10.997(12) \text{ \AA}$, $c = 10.181(77) \text{ \AA}$; $\alpha = \beta = \gamma 90^\circ$				
Atom	Wyckoff	x/a	y/b	z/c
Ca	4a	0.998(20)	0.668(85)	0.872(37)
Ba	4a	0.002(31)	0.666(27)	0.500(02)
Co1	4a	0.013(74)	0.999(75)	0.940(97)
Co2	4a	0.998(90)	0.172(76)	0.687(16)
Co3	4a	0.247(95)	0.089(35)	0.184(50)
Co4	4a	0.265(79)	0.917(10)	0.680(82)
O1	4a	0.065(78)	0.995(08)	0.251(60)
O2	4a	0.973(44)	0.492(33)	0.225(18)
O3	4a	0.774(12)	0.274(29)	0.777(97)
O4	4a	0.738(63)	0.751(23)	0.223(49)
O5	4a	0.950(81)	0.158(03)	0.494(62)
O6	4a	0.219(47)	0.092(59)	0.004(01)
O7	4a	0.273(13)	0.946(74)	0.488(61)

orthorhombic phase as function of doping (x).

The evolution of structural parameters across the $\text{Dy}_{1-x}\text{Ca}_x\text{BaCo}_4\text{O}_7$ series as a function of doping content (x) are illustrated in Figure 3.6(b). The lattice parameters are seen to vary systematically across the series with the possible exception of the $x = 0.1$ specimen. As a function of doping concentration x , the b parameter increases and both a and c decreases gradually within the orthorhombic phase. The lower panel of Fig. 3.6(b) depicts the evolution of the c/a ratio as a function of doping. At the critical value of the doping of $x = 0.4$, the c/a ratio exhibits a discontinuity due to the structural transition from the $P31c$ to $Pbn2_1$ symmetry. The orthorhombic structure results from the distortion of the hexagonal structure and the extent of distortion can be quantified using the distortion parameter $D = (b/\sqrt{3} - a)/a$. Within the hexagonal symmetry, the distortion occurs due to a contraction along the $[\bar{1}10]_H$ direction and an expansion along the $[110]_H$ direction. The distortion calculated for all the orthorhombic members of the $\text{Dy}_{1-x}\text{Ca}_x\text{BaCo}_4\text{O}_7$ series is shown in the lower panel of Fig. 3.6(b). The distortion is largest for CBCO with (D) $D = 1.14\%$ and is in agreement with the previously reported value of 1.05% [103]. With increasing Dy content the distortion (D) decreases monotonically, and falls to a value of $D = 0.47\%$ for the $\text{Dy}_{0.5}\text{Ca}_{0.5}\text{BaCo}_4\text{O}_7$ system. This is in agreement to that observed in other members of the $R^{3+}\text{BaM}_4\text{O}_7$ family. For instance, the value of D in

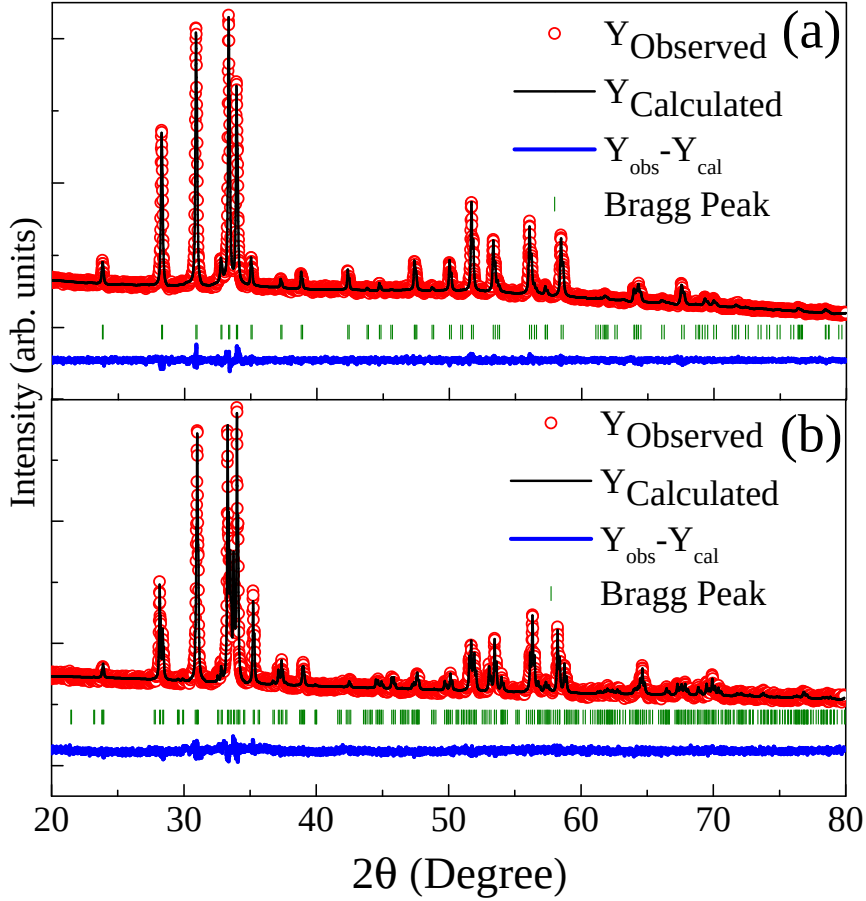


Figure 3.4: Rietveld refinement of room temperature X-Ray diffraction patterns of (a) $\text{DyBaCo}_4\text{O}_7$ and (b) $\text{CaBaCo}_4\text{O}_7$

the Yb [101], Tm [110] and Ho [111] systems have been calculated to be 0.67%, 0.53% and 0.44% respectively at different temperatures.

3.3.2.3 Structural transition as a function of temperature

A temperature driven structural transition from a high symmetry $P31c$ or $P6_3mc$ (at ambient temperature) to the low symmetry $Pbn2_1$ phase (at low temperature) have been explicitly reported for the RBaCo_4O_7 series. However, $\text{CaBaCo}_4\text{O}_7$ stabilizes already in low symmetry in ambient temperature. Hence one would expect a structural transition to high symmetry at high temperature. Interestingly, in spite of a large number of experimental reports on $\text{CaBaCo}_4\text{O}_7$, the presence of such a structural transition remains to be verified. We have performed high temperature X-Ray diffraction measurements on all orthorhombically distorted specimens to explore this structural transition as a function of temperature. A $Pbn2_1 \rightarrow P31c$ structural transition was observed for all the specimen with $x \geq 0.4$ as depicted in Fig.3.7(a), where a narrow region between

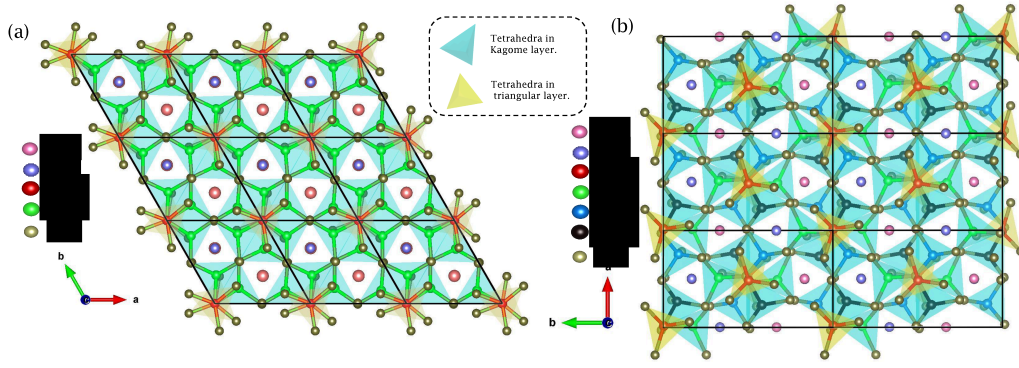


Figure 3.5: The crystal structure of the trigonal (a) $\text{DyBaCo}_4\text{O}_7$ and orthorhombic $\text{CaBaCo}_4\text{O}_7$ as viewed from crystallographic c axis.

33.8° to 34.5° is expanded for the sake of clarity. The Bragg peaks (221) and (041) in the low symmetry phase were merged as to the (201) Bragg peak at high temperature. Similar structural transition was also observed for the $\text{Dy}_{0.4}\text{Ca}_{0.6}\text{BaCo}_4\text{O}_7$ sample, as is depicted in Fig.3.7(b). For several members of RBaCo_4O_7 , it has been suggested that the temperature of this structural transition scales linearly with the ionic radii of the R site ion [94, 95]. We have verified this relationship, as is shown in Fig.3.8(a), where the transition temperature is plotted as a function of the mean ionic radii of the R site ion. The mean ionic radii have been calculated for the specimen in orthorhombic phase using the formula

$$\langle r_R \rangle = (1 - x) \langle r_{\text{Dy}} \rangle + x \langle r_{\text{Ca}} \rangle$$

High temperature X-ray diffraction measurements performed on specimens with orthorhombic structure of the $\text{Dy}_{1-x}\text{Ca}_x\text{BaCo}_4\text{O}_7$ family indicate that this quasi-linear relationship is satisfied for systems with different ionic radii as well as with varying $\text{Co}^{2+}:\text{Co}^{3+}$ ratios. Interestingly, the behavior of CBCO is clearly anomalous and violates this quasilinear relationship where the structural transition is relatively higher as is expected solely on the basis of its R site ionic radius. For instance, the structural transition temperature of $\text{CaBaCo}_4\text{O}_7$ is 1.48 times larger than $\text{Dy}_{0.1}\text{Ca}_{0.9}\text{BaCo}_4\text{O}_7$ despite of the difference in the mean ionic radii between them is only by 0.88%. CBCO has been identified to exhibit charge ordering, with the Co^{2+} and Co^{3+} ions exclusively occupying the Kagome and triangular layers respectively [103]. Also the fact that tetrahedral coordination of Co^{3+} is rare, the possibility of a metal to ligand charge transfer similar to that observed in layered cuprates has also been suggested [112]. Our observations indicate that these factors could possibly play a crucial role in stabilizing the large structural distortion observed in this system and causes it to stabilize in the high symmetry $P31c$ phase at temperature

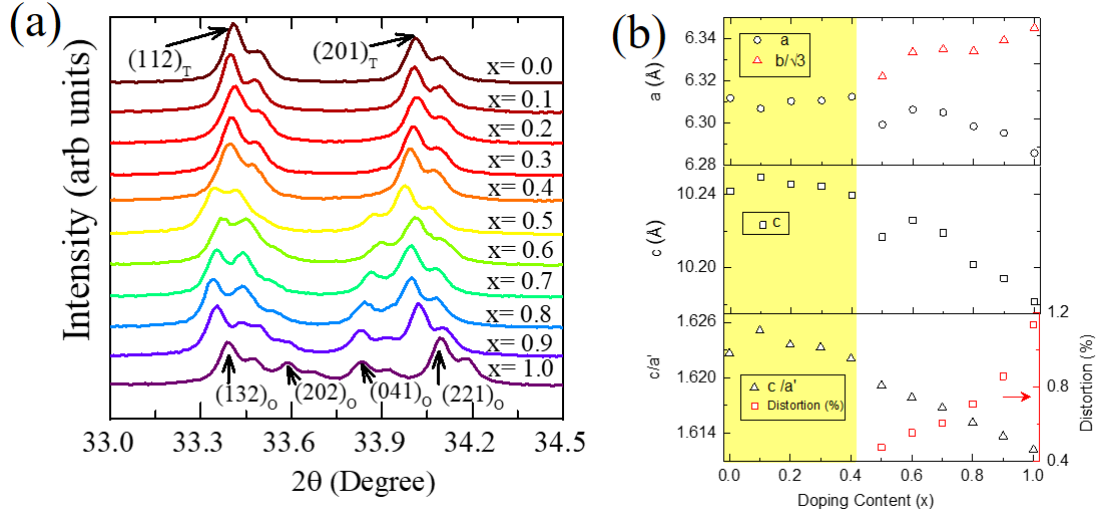


Figure 3.6: (a) Evolution of the Bragg Peak (112) and (201) from high symmetry $P31c$ to low symmetry $Pbn2_1$ with chemical doping. Where the suffix T and O imply Trigonal and Orthorhombic structure (b) The variation of the lattice parameters a , b , and c , across the $\text{Dy}_{1-x}\text{Ca}_x\text{Co}_4\text{O}_7$ series. The lattice parameter b is replaced by the reduced lattice parameter $b/\sqrt{3}$ for all the orthorhombically distorted members of the series. The shaded region corresponds to the specimens crystallizing in the high symmetry $P31c$ space group. The right axis of the lower panel exhibits the variation of the orthorhombic distortion ($D = (b/\sqrt{3} - a)/a$) for all the specimens crystallizing in the $Pbn2_1$ space group.

of the order of 1073K.

3.3.2.4 Effect of doping in $\text{Dy}_{1-x}\text{Ca}_x\text{BaCo}_4\text{O}_7$ series

The occurrence of the ($P31c \rightarrow Pbn2_1$) structural transition has been ascribed to the under bonding of the BaO_{12} polyhedra in some of the $R^{3+}\text{BaCo}_4\text{O}_7$ systems [101]. The Ba^{2+} ion occupies an anticubooctahedral site as shown in Fig.3.8(b). Our structural refinement models indicate a number of bonds with unphysical bond lengths ($>3 \text{ \AA}$). This causes a distortion of the anticubooctahedron resulting in an equal number of small (and large) Ba-O bond lengths, such that the average Ba-O bondlength is invariant. In $\text{YbBaCo}_4\text{O}_7$ the high symmetry structure is associated with three long and three short bonds, with the other six bonds being close to 3.14 and results in the bond ratio of 3 : 3 : 6. The structural transition to low symmetry as a function of temperature is associated with a change in this ratio to 6 : 6 : 0, with the distorted orthorhombic structure being characterized by an equal number of large and short bonds [101]. Our analysis of room temperature diffraction data shows that the scenario is similar in the $\text{Dy}_{1-x}\text{Ca}_x\text{BaCo}_4\text{O}_7$ series, where this structural transition is observed as a function of doping. The specimens with doping content $x = 0$, to $x = 0.4$ crystallizes in the high symmetry phase and comprises 3 long

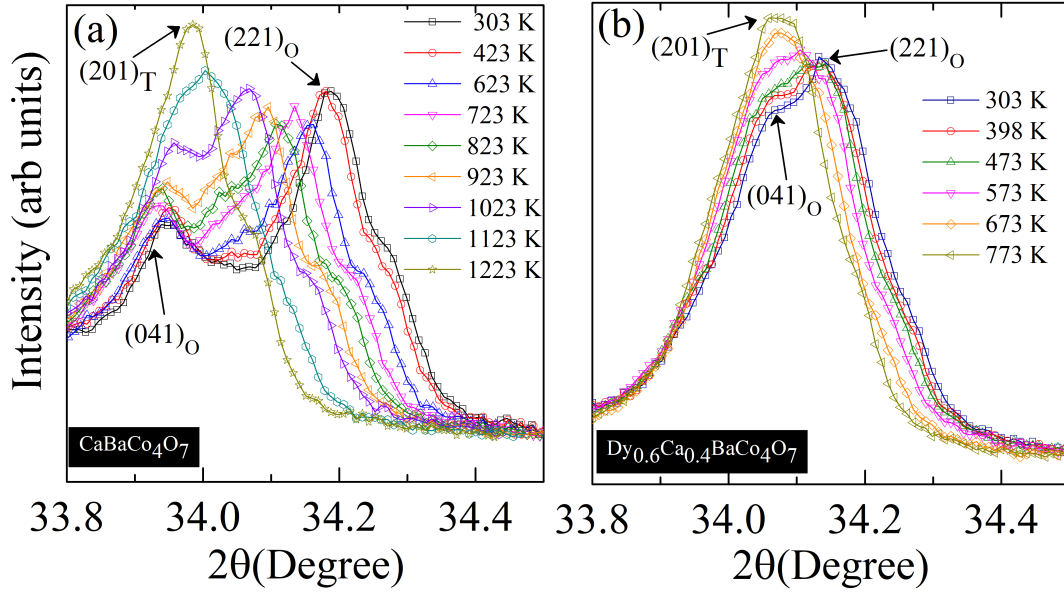


Figure 3.7: The structural transition from the high symmetry $P31c$, Trigonal (T) $\rightarrow$ low symmetry $Pbn2_1$, Orthorhombic (O) phase as observed from high temperature X-ray diffraction pattern in a narrow region for (a) $\text{CaBaCo}_4\text{O}_7$ and (b) $\text{Dy}_{0.4}\text{Ca}_{0.6}\text{BaCo}_4\text{O}_7$ specimens.

and short bonds each with average lengths of 3.45 ± 0.02 and 2.85 ± 0.02 and other 6 bonds with an average value of 3.15 ± 0.02 . However, the average Ba-O bondlength of 3.14 ± 0.02 is invariant across the whole series. For samples with $x > 0.4$ which crystallize in the low symmetry $Pbn2_1$ space group, the BaO_{12} polyhedra is characterized by 6 large and short bonds each with average lengths of 3.50 ± 0.02 and 2.78 ± 0.02 respectively. Thus, the underbonding of Ba^{2+} which possibly drives this structural transition, is clearly endemic in both the high symmetry and low symmetry members of the Swedenborgite family. Hence the underbonding in BaO_{12} polyhedra can not be assigned as the possible origin of such structural transition in this series. The charge redistribution between the kagome and triangular could be the possible driving factor of the observed structural transition [104].

3.3.3 DC magnetization

The ZFC-FC magnetic measurements reveal that DBCO exhibits an antiferromagnetic transition at 76 K, as is shown in main panel of Figure 3.9(a). Some of the RBaCo_4O_7 member has been reported to exhibit spin/cluster glass like freezing [97, 98]. However, ac susceptibility measurement shows that the observed peak in the magnetic susceptibility of DBCO is frequency independent (inset of Fig. 3.9(a)), thus ruling out the possibility of a

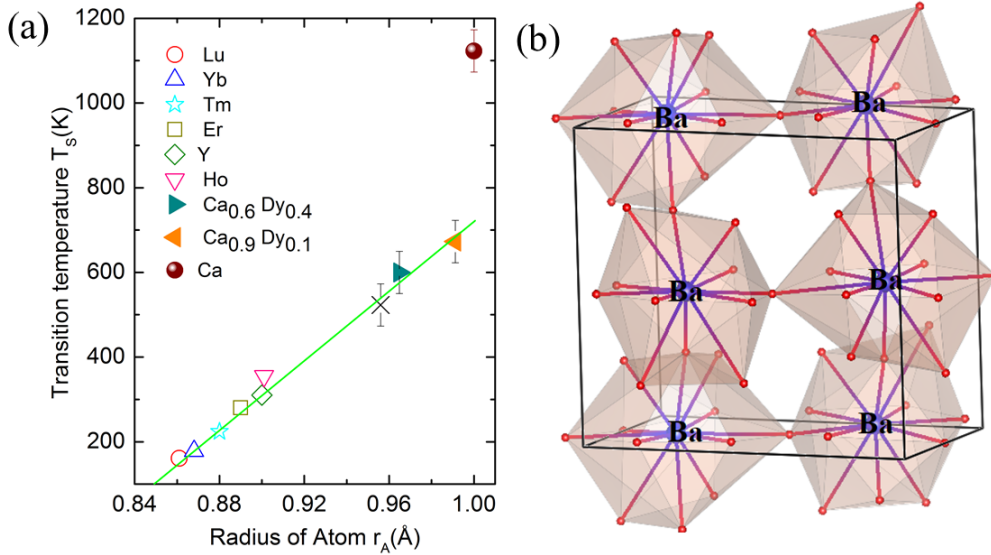


Figure 3.8: (a) The variation of the structural transition (high symmetry to low symmetry) temperature as a function of the mean R site ionic radii (r_R) for all cobalt based Swedenborgites reported till date. As is evident, a quasilinear relationship between this transition temperature and r_R is seen for all members of this family, except $\text{CaBaCo}_4\text{O}_7$ (b) BaO_{12} polyhedra of RBaCo_4O_7 , where the Ba^{2+} ion occupy an anticubooctahedral site with coordination number 12.

glassy phase in DBCO. The ZFC-FC magnetic measurements of $\text{Dy}_x\text{Ca}_{1-x}\text{BaCo}_4\text{O}_7$ series are shown in Fig. 3.9(b). $\text{CaBaCo}_4\text{O}_7$ exhibits a ferrimagnetic ordering at 65K, which is in agreement with previous reports [99, 100]. The structural distortion along with the preferential occupation of the Kagome and triangular layers by Co^{2+} and Co^{3+} ions is proposed as the driving factor for the observed ferrimagnetic ground state in CBCO. The ferromagnetic structure of $\text{CaBaCo}_4\text{O}_7$ is unique compared to other members of RBaCo_4O_7 , where a ferromagnetic coupling among the cobalt spin occurs along the b axis instead of antiferromagnetic coupling [103].

According to Hund's rule, the effective paramagnetic moment ($p_{\text{calc}} = g\sqrt{S(S+1)}$) of Dysprosium ($4f^9 5s^2 6p^6$) is $10.63\mu_B$, which is the highest among the rare earth ions. As is clearly evident, ZFC magnetic measurements are plagued by the presence of such large Dy^{3+} paramagnetic moment and no order is seen within the Dy^{3+} sub-lattice down to the lowest measured temperatures. Due to this large paramagnetic background, the transition within the Co sublattice is barely discernible. This problem is more prominent in the other members of the $\text{Dy}_{1-x}\text{Ca}_x\text{BaCo}_4\text{O}_7$ series as is shown in Fig. 3.9(b). Hence, conventional Zero Field cooled measurements are unable to pick up the onset of magnetic ordering in these specimens due to the large Dy^{3+} paramagnetic moment.

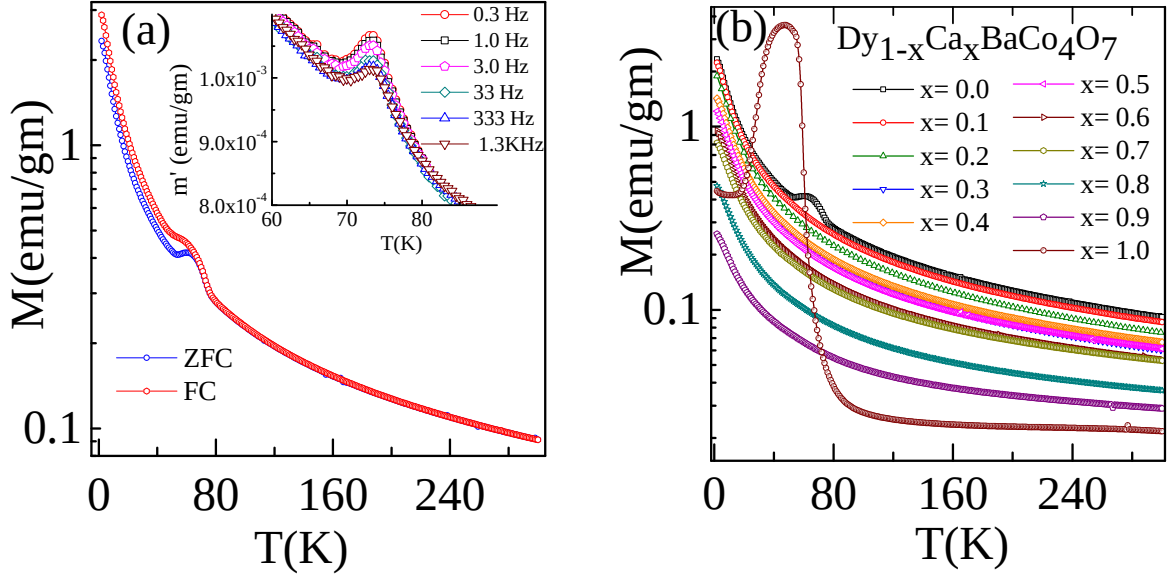


Figure 3.9: (a) exhibits the magnetization of the $\text{DyBaCo}_4\text{O}_7$ system measured using the Zero Field Cooled (ZFC) and Field Cooled (FC) protocols at a field of 100 Oe. The inset shows the ac susceptibility measurement of the same system at varying frequencies. (b) depicts the ZFC curves of all members of the $\text{Dy}_{1-x}\text{Ca}_x\text{Co}_4\text{O}_7$ series as measured at 100 Oe.

3.3.4 TRM measurements

To resolve the issue of the paramagnetic moment of Dy^{3+} in ZFC measurement protocol, we have utilized the relatively underutilized technique of Thermo-remnant Magnetisation (TRM) to identify the magnetic ordering temperatures in the $\text{Dy}_{1-x}\text{Ca}_x\text{BaCo}_4\text{O}_7$ series. The protocol used for our TRM measurements is schematically shown in figure 3.10(a). It involves, applying a DC field (H_{app}) at room temperature, and the system is cooled to a temperature (5K in our case) well below the magnetic transition temperature (T_N) of the specimen (1 $\rightarrow$ 2). Next, the field is reduced to zero (2 $\rightarrow$ 3), and the remanent magnetization $M_{TRM}(T)$ is measured during warming at a constant rate (3 $\rightarrow$ 4). TRM measurement have been extensively used in the investigation of spin glasses [113], studying domain dynamics of AFM, piezomagnetism [114] etc. In the case of spin glasses, $M_{TRM}(T)$ is seen to be zero in the paramagnetic region, and the magnetic transition temperature is identified in the form of an upturn in the magnetization [115]. Temperature dependent M_{TRM} measurements performed after a field cool of 100 Oe is shown in Fig.3.10(b). As is evident, TRM measurements are relatively insensitive to the Dy^{3+} paramagnetic background, and clearly identifies magnetic transitions in all the members of the $\text{Dy}_{1-x}\text{Ca}_x\text{BaCo}_4\text{O}_7$ series. $M_{TRM}(T)$ measurements indicate that the

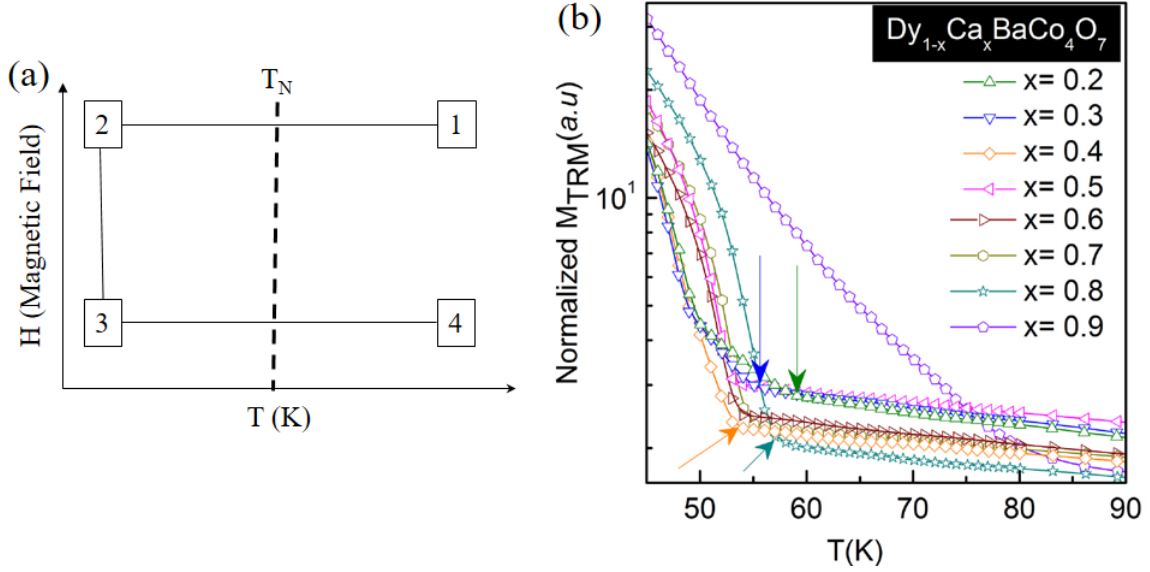


Figure 3.10: (a) Schematic representation of the thermo remanent magnetization (TRM) measurement protocol. (b) The temperature dependence of the thermoremanent magnetization ($M_{TRM}(T)$) as measured for all members of the $\text{Dy}_{1-x}\text{Ca}_x\text{BaCo}_4\text{O}_7$ series. All the measurements are normalized with $M_{TRM}(300\text{K})$ for the sake of clarity. The onset of the magnetic transitions is clearly evidenced by a sharp upturn in $M_{TRM}(T)$.

antiferromagnetic T_N varies smoothly among the intermediate compositions. Interestingly, the only exception to this rule is the ferrimagnetic $\text{CaBaCo}_4\text{O}_7$, where long range order sets in at a temperature (T_C) lower than that observed for the $x = 0.9$ member of the $\text{Dy}_{1-x}\text{Ca}_x\text{BaCo}_4\text{O}_7$ series. However, for systems with multiple magnetic sub-lattices, identifying the onset of magnetic order in one of the sub-lattices is non-trivial issue. We found that in such cases, TRM measurements would be more effective than conventional Field cooled or Zero field cooled measurement protocols for identifying magnetic transitions.

3.3.5 Dielectric measurements

The dielectric measurement performed on CBCO exhibits a sharp peak in the real part of the dielectric permittivity (ϵ') in the vicinity of magnetic transition, indicating the presence of a large coupling of the spin and charge degrees of freedom. The main panel of Fig. 3.11(a) shows the temperature dependence of (ϵ') as measured for all the orthorhombic members of the $\text{Dy}_{1-x}\text{Ca}_x\text{BaCo}_4\text{O}_7$ series. Interestingly, with the substitution of Dy^{3+} in Ca^{2+} sites, the feature in the dielectric permittivity vanishes and the onset of the magnetic transition for all the compositions are barely discernible. The magnitude of ϵ' does not change appreciably with doping in comparison to CBCO. This reaffirms the anomalous

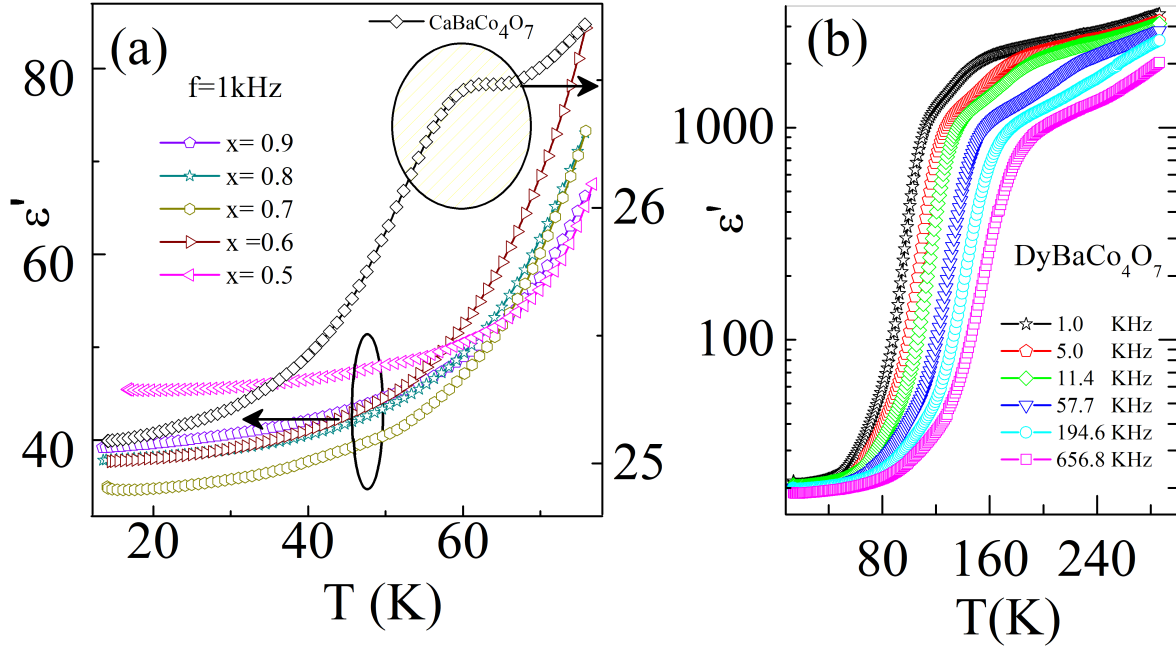


Figure 3.11: (a) The temperature dependence of the dielectric constant $\epsilon'(T)$ as measured for all the orthorhombic members of the $\text{Dy}_{1-x}\text{Ca}_x\text{Co}_4\text{O}_7$. (b) The frequency dependent measurements of $\epsilon'(T)$ for the $\text{DyBaCo}_4\text{O}_7$ system.

behavior of the charge ordered CBCO with its large magneto-elastic coupling from the doped members of the $\text{Dy}_{1-x}\text{Ca}_x\text{BaCo}_4\text{O}_7$ series [100]. However the parent specimen $\text{DyBaCo}_4\text{O}_7$ does not exhibit any signatures of (long or short range) electrical ordering at the magnetic ordering temperature as is shown in the Fig.3.11(b). Interestingly, the dielectric permittivity of $\text{DyBaCo}_4\text{O}_7$ exhibits a high dielectric constant of the order of several thousand near room temperature. A frequency-dispersive sharp drop (below 200K) and an almost T and ω insensitive plateau in the higher temperature regime was observed in $\text{DyBaCo}_4\text{O}_7$. Such observation is similar to the behavior of colossal dielectric constant (CDC) materials [116, 117]. In many strongly correlated oxide polycrystalline materials, the electrical heterogeneity originating from the semi-conducting grains and insulating grain boundaries leads to the appearance of CDC [118, 119].

3.4 Phase diagram of the $\text{Dy}_{1-x}\text{Ca}_x\text{BaCo}_4\text{O}_7$ series

We have charted out the phase diagram of the Swedenborgite $\text{Dy}_{1-x}\text{Ca}_x\text{BaCo}_4\text{O}_7$ series using x-ray diffraction, magnetization, and dielectric measurements, as shown in Fig.3.12. One end member DBCO ($x=0$) crystallizes in the trigonal $P31c$ whereas the other end member CBCO ($x=1$) stabilizes in orthorhombic $Pbn2_1$. The evolution of structure as

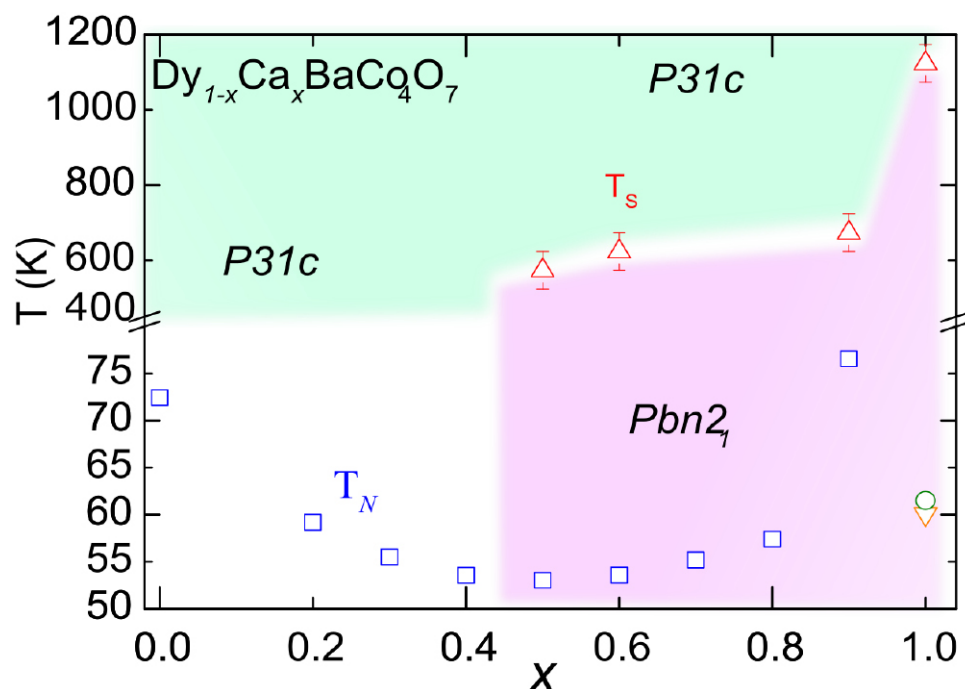


Figure 3.12: The phase diagram for the $\text{Dy}_{1-x}\text{Ca}_x\text{Co}_4\text{O}_7$ series as determined by x-ray diffraction ($\triangle$), magnetization (T_N : $\square$, T_C : ∇) and dielectric ($\circ$) measurements.

a function of doping (x) and temperature are shown with two different colors. For the specimens with $x > 0.4$, structural transition $P31c \rightarrow Pbn2_1$ occurs both as function of doping and temperature. $\text{CaBaCo}_4\text{O}_7$ exhibits concurrent dielectric and magnetic transitions.

3.5 $\text{SrBaCo}_4\text{O}_7$ - a new addition to the Swedenborgite family

In the Swedenborgite cobaltites RBaCo_4O_7 , the R site has been substituted with several lanthanides in trivalent charge states [92, 93, 94, 95, 96]. However, Calcium (Ca) is the only cation reported with R site in the divalent charge state [120]. We have attempted to substitute the R site with Sr^{2+} and successfully synthesized polycrystalline $\text{SrBaCo}_4\text{O}_7$ by solid state reaction. ¹

¹An attempt to substitute with Mg^{2+} was not successful. A number of trial leads to an end product of $\text{MgO} + \text{BaCoO}_{2.6} + \text{CoO}$

3.5.1 Synthesis of $\text{SrBaCo}_4\text{O}_7$

Stoichiometric amounts of the high purity precursors SrCO_3 , BaCO_3 and Co_3O_4 were thoroughly ground using mortar and pestle. The mixture was then heat treated at 800°C in the air. Next, the powders were cold pressed to form pellets and calcined at 950°C for 24 hrs. The end product of the solid state reaction was highly influenced by the cooling. The phase was formed by quenching in the air down to room temperature.

3.5.2 Indexing the diffraction profile of $\text{SrBaCo}_4\text{O}_7$

The observed Bragg peaks in the collected X-ray diffraction profile could not be assigned with any of the starting precursors phase or any of existing phase reported in the literature with a combination of Sr, Ba, Co and O (Sr-O, Co-O, Ba-O, Sr-Co-O, Sr-Ba-O, Ba-Co-O etc). Moreover, the EDAX study of the polished powder exhibit the cation ratio of Sr: Ba :Co = 1:1:4 confirming the formation of SrBaCo_4 phase. A profile refinement with the space group orthorhombic $Pbn2_1/Cmc2_1$ was not successful.

Possible space group for the diffraction profile of $\text{SrBaCo}_4\text{O}_7$ was determined using

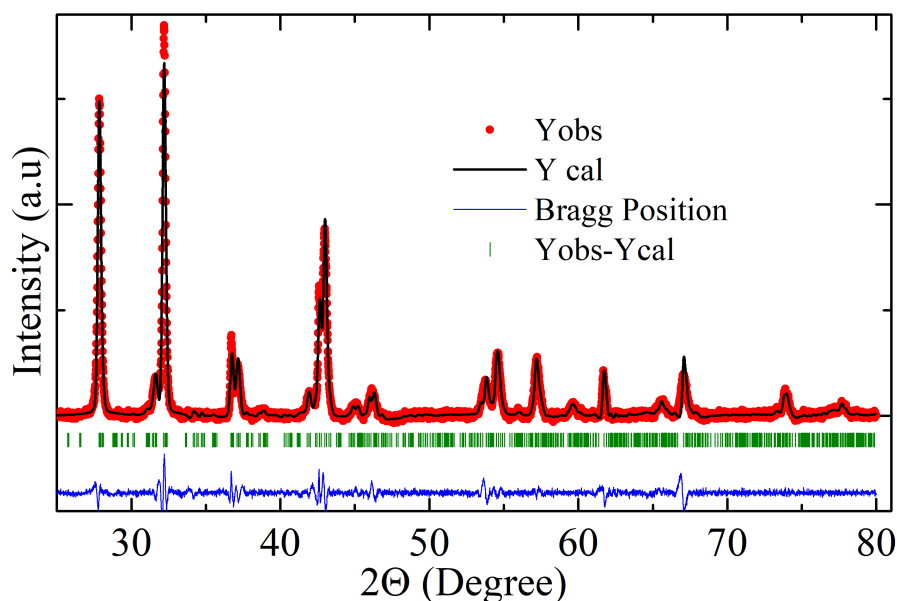


Figure 3.13: Le Bail fitting of the room temperature powder diffraction of $\text{SrBaCo}_4\text{O}_7$

DICVOL06 [79] from the Fullprof Suite toolbar. An exhaustive study with possible space group has resulted in the best LeBail profile fit with the orthorhombic $Pnma$, as depicted in Fig.3.13. The obtained unit cell parameters are $a = 12.36 \text{ \AA}$, $b = 10.45 \text{ \AA}$, $c = 8.00 \text{ \AA}$ and $\alpha = \beta = \gamma = 90^\circ$. The obtained structure of $\text{SrBaCo}_4\text{O}_7$ is similar to the structure of

off-stoichiometric YBaCo_4O_7 [121] with the unit cell parameter related with the parent hexagonal phase as $a_0 \approx \sqrt{3}a_h$, $b_0 \approx c_h$ and $c_0 \approx a_h$.

3.5.3 Magnetic measurements

The magnetic measurements performed in ZFC-FC protocol exhibits an anomaly at 270K (inset of Fig.3.14(a)) and another low temperature anomaly at 37K, as is shown

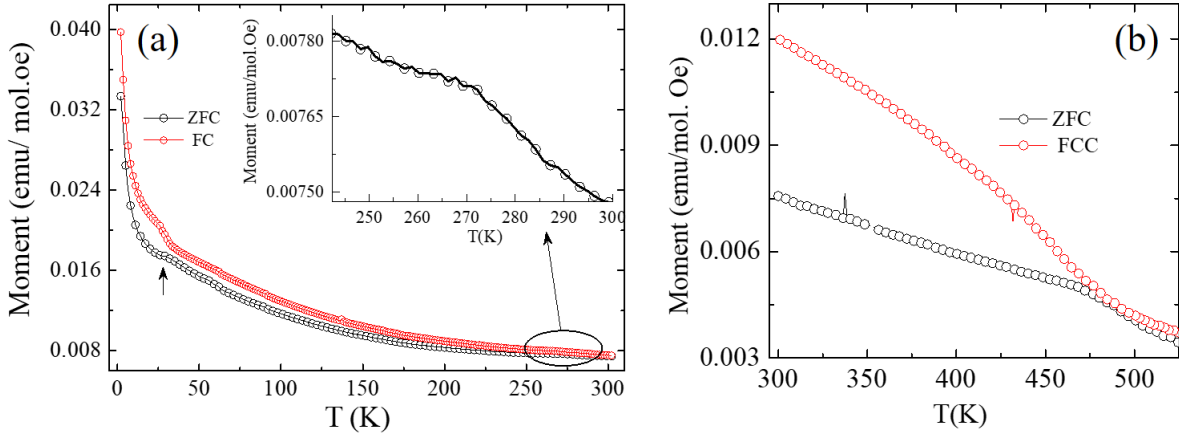


Figure 3.14: ZFC-FC magnetic measurement performed in the powder $\text{SrBaCo}_4\text{O}_7$ specimen. The inset shows a magnified view of the high temperature anomaly in ZFC measurement. (b) High temperature magnetic measurement in MPMS with oven attachment on the polycrystalline $\text{SrBaCo}_4\text{O}_7$ pellet

in Fig.3.14(a). Interestingly, the magnetization measured in ZFC-FC protocols do not merge together even at room temperature. High temperature magnetic measurement performed in ZFC-FCC protocol shows another magnetic transition at 475K, as shown in Fig.3.14(b). Prior investigations of Swedenborgite members have revealed that the high temperature transition is associated with a structural transition and a long range magnetic ordering sets in at the low temperature transition [122]. Temperature dependent X-ray diffraction measurement across the observed transition could reveal the occurrence of structural transition on $\text{SrBaCo}_4\text{O}_7$.

3.5.4 Specific heat measurements

The specific heat measurement exhibits a discernible anomaly at the low temperature magnetic transition, as depicted in Fig.3.15. However, there is no significant change in the specific heat across the high temperature transition, implying the change in entropy across this transition might be smaller.

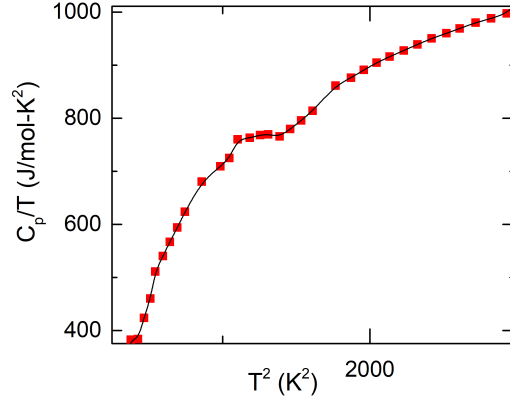


Figure 3.15: Specific heat measurement performed on the polycrystalline $\text{SrBaCo}_4\text{O}_7$.

3.6 Conclusions

The $\text{DyBaCo}_4\text{O}_7$ system crystallizes in the trigonal $P31c$ phase. Substitution of Ca^{2+} on Dy^{3+} sites in the $\text{Dy}_{1-x}\text{Ca}_x\text{BaCo}_4\text{O}_7$ series ($x=0$ to 1) results in a structural transition from the high symmetry Trigonal to $P31c \rightarrow$ low symmetry $Pbn2_1$ phase at doping concentration $x = 0.4$. All the orthorhombic members of this series undergo a transition to the high symmetry $P31c$ phase at elevated temperatures. The temperatures at which this transition occurs is seen to scale linearly with the average ionic radii of the R site ion. The orthorhombically distorted $\text{CaBaCo}_4\text{O}_7$, which comprises an equal number of Co^{3+} and Co^{2+} ions clearly violates this rule, indicating that the charge ordering scenario also possibly plays a role in stabilizing the structural distortion in this compound. The large paramagnetic background of Dy^{3+} masks the magnetic transitions occurring within the Co sublattice, and we demonstrate the utility of temperature dependent thermo-remanent magnetization (TRM) measurements in identifying the phase transition temperatures in such systems.

$\text{SrBaCo}_4\text{O}_7$, a new member of the Swedenborgite family was synthesized successfully. The profile matching of the diffraction profile indicates that unlike $\text{CaBaCo}_4\text{O}_7$, it crystallizes in the space group $Pnma$. The magnetic and specific heat measurement reveals multiple phase transitions in this specimen.

Chapter 4

A near room temperature magneto-dielectric Fe_2WO_6

4.1 Summary

We report on the synthesis and characterization of the $\gamma\text{-Fe}_2\text{WO}_6$ system. Crystallizing in the non-polar $Pbcn$ space group, this system exhibits a number of magnetic transitions as a function of decreasing temperatures, with long range antiferromagnetic order setting at temperatures as high as 280K. From the Curie-Weiss fit of the high temperature paramagnetic susceptibility, we infer that our specimen possibly comprises of Fe^{3+} and Fe^{2+} which is in agreement with earlier reports. This system also exhibits the appearance of a weak ferromagnetic component within the anti-ferromagnetic order which sets in at 280K. Dielectric measurements performed under magnetic field reveals that these transitions, especially the high temperature ones, are also associated with a finite magneto-dielectric effect. Absence of a noticeable change in the DC resistivity measurement performed under zero field and applied magnetic field rules out a possible magneto-resistance contribution and implies that the observed magneto-dielectricity is intrinsic to the system. From aging and magnetic viscosity measurements, we reckon that the low temperature state is associated with a magnetic glass-like state, apparently arising as a consequence of the freezing of magnetic clusters, the existence of which is also suggested by the frequency dependent peak in the imaginary part of the measured dielectric susceptibility.

4.2 Introduction

The specimen Fe_2WO_6 is a prototype belonging to the structural type $\text{tri-}\alpha\text{PbO}_2$. This may be considered as variants of Columbite and the super lattice variants of the $\alpha\text{-PbO}_2$ structure. The 2:1 cation ordering in a Columbite structure results in a tripling of the b parameter of the unit cell. The chemical phase diagram of the Fe-W-O system is characterized by the presence of a number of polymorphic modifications, which makes the selective synthesis of Fe_2WO_6 non-trivial [123]. Depending on the synthesis conditions, Fe_2WO_6 can exist in three distinct structures labeled as α , β and γ - Fe_2WO_6 [124, 125, 126]. These polymorphs are typically stabilized as a function of increasing reaction temperatures, with ill-defined phase boundaries. A detailed investigation of the synthesis condition and the stabilization of the different polymorphs of Fe_2WO_6 is illustrated in Fig.4.1 [124]. For instance, $\alpha\text{-Fe}_2\text{WO}_6$ crystallizing in the orthorhombic

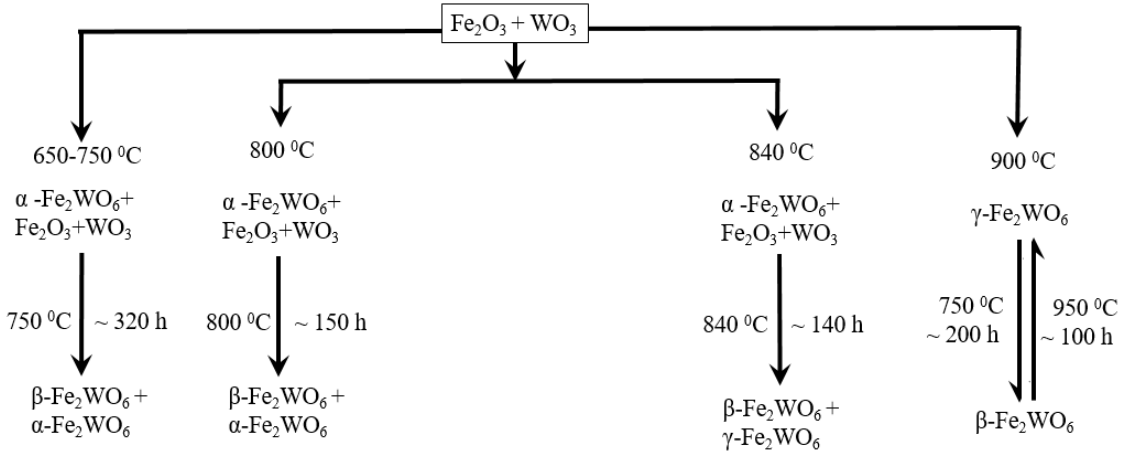


Figure 4.1: The stabilization of different phases of Fe_2WO_6 depending upon the temperature range of the synthesis condition [124].

columbite ($Pbcn$) symmetry, is stabilized at reaction temperatures lower than 800°C. At reaction temperatures between 750-900°C, the monoclinically distorted $\beta\text{-Fe}_2\text{WO}_6$ is favored, whereas at reaction temperatures in excess of 900°C, the γ phase is reported to be stabilized. This high temperature γ phase is known to crystallize in the tri- $\alpha\text{-PbO}_2$ structure, where the orthorhombic $Pbcn$ symmetry of the $\alpha\text{-Fe}_2\text{WO}_6$ phase is preserved, but with a tripling of the unit cell along one of the crystallographic directions ($a' = a, b' = 3b, c' = c$).

The member Cr_2WO_6 stabilizing in the inverse tri-rutile structure and space group $P4_2/mmm$, has been reported to exhibit a large magnetodielectric effect along with a magnetic field induced polarization at $\approx 45\text{K}$ [127]. This is in sharp contrast with the

observed structure and crystal chemistry of the Fe_2WO_6 . Also the systems of the form $R\text{FeWO}_6$ have recently been found to be multiferroic [128], crystallizing in the polar $Pna2_1$ structure. The system exhibits low temperature multiferroic transitions between 15-18K, which involve a complex interplay between the Fe and the magnetic R ions. However, the properties of Fe_2WO_6 is remain unexplored.

4.3 Results & Discussions

4.3.1 Synthesis of $\gamma\text{-Fe}_2\text{WO}_6$

Polycrystalline specimens of $\gamma\text{-Fe}_2\text{WO}_6$ were synthesized using the standard solid state ceramic method. A stoichiometric mixture of previously preheated Fe_2O_3 (Sigma Aldrich, $\geq 99\%$) and WO_3 (Alfa Aesar, $\geq 99.8\%$) precursors were thoroughly ground for several hours using a dry ball mill. The fine and homogenous mixture was pressed into pellets and loaded into a preheated alumina boat. The mixture was slowly heated to 800°C , kept there for 24 hours and then gradually cooled down to room temperature. These pellets were repeatedly reground, palletized and sintered for several times at 950°C in air. After about 100 hours at this temperature we obtained a well crystallized single phase of $\gamma\text{-Fe}_2\text{WO}_6$. However, we found that the $\gamma\text{-Fe}_2\text{WO}_6$ specimens were slightly degraded with time, though no appreciable changes were observed in their XRD patterns taken after a few months.

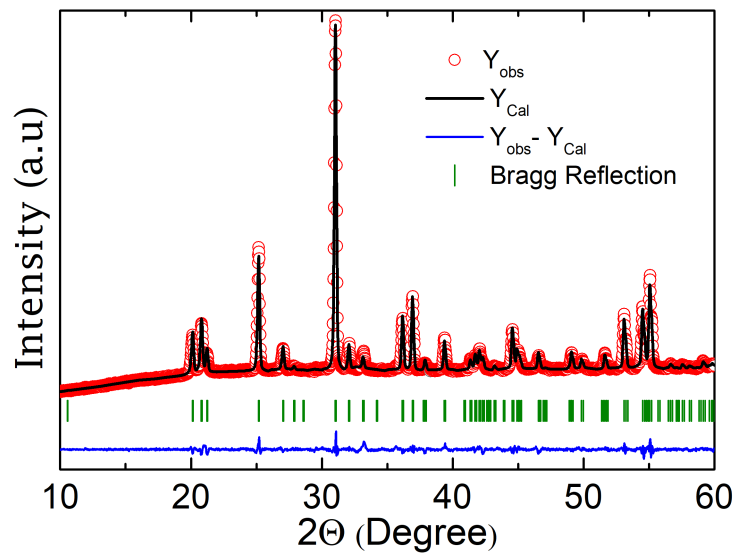


Figure 4.2: A Rietveld fit to the room temperature x-ray diffraction data of $\gamma\text{-Fe}_2\text{WO}_6$. This corresponds to a fit with R parameters of $R_{wp} = 11.3$, $R_e = 6.10$.

4.3.2 Structural Characterization

The Rietveld refinement of room temperature X-ray diffraction pattern of our polycrystalline specimen is as shown in Fig.4.2. Successful refinement with goodness of fit (GOF) value (R_{wp}/R_e) of 1.85 could be obtained, confirming a single phase $\gamma\text{-Fe}_2\text{WO}_6$.

4.3.2.1 Crystal structure

The unit cell of $\gamma\text{-Fe}_2\text{WO}_6$ contains four formula units crystallizing in the $Pbcn$ space group, with lattice parameters $a = 4.575(1)$, $b = 16.747(4)$, $c = 4.965(1)$, and $\alpha = \beta = \gamma = 90^\circ$. A schematic of this tri- $\alpha\text{-PbO}_2$ structure along the **a**, **b** and **c** axis is depicted

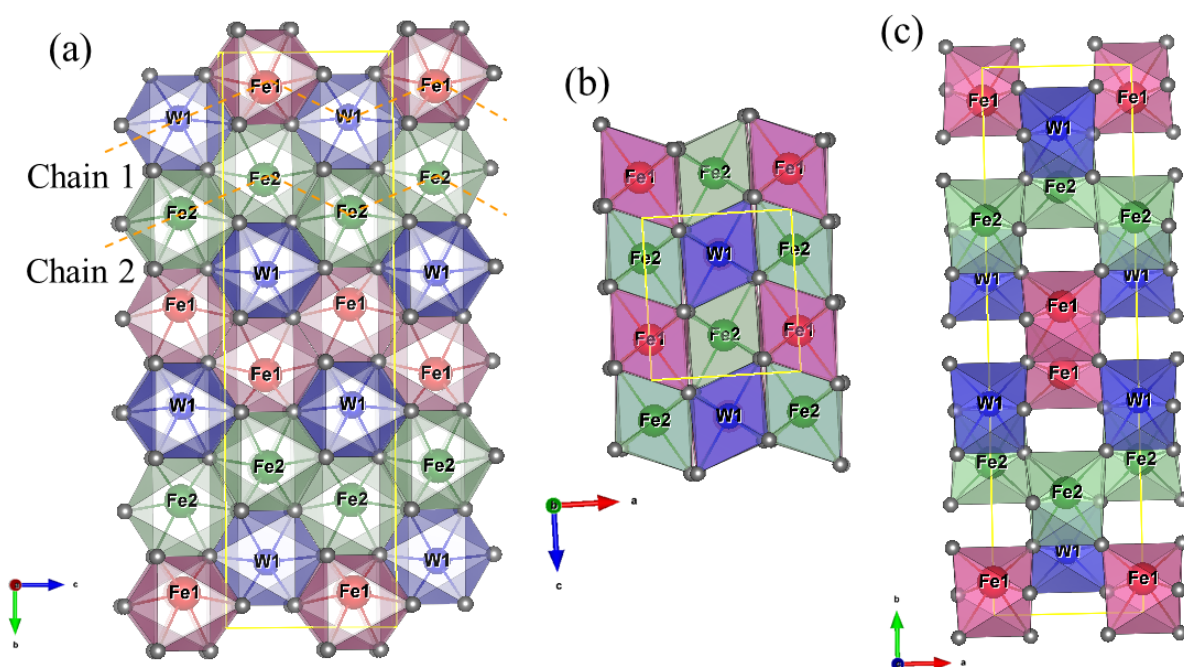
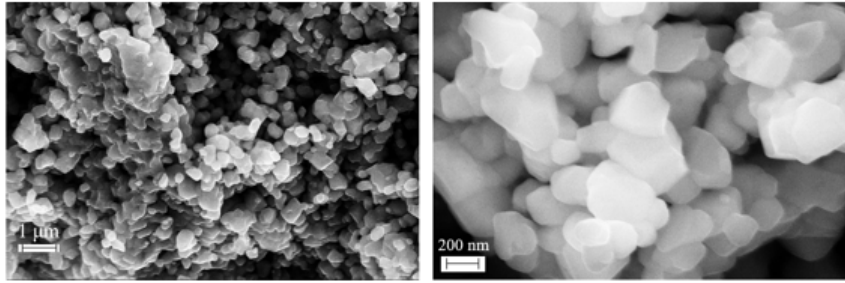


Figure 4.3: Crystal structure of Fe_2WO_6 comprises FeO_6 and WO_6 octahedra. The crystal structure viewed along (a) 100 (b) 010 and (c) 001 direction.

in Fig.4.3, and comprises of layered corner-shared FeO_6 octahedra, with Fe occupying two distinct crystallographic sites. The scanning electron micrograph images exhibit distinguishable homogeneous particles in our specimen further reconfirming the absence of secondary/amorphous phases, as depicted in Fig.4.4. The obtained stoichiometry from the EDAX analysis for cation is $\text{Fe}_{1.98 \pm 0.06} \text{W}_{1.02 \pm 0.06}$. The atomic position of the several atoms within the unit cell is tabulated in Table.4.1. The structure consists of two zig-zag chains, where one of the chain (chain 1) is purely occupied by octahedra of iron and another chain (chain 2) comprises of alternate iron and tungsten octahedra.

Table 4.1: Structural parameters of γ - Fe_2WO_6 as obtained from Rietveld refinement of room temperature X-Ray diffraction data

Atom	Wyckoff	x/a	y/b	z/c
Fe1	4c	0.0000	0.0594	0.2500
Fe2	4c	0.0000	-0.2763	0.2500
W	4c	0.0000	0.3868	0.2500
O1	8d	0.2365	0.0412	0.5713
O2	8d	0.2700	0.1250	0.0900
O3	8d	0.2901	0.2043	0.5822

Figure 4.4: SEM image of a polished γ - Fe_2WO_6 pellet

4.3.3 DC magnetic measurements

The magnetic properties of several Fe_2WO_6 polymorphs appearing to depend solely on the synthesis conditions [129, 130]. For instance, both the α and γ - modifications of Fe_2WO_6 are reported to exhibit two magnetic transitions, with a high temperature transition at $T_1 \approx 240$ -260K, and a lower temperature transition $T_2 \approx 200$ -220K, as tabulated in Table.4.2. In addition, the presence of an additional low temperature feature at ≈ 20 K

Table 4.2: Magnetic transition as observed in several phases of Fe_2WO_6 from ZFC magnetic measurements.

Phase	T_1 (K)	T_2 (K)	T_3 (K)	Reference
α	260	≈ 200	≈ 15 K	[129]
β	260	-	-	[129]
γ	240	≈ 220	-	[130]
	260	≈ 200	≈ 15	[129]
	282	≈ 228	≈ 20	This work

has also been reported in both these polymorphs. However, the $\beta\text{-Fe}_2\text{WO}_6$ is reported to exhibit a solitary magnetic transition at 260K.

The DC magnetic susceptibility measured in the Zero Field Cooled (ZFC) and Field Cooled (FC) protocols at 10 Oe magnetic field on our $\gamma\text{-Fe}_2\text{WO}_6$ specimen is shown in Fig.4.5(a). Two distinct anomalies observed at $T_1=282\text{K}$, and $T_2=228\text{K}$ can be discerned

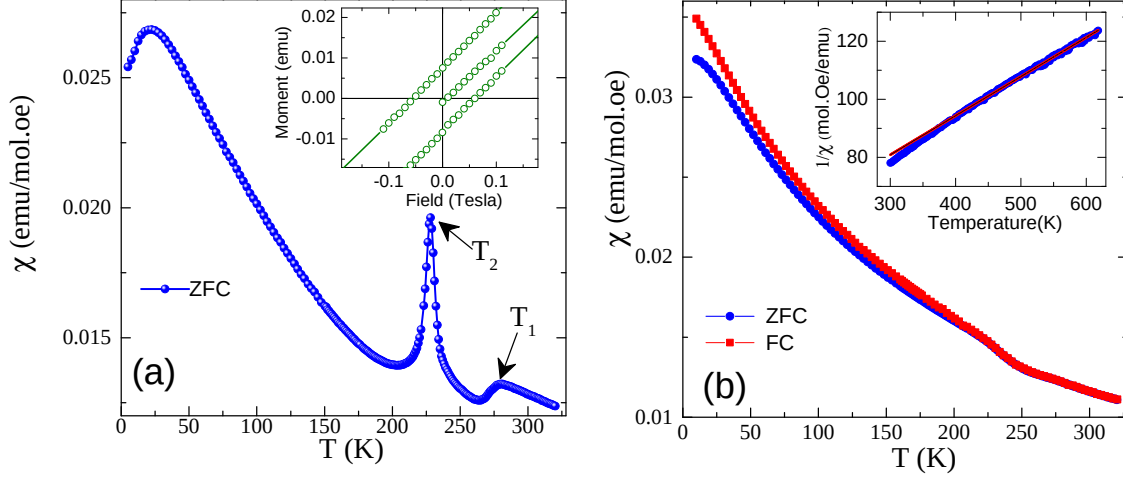


Figure 4.5: (a) depicts the temperature dependence of dc magnetization as measured in $\gamma\text{-Fe}_2\text{WO}_6$ in the Zero Field Cooled (ZFC) protocol at an applied field of 10 Oe. The inset depicts M-H isotherm measured at 2K. (b) depicts the ZFC and FC measured at an applied field of 1 Tesla. The inset shows the Curie-Weiss fit to the high temperature magnetization data

from the magnetization measurement, with a down turn in magnetization at T_1 and a broad peak at T_2 . An increase in the applied magnetic fields results in broadening the high temperature transitions Fig.4.5(b), without a pronounced change in the transition temperatures. Prior neutron diffraction investigations on $\gamma\text{-Fe}_2\text{WO}_6$ has revealed that the magnetic structure comprises of ferromagnetic (100) planes coupled antiferromagnetically, with the spins lying along the (001) direction [130]. It was also suggested that a finite ferromagnetic component may appear along one of the crystallographic axes with the magnetic space group ($Pbc'n'$). The transition T_2 has been associated with shift in ionic positions [130]. M - H isotherm measured at different temperatures indicate that the magnetization does not saturate up to the highest measured field of 7 Tesla. However, a finite opening of the hysteresis loop exists down to the lowest measured temperatures of 2K. This implies that a weak ferromagnetic component coexists along with the antiferromagnetic order which appears to set in at 280K. On further reducing the temperature, the magnetization increases monotonically, and exhibits a cusp like feature at $\approx 22\text{K}$, which possibly corresponds to the low temperature transition as specified in earlier re-

ports. The DC magnetic measurement performed at high magnetic field up to 1 Tesla exhibits a bifurcation in the FC and ZFC magnetization at very low temperatures, as is evident from Fig.4.5(b). Presence of such bifurcation even at high magnetic field indicates possible existence of magnetic glass like state at the transition $T_3 \approx 20\text{K}$.

A Curie Weiss fit to the high temperature DC magnetization data (inset of 4.5(b)) at temperatures in excess of 450 K, giving Curie temperature $\Theta_C = -299.7\text{K}$. The effective magnetic moment per Fe ion is $1.22\mu_B$. The calculated spin only moment of Fe³⁺, as-

Table 4.3: Spin only moment of Fe³⁺ (3d⁵) in high and low spin states under an octahedral crystal field.

	Spin state	Electronic configuration	Calculated Spin only moment (S_μ / Fe^{2+})
Fe ³⁺ (3d ⁵)	Low Spin	↑↓ ↑↓ ↑ t_{2g} ↑ ↑ e_g	1.73
	High Spin	↑ ↑ ↑ t_{2g} ↑ ↑ e_g	5.91

suming the orbital moment fully quenched, both in high spin and low spin states are tabulated in Table. 4.3. Thus a finite fraction of the Fe ions are in the low spin ($S = 0$) Fe²⁺ state. Prior report of Electron Paramagnetic Resonance (EPR) measurement has also speculated on the possibility of the existence of Fe²⁺ ions in the Fe₂WO₆ system [129], indicating that oxygen non-stoichiometry could be endemic to this class of materials.

4.3.4 Aging effect

One of the remarkable aspects of any magnetic glassy system is the presence of an aging effect in time dependent ZFC magnetization. These measurements were performed by cooling the system in zero magnetic field from room temperatures down to the lowest temperature of 2 K across the magnetic transition (T_3). Maintaining the zero field at the lowest temperature, the system was left for different waiting times (t_w) (called *aging*). The evolution of the DC magnetization as a function of time was then measured in the presence of a magnetic field of $H=100$ Oe. The measurement was performed for three different values of t_w , namely 100, 1000 and 5000 seconds. Fig.4.6(a) shows the evolution of magnetization as a function of time in γ - Fe₂WO₆. The time slow evolution dynamics

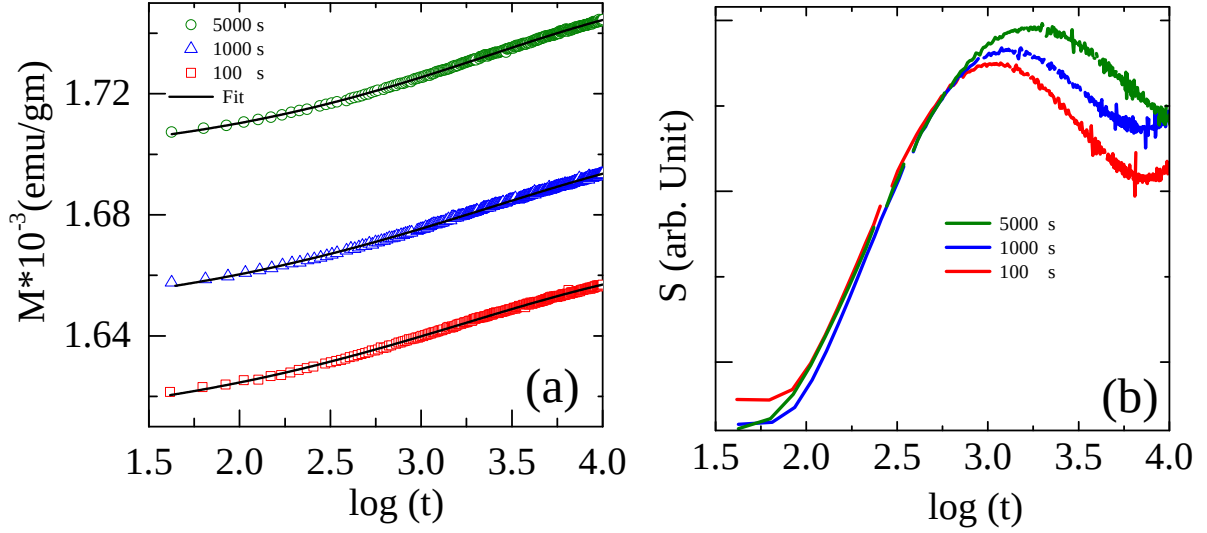


Figure 4.6: (a) shows the evolution of the dc magnetization at an applied field of 100 Oe, after soaking the system for different waiting times. The solid lines are fits to a stretched exponential function. (b) depicts the shift of the magnetic viscosity $S(t)$ as a function of the waiting time.

of M has been modeled to show a power law ($t^{\pm\alpha}$) [131] or a Kohlrausch-Williams-Watt (KWW) stretched exponential behaviour ($\approx \exp[-(t/\tau)^\beta]$) [132]. We observe that the data fits well to a modified *stretched* exponential of the form:

$$M(t) = M_0 - M_g \exp\left(\frac{-t}{\tau}\right)^\beta \quad (4.1)$$

Equation 4.1 has been used earlier in fitting the magnetic relaxation in a number of spin/cluster glasses [133, 134, 135, 136, 137]. Here, β is a temperature dependent exponent, τ is the time constant, and M_0 and M_g refer to the contributions from the long range ordered and glassy components of the system respectively. In this model, the exponent β has a value in between 0 and 1 depending upon the class of magnetically inhomogeneity. These fits are depicted as solid lines in Fig. 4.6(a). The values of M_0 , β and τ deduced from our fit range from 0.00167 to 0.00175 emu/gm, 0.35 to 0.41 and 1771 s to 2402 s respectively for different waiting times. The small value of M_0 in our case could be a consequence of the fact that the long range ordered component in our case is antiferromagnetic [134].

The relaxation rate of magnetization, called magnetic viscosity is expressed as [135, 136, 137]

$$S(t) = \frac{1}{H} \left[\frac{\partial M}{\partial (\ln t)} \right] \quad (4.2)$$

Magnetic viscosity as deduced for our measurements with different waiting times (t_w) is depicted in Fig.4.6(b). The $S(t)$ curves reaches a maximum and shifts towards longer observation time for longer aging time t_w . Such observations are in agreement with that observed for glassy systems and reinforcing the glass like nature of this low temperature state T_3 . As mentioned earlier, the γ - Fe_2WO_6 specimens appear to slightly change with time. Our measurements indicate that even after a few months after synthesis, the temperatures of the high temperature magnetic transitions remain relatively invariant. However, the temperature of the low temperature glass like transition appears to shift to lower temperatures as a function of the elapsed time.

4.3.5 Specific heat measurements

Specific heat measurements on γ - Fe_2WO_6 reveals a solitary feature in the vicinity of the

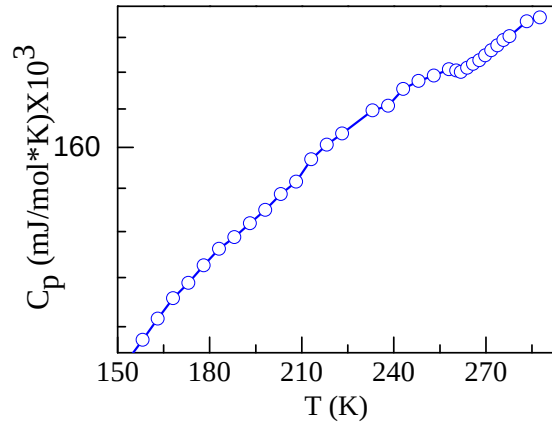


Figure 4.7: Specific heat measurement performed on γ - Fe_2WO_6 .

high temperature transition, as is shown in the main panel of Fig.4.7. The fact that the other two transitions are not picked up in the heat capacity measurements indicate that the change in entropy associated with these transitions is quite small.

4.3.6 Magneto-dielectric measurements

Dielectric measurements were performed under zero magnetic field at frequencies varying from 0.1 to 100 kHz. Fig.4.8 depicts the real part of the dielectric constant (ϵ') as a function of temperature. A pronounced dielectric anomaly is observed in the vicinity of the high temperature magnetic transition at 282K, indicating a substantial coupling between the spin and electronic degrees of freedom in this system.

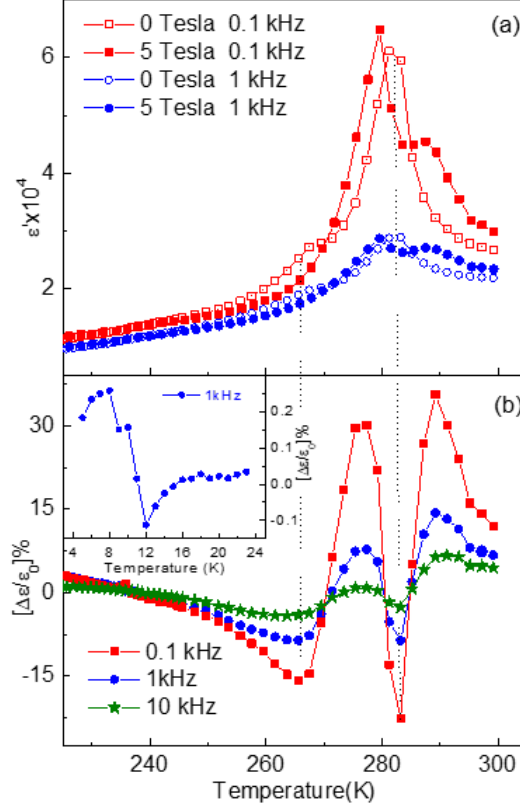


Figure 4.8: (a) The magnetic field dependence of the real part of the dielectric susceptibility $\epsilon'(T)$ as measured at 0 and 5 Tesla magnetic field. (b) Percentage change of magneto-dielectricity ($|\Delta\epsilon/\epsilon_0|\%$) in presence of magnetic field. The upper inset depicts $|\Delta\epsilon/\epsilon_0|\%$ as measured at 1 kHz.

The dielectric measurements performed in the presence of a magnetic field shows a suppression of $\epsilon'(T)$. The temperature dependence of the real part of the dielectric susceptibility $\epsilon'(T)$ as measured in $\gamma\text{-Fe}_2\text{WO}_6$ at 5 Tesla magnetic field is depicted in Fig. 4.8(a). The percentage of the change of magneto-dielectric effect ($|\Delta\epsilon/\epsilon_0|\%$) across these transitions are depicted in 4.8(b). A finite magneto-dielectric effect is clearly seen till room temperature. Two negative cusps in the magneto-dielectric effect are observed at 282 K and at 265 K, which corresponds to the peak temperature of one magnetic transition, and the onset temperature of the other one respectively. The $|\Delta\epsilon/\epsilon_0|$ decreases sharply with the probing frequency, and varies from $\approx 10\%$ at 1 kHz to $\approx 0.75\%$ at 0.1 MHz. Such a pronounced frequency dependence of the dielectric permittivity as a function of the measurement frequency has been earlier reported in polar dielectrics [138, 139]. However, our observation of a noticeable alteration of the dielectric permittivity in the presence of magnetic field in the vicinity of the magnetic transition implies a significant contribution of magneto-dielectric coupling in this system. In addition, we also observe an anomaly in the measured magneto-dielectricity in the vicinity of the low temperature (glass like)

magnetic transition, as is depicted in the lower inset of Fig.4.8(b). This reinforces the presence of finite magnetodielectric coupling and the magnetic ground state appears to tune the dielectric properties in the $\gamma\text{-Fe}_2\text{WO}_6$ system.

The temperature dependence of the imaginary part of the dielectric permittivity (ϵ'') exhibits a pronounced frequency dependent peak as shown in Fig.4.9. The observed peak position shifts to higher temperatures with increase in the probing frequencies. However,

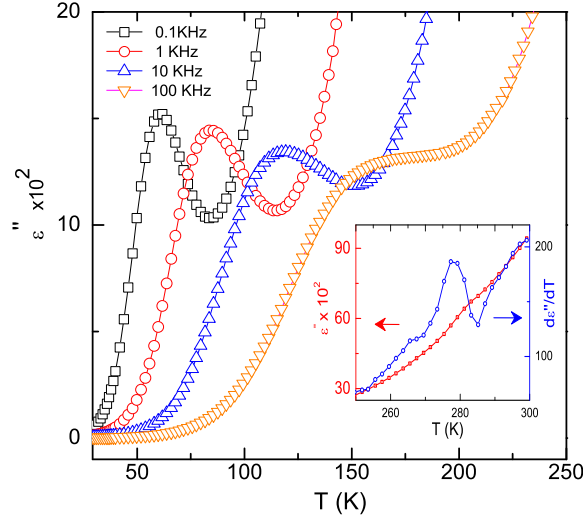


Figure 4.9: Temperature dependence of the dielectric loss $\epsilon''(T)$ at different probing frequencies as measured in $\gamma\text{-Fe}_2\text{WO}_6$. A frequency dependent peak, typical of charge relaxation processes is observed. The inset depicts $\epsilon''(T)$ and its temperature derivative in the vicinity of the high temperature magnetic transitions.

these features are not associated with the magnetic ordering (signatures corresponding to which are depicted in the inset of Fig.4.9) and is representative of a charge relaxation process. Similar features have been observed in a number of other strongly correlated oxides, especially within the magnetic state of the phase separated manganites [140, 141, 142]. In the mixed valent manganites, electronic phase separation typically gives rise to regions with ferromagnetic and antiferromagnetic correlations, the competition between which is known to result in glassiness in both the magnetic and electronic sectors [143]. This electronic phase separation which results in phase co-existence over a wide range of length scales then manifests itself in the form of frequency dependent dielectric properties. In the case of the $\gamma\text{-Fe}_2\text{WO}_6$ system investigated here, this dispersion observed in the dielectric susceptibility could arise as a consequence of the oxygen non-stoichiometry. This could also be intimately tied with the low temperature magnetic glass state which sets in at lower temperatures. For instance, early Electron Paramagnetic Resonance (EPR) measurements have speculated on the possibility of magnetic clusters (presumably arising

ing from anti-site disorder) in the Fe_2WO_6 polymorphs [129]. More recent measurements [144] have also indicated the presence of short range correlations extending well above the magnetic ordering temperatures in the $\beta\text{-Fe}_2\text{WO}_6$ polymorph, indicating that this cluster formation could be generic to the Fe-W-O systems.

4.3.7 Resistivity measurements

Though the observed dielectric anomaly is reminiscent of that seen in many multiferroic systems, the overall resistivity values are quite low, especially in the high temperature regime, where these features are observed. Thus, the possibility of a magnetically induced robust ferroelectric state can be ruled out. It is known that strong magneto-dielectric effects could arise through a combination of the magneto-resistance and the Maxwell-Wagner effect [145].

The resistivity measurement was performed in that standard 4-probe method on a bar shaped pellet under zero magnetic field and 5 Tesla down to 200K. We have not observed any contribution of magneto resistance across the magnetic anomalies (T_1 and T_2), as is shown in Fig.4.10. The fact that there is no noticeable change in the electronic con-

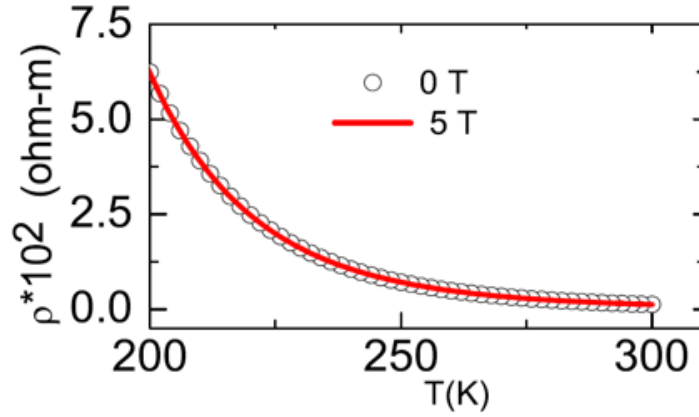


Figure 4.10: Resistivity measurement performed at 0 Tesla and 5 Tesla magnetic field in 4-contacts mode across the high temperature transitions. Absence of any noticeable change in the measurement rules out the possible contribution of magneto-resistance to the observed magneto-dielectric effect.

ductivity, and the absence of a magnetoresistive component suggests that the observed magneto-dielectricity appears to be intrinsic to the system.

4.4 Conclusions

We have synthesized the relatively unexplored Iron-Tungsten-Oxygen system (γ Fe_2WO_6) and investigated it using magnetic, thermodynamic and dielectric measurements. Crystallizing in the non-polar $Pbcn$ space group, this system exhibits a number of magnetic transitions as a function of decreasing temperatures, with long range antiferromagnetic order setting in at temperatures as high as 280K. From the Curie-Weiss fit of the high temperature paramagnetic susceptibility, we infer that our specimen has the possible coexistence of Fe^{3+} and Fe^{2+} . This system also exhibits appearance of a weak ferromagnetic component along with the anti-ferromagnetic order which sets in at 280K. Dielectric measurement performed under magnetic field reveals the presence of a finite magneto-dielectric effect till room temperature. DC resistivity measurement performed across the observed transitions under zero field and applied magnetic field rules out possible magneto-resistance contribution and implies that the observed magneto-dielectricity is intrinsic to the system. The presence of a low temperature magnetic glass like state is also inferred from aging and magnetic viscosity measurements. These presumably arise as a consequence of the freezing of magnetic clusters, the existence of which is also suggested by a frequency dependent peak in the imaginary part of the measured dielectric susceptibility.

Chapter 5

Coupled magnetic and ferroelectric states in distorted honeycomb

$\text{Fe}_4\text{Ta}_2\text{O}_9$

5.1 Summary

We have studied the corundum related member $\text{Fe}_4\text{Ta}_2\text{O}_9$ through magnetic, thermodynamic, dielectric, and pyroelectric measurements. This system crystallized in the Trigonal $P-3c1$ symmetry and was seen to exhibit a series of magnetic transitions, many of which are associated with the emergence of ferroelectric order. Our study unveils $\text{Fe}_4\text{Ta}_2\text{O}_9$ as the only genuine multiferroic in its material class. Pyroelectric measurement performed under zero magnetic field exhibits the appearance of spontaneous polarization at $T_1=80\text{K}$ (AFM1 FE1) and $T_2=60\text{K}$ (AFM2 FE2) concomitant with the observed magnetic transitions. On cooling further, a field induced multiferroic state is observed (AFM3 FE3) and within this state, a metamagnetic (spin-flop) transition appears with no discernible influence on this polar state (SF- AFM3 FE3). The dielectric and magnetic measurement further evidenced a transition $\approx 5\text{K}$, which remains robust under an applied magnetic field. We suggest that the observed properties arise due to an effective reduction in the dimensionality of the magnetic lattice, with the magnetically active Fe^{2+} ions preferentially occupying a quasi 2D buckled honeycomb structure. The low temperature H - T phase diagram of $\text{Fe}_4\text{Ta}_2\text{O}_9$ reveals a rich variety of coupled magnetic and ferroelectric phases, in similarity with that observed in the distorted Kagome systems.

5.2 Introduction

$\text{Fe}_4\text{Ta}_2\text{O}_9$ belongs to the compound type $\text{A}_4\text{X}_2\text{O}_9$ ($\text{A}=\text{Mn, Fe, Co, Ni, Cu, Mg, Zn}$; $\text{X}=\text{Ta, Nb}$) closely related to the corundum structure ($\alpha\text{-Al}_2\text{O}_3$). First synthesized by Bertaut *et. al* [146], this family of compounds crystallizes in the Trigonal $P\text{-}\bar{3}c1$ space group.

Possible variation of corundum structures and $\text{Fe}_4\text{Ta}_2\text{O}_9$:

In $\alpha\text{-Al}_2\text{O}_3$ the pair of face sharing AlO_6 octahedra alternate along with the empty octahedra forming a $-(\text{AA})\text{-(AA)}-$ chain along the c axis (Fig.5.1(a)). If we consider a system with general formula ABO_3 , where both the A and B cations occupy the Al sites in $\alpha\text{-Al}_2\text{O}_3$ type corundum structure, then two possible packing sequence of face sharing AO_6 and BO_6 octahedra along the c axis is possible [147], namely

Type (I) $-(\text{AB})\text{-(AB)}-$

Type (II) $-(\text{AB})\text{-(BA)}-$

The Type-I is described by rhombohedra LiNbO_3 type corundum structure where each layer contains octahedra of both Li and Nb cation, as depicted in Fig.5.1(b). On the other hand, the Trigonal FeTiO_3 describes the Type-II corundum structure, where the Fe and Nb octahedra are distributed in alternate layers (Fig.5.1(c)). However, a change

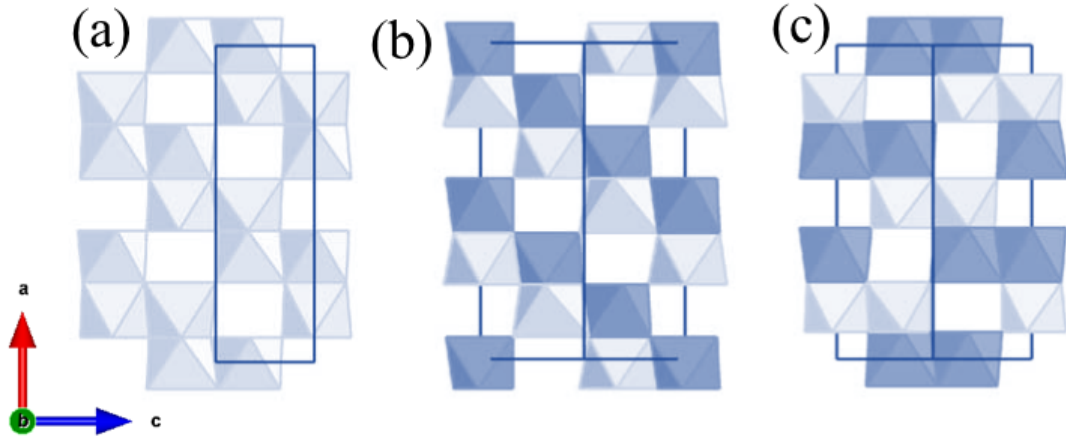


Figure 5.1: Crystal structures of different corundum related members. Dark and light color represents two different types (A and B) of octahedra. (a) Face sharing AlO_6 octahedral network of $\alpha\text{-Al}_2\text{O}_3$ (b) Coexistence of both Li and Nb octahedra in each layer of LiNbO_3 type corundum structure (c) Preferential occupation of Fe and Ti octahedra in distinct layers of FeTiO_3 type corundum structure

in the ratio of A and B site could give rises to change in the distribution of octahedra. For $\text{Fe}_4\text{Ta}_2\text{O}_9$ the ratio is $\text{A:B (Ta:Fe)} = 1:2$ and this results in two different chains of octahedra within the corundum structure namely, one $-(\text{AA})\text{-(AA)}-$ and two $-(\text{BB})\text{-(BB)}-$

layers along the c axis.

S.C. Abraham based on purely structural origin proposed that the member $\text{Mn}_4\text{Ta}_2\text{O}_9$ crystallizing in the space group $R\bar{3}c$ could possess a potential ferroelectric state [148]. However, the $\text{A}_4\text{X}_2\text{O}_9$ stabilizing in the trigonal $P\bar{3}c1$ symmetry has been popular recently due to their potential magneto-electric (ME) properties [149]. For instance, both the compounds $\text{Co}_4\text{Ta}_2\text{O}_9$ [150] and $\text{Co}_4\text{Nb}_2\text{O}_9$ [151, 152, 153] exhibits a magnetic field induced polarization at $T_N = 20.5\text{K}$ and 27.5K respectively. Whereas, $\text{Mn}_4\text{Ta}_2\text{O}_9$ [154] and $\text{Mn}_4\text{Nb}_2\text{O}_9$ [155] shows magnetoelectric coupling at $T_N = 103\text{K}$ and 109K respectively. One of the remarkable aspects of this compound is that it comprises of two magnetic sublattices which contribute independently to the ME effect. An opposite sign of ME effect of the individual magnetic sublattice has been suggested to give rise a lesser value of the resultant ME effect [156]. At zero magnetic field, the opposite magnetoelectric effect of the two sublattices balance each other and the magnetoelectric effect vanishes.

The iron member of the family $\text{A}_4\text{X}_2\text{O}_9$ remains unexplored due to the unavailability

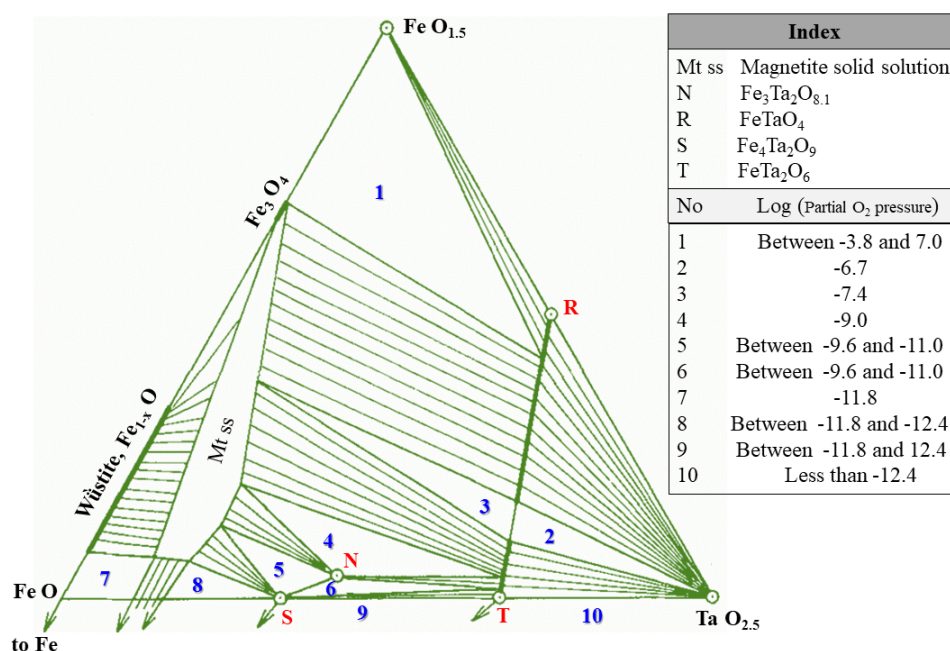


Figure 5.2: Isothermal projection in the three solid phase triangles of the Fe-Ta-O system. The tie lines with different compositional ranges corresponds to various phases formed during solid state synthesis under oxygen pressure [157]. Figure adapted with permission from Ref. [157], copyright (2006) John Wiley and Sons

of phase pure specimen. An isothermal projection of the FeO - $\text{FeO}_{1.5}$ - $\text{TaO}_{2.5}$ with tie lines shows the complexity of phase stability depending upon the partial oxygen pressure during a solid state reaction [157]. However, in this study, the synthesis of $\text{Fe}_4\text{Ta}_2\text{O}_9$ at 1200°C in the range of oxygen partial pressure of 2.6×10^{-11} to $2.7 \times 10^{-13} \pm 2.6 \times 10^{-1}$

atm was reported along with parasitic phases (S in Fig. 5.2). These partial pressure values were obtained using various mixtures of CO_2 and CO . Here, we present a novel synthesis protocol which is safer and easier as compared to dynamic reactions under reducing gas atmosphere.

5.3 Results and Discussions

5.3.1 Synthesis of single phase polycrystalline $\text{Fe}_4\text{Ta}_2\text{O}_9$

Polycrystalline samples of $\text{Fe}_4\text{Ta}_2\text{O}_9$ were prepared using encapsulation synthesis technique, employing a sealed quartz ampoule which contained the homogeneous mixture of precursors and Fe granules as an oxygen getter. Such configuration facilitates in-situ control of the partial oxygen pressure, as schematically shown in Fig.5.3. A stoichiometric ratio of previously preheated Fe_2O_3 (Sigma Aldrich, $\geq 99\%$) and Ta_2O_5 (99.993%, Alfa Aesar) was manually ground for few hours in a glove box filled with argon (moisture content is 0.1 ppm). Next, the mixture was ground using a ball mill and further mechanically

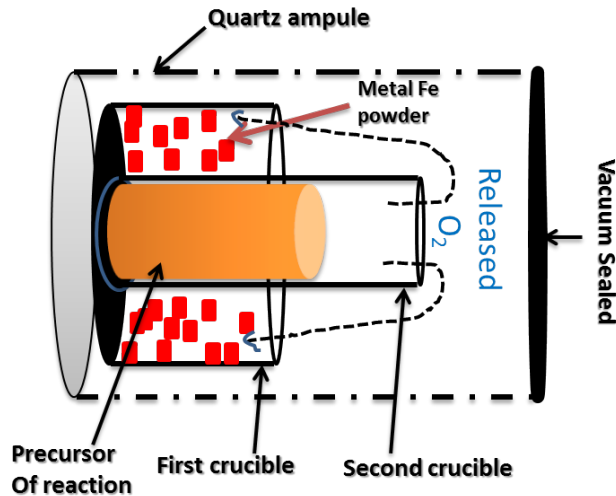


Figure 5.3: Schematic diagram of encapsulation synthesis assembly used for the synthesis of polycrystalline $\text{Fe}_4\text{Ta}_2\text{O}_9$. The precursors filled in a crucible were placed in a larger crucible containing the oxygen getter (Fe grains). Both of these crucibles were vacuum sealed inside a quartz ampoule. The extra oxygen released during the reaction is absorbed by the getter.

ground under a static argon atmosphere. A preheated quartz ampoule (approximately 25 cm^3) with two alumina crucibles was used for the sintering treatment. One alumina crucible was larger in diameter and can accommodate the oxygen getter (Fe grains (Alfa

Aesar, (99.998%, 1-2mm)) along with the other alumina crucible which was filled with mechanically homogenized mixture of precursors. The ampoule charged in this fashion was evacuated and then sealed under vacuum. The ampoule with reaction mixture and getter was slowly heated to 1100°C and kept there for 48h, and thereafter slowly cooled down to room temperature. The exact partial oxygen pressure inside of the ampoule depends on the redox couple used and on the temperature profile. In our case, using Fe/FeO as a redox couple and under these temperature conditions, the oxygen partial pressure is expected to equilibrate at around 2.7×10^{-14} atm [158]. For each 2 moles of Fe_2O_3 one mole of oxygen is expected to be released during the reaction of the stoichiometric precursors of Fe_2O_3 with Ta_2O_5 . The extra oxygen released during the reaction process is absorbed by the getter. The absorption of released oxygen gas by the getter is coupled with a reducing process of Fe^{+3} to Fe^{+2} resulting in the formation of $\text{Fe}_4\text{Ta}_2\text{O}_9$ phase. Using this synthesis protocol, the formation of parasitic phases as FeTa_2O_6 [159], FeTaO_4 [160], $\text{Fe}_3\text{Ta}_2\text{O}_8$, etc can be avoided, resulting in a single phase material.

5.3.2 Structural characterization

The Rietveld refinement of the room temperature powder X-Ray diffraction data is shown in Fig. 5.4. In similarity to the other members of the $A_4\text{Ta}_2\text{O}_9$ family, this system is also

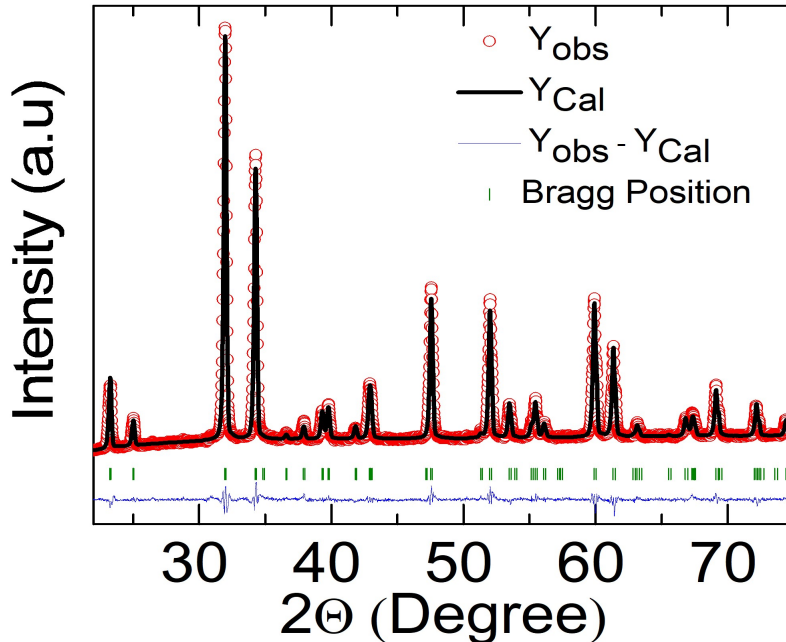


Figure 5.4: Rietveld refinement of room temperature X-ray diffraction data of $\text{Fe}_4\text{Ta}_2\text{O}_9$. This corresponds to a fit with R parameters of $R_{wp} = 9.13$, $R_e = 5.55$, and $\chi^2 = 2.7$.

seen to crystallize in the centrosymmetric Trigonal ($P\bar{3}c1$) symmetry. The structural

details as obtained from the Rietveld refinement of room temperature diffraction data are summarized in Table 5.1. The chemical composition as obtained from the Rietveld analysis was found to be $\text{Fe}_{3.9 \pm 0.1}\text{Ta}_{1.9 \pm 0.1}\text{O}_9$. This was in agreement with the elemental composition determined using Energy Dispersive X-ray analysis, which indicated a Fe:Ta ratio of $(3.93 \pm 0.12):(2.06 \pm 0.12)$.

Table 5.1: Structural parameters of $\text{Fe}_4\text{Ta}_2\text{O}_9$ as determined from Rietveld refinement of room temperature X-Ray diffraction data

Space Group : $P\bar{3}c1$, Crystal System: Trigonal				
$a = b = 5.232(4) \text{ \AA}$, $c = 10.238(1) \text{ \AA}$; $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$				
Atom	Wyckoff	x/a	y/b	z/c
Fe1	4d	0.3333	0.6667	0.5172
Fe2	4d	0.3333	0.6667	0.3079
Ta	4c	0.00000	0.00000	0.8567
O1	6f	0.3112	0.00000	0.2500
O2	12g	0.3288	0.2869	0.0817

5.3.2.1 Crystal Structure

In comparison with the corundum structure (ABO_3 type) in $\text{Fe}_4\text{Ta}_2\text{O}_9$, the A and B cation ratio is A (Fe):B (Ta)=2:1. The Fe^{2+} ion occupies two distinct crystallographic sites. The structure is made of an alternating sequence of pure Fe layer (Layer A) and mixed Fe,Ta layers along the c axis. The first layer (A) comprises of hexagonal rings of edge sharing FeO_6 octahedra, with the adjacent layer (B) being made up of alternating edge sharing Fe_2O_6 and TaO_6 octahedra, as is schematically shown in Fig. 5.5 [161].

5.3.3 DC magnetization

The Zero Field Cooled (ZFC)- Field Cooled (FC) measurements performed at 100 Oe on polycrystalline $\text{Fe}_4\text{Ta}_2\text{O}_9$ is depicted in Fig. 5.6. On cooling from room temperatures, two magnetic transitions at 80 K (T_1) and 60 K (T_2) are observed. These transitions are more clearly visible from the temperature dependence of $d\chi/dT$ plot as depicted in the inset of Fig. 5.5. On further cooling, a splitting between the ZFC and FC curves appear, with the magnetization increasing monotonically till a low temperature magnetic transition (T_3) at 5K. The inverse of the dc magnetic susceptibility $[\chi_{dc}^{-1}(T)]$ is linear

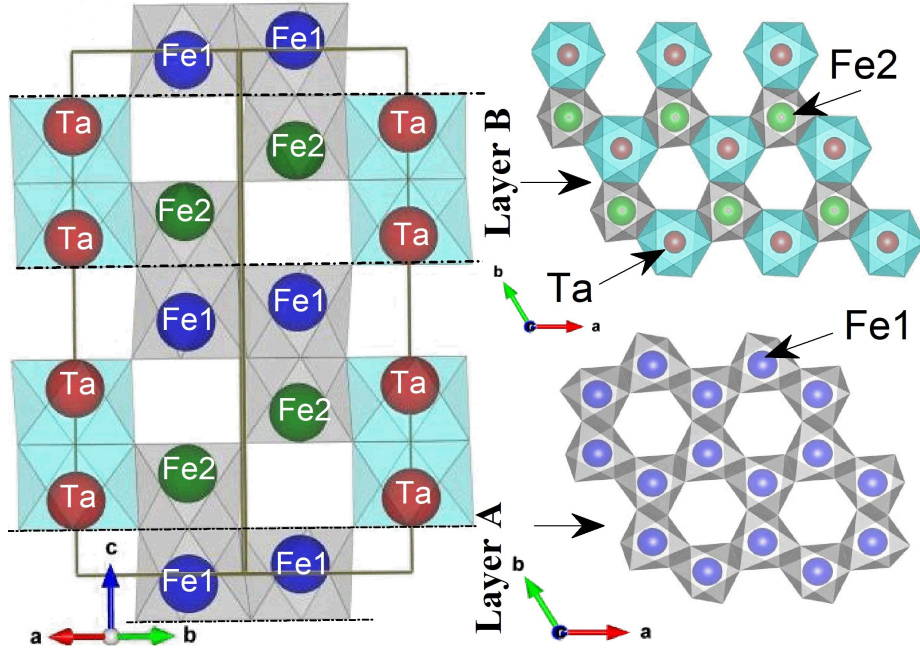


Figure 5.5: The structure of corundum related $\text{Fe}_4\text{Ta}_2\text{O}_9$ as obtained from the Rietveld refinement of room temperature X-ray diffraction profile. The structure comprises of edge sharing FeO_6 octahedra (Layer A) and the adjacent layer constitutes of edge sharing TaO_6 , FeO_6 octahedra (Layer B).

only above 150 K, as is shown in the inset of Fig. 5.6(b), indicating the presence of short range correlations well above the transition temperature. The linear fit to $\chi_{dc}^{-1}(T)$ gives a Curie-Weiss temperature $\theta_{CW} = -45.33\text{K}$, indicating the coexistence of ferromagnetic and antiferromagnetic interactions. The effective magnetic moment μ_B/Fe^{2+} calculated from the Curie-Weiss fit is only $2.69 \mu_B$. The spin only moment $S_\mu = \sqrt{n(n+2)} \mu_B$ where n is number of the unpaired electrons (assuming a fully quenched orbital moment) for Fe^{2+} in octahedral environment are tabulated in Table 5.2. This is significantly less than

Table 5.2: Spin only moment of Fe^{2+} ($3d^6$) in high and low spin states under an octahedral crystal field.

	Spin state	Electronic configuration	Calculated Spin only moment (S_μ/Fe^{2+})
Fe^{2+} ($3d^6$)	Low Spin	e_g ↑↓ ↑↓ ↑↓ t_{2g}	0
	High Spin	↑ ↑ e_g ↑↓ ↑ ↑ t_{2g}	4.89

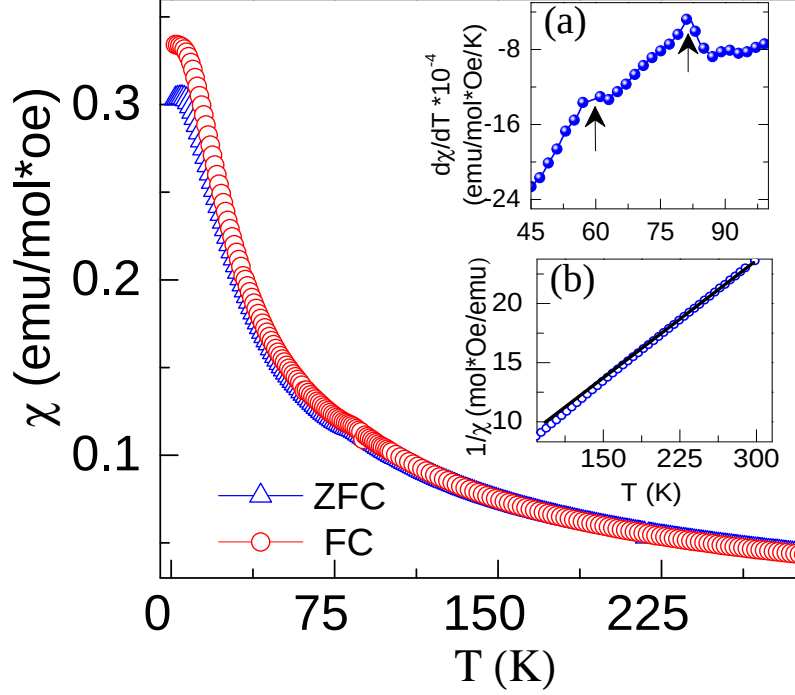


Figure 5.6: Main panel shows temperature dependence of DC magnetic susceptibility measured under ZFC-FC protocols. The inset (a) shows $d\chi/dT$ Vs T plot which clearly identifies the presence of magnetic anomalies at $T_1=80\text{K}$ and $T_2=60\text{K}$. The inset (b) represents the Curie-Weiss linear fit of the $1/\chi$ Vs T plot in the paramagnetic region.

the spin only ($S=2$) value of Fe^{2+} in its high spin state. This observation implies that Fe^{2+} coexists in both the high spin ($S=2$) and the low spin ($S=0$) state in this system. Our Curie Weiss fit indicates that the ratio of the high spin:low spin of Fe^{2+} species is in the ratio $\approx 0.55:0.45$. This is in sharp contrast to that observed in other members of the $A_4\text{Ta}_2\text{O}_9$ family, where the effective spin only $S_\mu/\text{magnetic ion}$ is always larger than the corresponding spin only value. This has been ascribed to the presence of an unquenched orbital momentum contribution, which is also intimately related to the observed linear magnetoelectricity in many other members of this family. [152, 156, 162].

DC magnetic measurements performed in magnetic fields in excess of 1 Tesla exhibits additional field induced transition ($T_3(H)$), which is depicted in Fig.5.6(a). At 1 Tesla magnetic field, the anomaly occurs at 22K and shifts towards higher temperature with increasing the magnetic field strength. At the highest possible applied magnetic field of 7 Tesla it reaches $\approx 35\text{K}$, which is prominently observed in the form of peak, as depicted in $d(1/\chi)/dT$ vs T plot shown in Fig.5.7(b). Below this field induced transition the ZFC magnetic susceptibility increases monotonically until another magnetic anomaly at $T_4 \approx 5\text{K}$, as is shown in Fig.5.7(c).

Low temperature M - H isotherms exhibit a non-saturating behavior upto the highest pos-

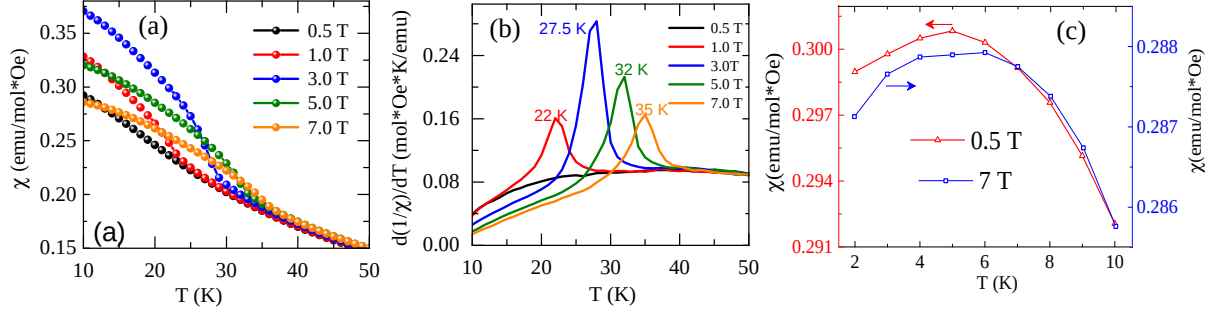


Figure 5.7: (a) The ZFC magnetic measurement performed under magnetic field exhibits a field induced transition. (b) Such field induced transition clearly identified in the plot of $d(1/\chi)/dT$ Vs dT plot. (c) DC magnetic susceptibility measurement at 100 Oe and 7 Tesla shows appearance of a low temperature magnetic transition at 5K.

sible applied magnetic field of 7 Tesla as is expected for an AFM system, and is depicted in Fig.5.8(a). Interestingly we have observed field induced meta-magnetic transitions as is clearly evident from a slope change in the M - H plot. This field induced transition is prominently observed in $\frac{dM}{dH}$ vs H plot with a broad peak, as is depicted in the Fig.5.8(b). The critical field of this meta-magnetic transition is 1.4 T (± 0.1 T) at 2K

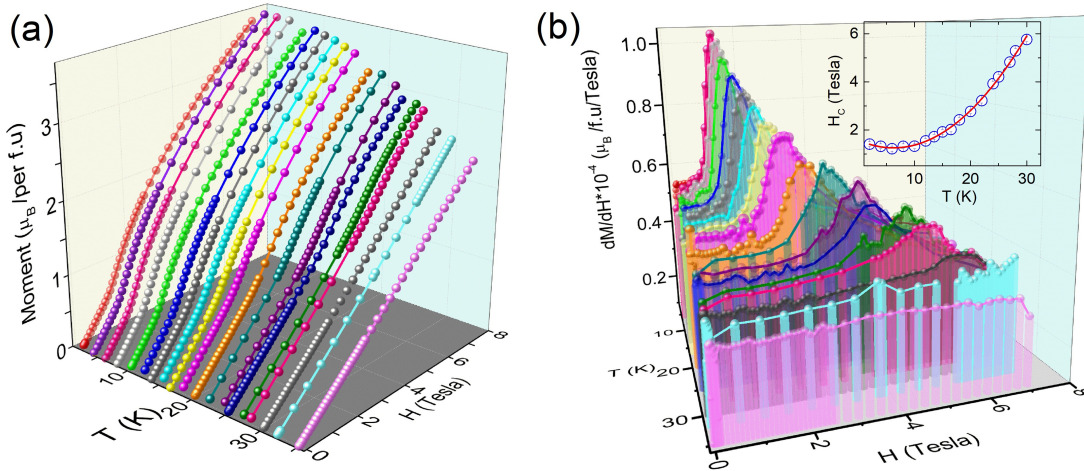


Figure 5.8: (a) Temperature evolution of M - H hysteresis loop. (b) A 3D view of dM/dH with respect to temperature and magnetic field. The meta-magnetic transition is clearly seen in form a peak. The inset illustrate the evolution of the critical field (H_c) of this metamagnetic transition with temperature.

and steadily increases as a function of temperature. The critical field (H_c) of the meta-magnetic transition is seen to have a T^2 dependence, as shown in the inset of Fig.5.8(b). This is in broad agreement with Yamada's theory [163] on field induced transition from paramagnetic to ferromagnet state in itinerant magnets. However, its applicability in the anti-ferromagnetic ordered insulating $\text{Fe}_4\text{Ta}_2\text{O}_9$ is likely to be limited.

5.3.4 Specific heat Measurements

Specific heat measurements reconfirm the presence of transitions at $T_1 = 80$ K and $T_2 = 60$ K (Fig.5.9 (a)). Both these anomalies remain insensitive to the application of magnetic fields up to 7 Tesla. The non-magnetic structural specimens corresponding to $\text{Fe}_4\text{Ta}_2\text{O}_9$

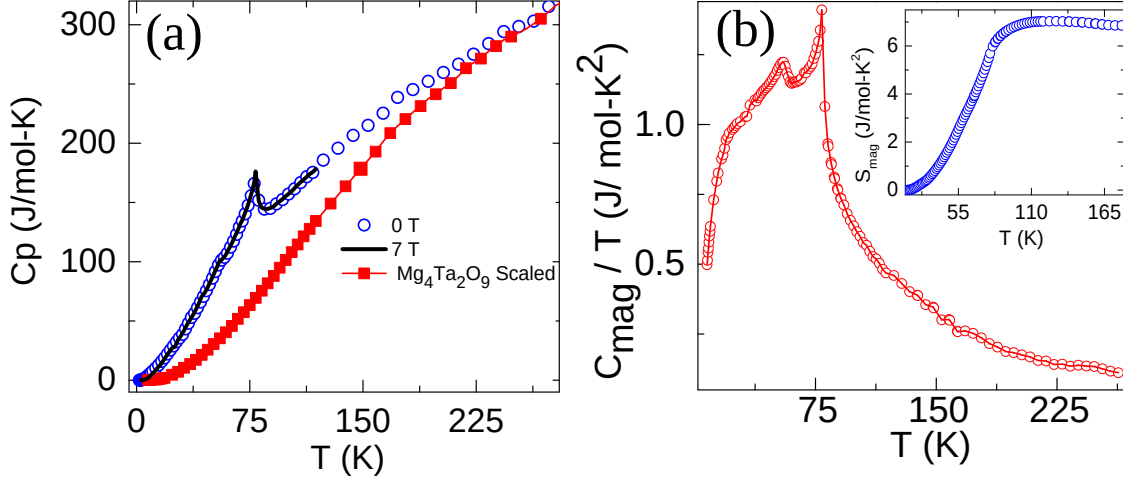


Figure 5.9: (a) Temperature dependence of specific heat of $\text{Fe}_4\text{Ta}_2\text{O}_9$ as measured at 0 and 7 Tesla magnetic field. Scaled specific heat of $\text{Mg}_4\text{Ta}_2\text{O}_9$ with respect to molecular weight of Fe representing the phonon contribution of specific heat in this structure is also seen. (b) The main panel shows the evolution of C_{mag}/T as a function of temperature. The inset depicts the temperature evolution of the magnetic entropy (S_{mag}).

are $\text{A}_4\text{Ta}_2\text{O}_9$ ($\text{A}=\text{Mg}, \text{Zn}$). The magnetic contribution to specific heat (C_{mag}) was calculated by subtracting phonon contribution as described in section.1.15.4 in Chapter2. We have prepared phase pure $\text{Mg}_4\text{Ta}_2\text{O}_9$ [164] by mixing the MgO and Ta_2O_5 in a stoichiometric ratio and sintering at 1350 °C, and 1400 °C for 24 hrs each. The temperature dependence of magnetic entropy (S_{mag}) is depicted in the inset of Fig.5.9(b). The magnetic entropy saturates at a value 7.12 J/mol-K². The expected magnetic entropy with 55% Fe^{2+} in high spin state ($S=2$) and 45% low spin state ($S=0$) is $S = R \ln(2S+1) = 7.359$ J/mol-K². The magnetic entropy at (T_1) 80 K is 5.69 J/mol-K², and at (T_2) 60 K is 3.14 J/mol-K² respectively. Hence 44% and 80% of the magnetic entropy is reached at the magnetic transitions at 60K and 80K respectively, and 20% of the entropy is released via short range correlations above the transition. This is also in agreement with our observation that the Curie-Weiss behavior is valid only at temperatures well above the magnetic transition.

5.3.5 Dielectric measurements

Dielectric measurements under zero magnetic field were performed in CCR. A weak anomaly is observed at $T_1 = 80\text{K}$ and a pronounced feature is observed at $T_2 = 60\text{K}$, as depicted in Fig. 5.10 (a). The field induced transitions as found in the magnetic mea-

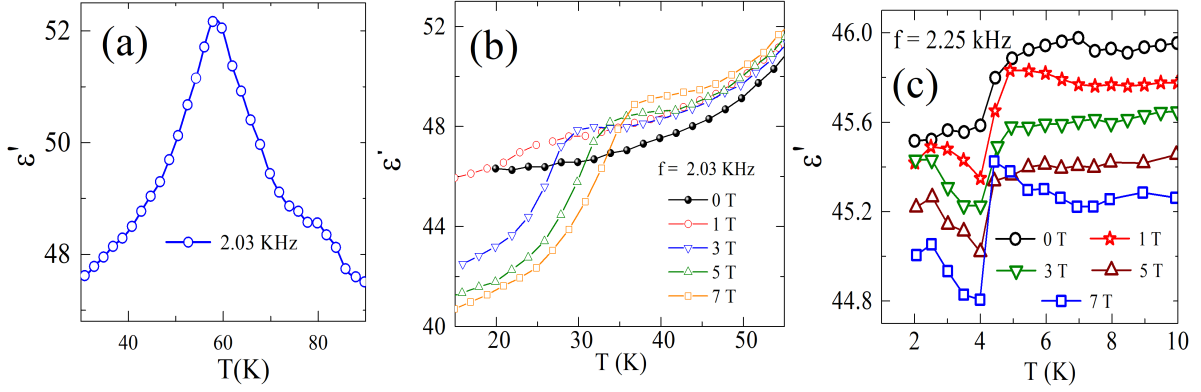


Figure 5.10: (a) Real part of dielectric constant (ϵ') measured under zero magnetic field across the transition T_1 and T_2 . (b) Dielectric measurement performed under magnetic field where the real part of dielectric constant exhibits a sharp down turn. (c) Real part of dielectric constant remain robust in presence of magnetic field across the transition T_4 .

surement, are also observed in dielectric measurements performed under a magnetic field. As depicted in Fig. 5.10(b), a downturn in the real part of dielectric susceptibility (ϵ') was observed and it shifts towards high temperature as a function of magnetic field ($T_3(H)$). Below the field induced magnetic state, the dielectric measurement exhibits a step like feature at $T_4 = 5\text{K}$. Measurements done at different magnetic fields show that there is no observable change in the nature of the magneto-dielectricity on either side of the phase transition, as is shown in Fig. 5.10(c). Hence, the presence of anomalies in dielectric measurements clearly implies the existence of coupling between the charge and spin degrees of freedom in $\text{Fe}_4\text{Ta}_2\text{O}_9$.

5.3.6 Pyroelectric measurements

5.3.6.1 Pyroelectric measurements without a magnetic field

The presence of possible ferroelectric order at the observed dielectric anomalies are further confirmed by performing pyrocurrent measurements as depicted in Fig. 5.11(a). Poling the sample from $T_i = 90\text{K}$ to $T_f = 30\text{K}$ and performing the pyrocurrent measurement shows two anomalies at $T_2 = 60\text{K}$ and $T_1 = 80\text{K}$ reconfirming the presence of ferroelectric

states. Polarization across each phase transitions was evaluated by performing independent pyrocurrent measurements with selective poling temperature (T_i and T_f). Poling

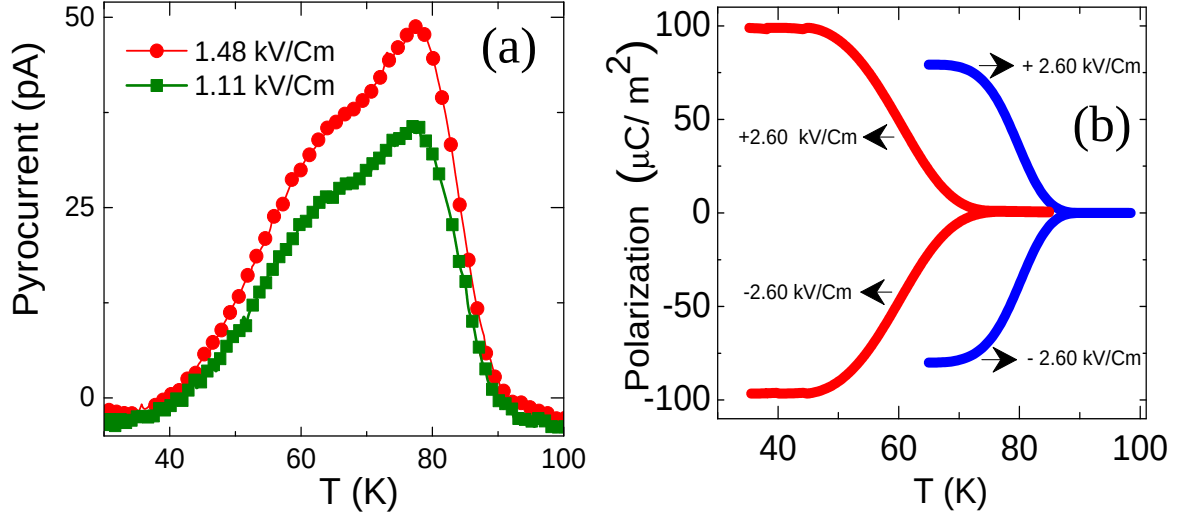


Figure 5.11: (a) Pyrocurrent measurements performed across the transitions T_1 and T_2 after poling under different values of electric field and a zero magnetic field. (b) Electrical polarization calculated across both these transitions. Flipping of polarization by changing the direction of electric field, indicates the true ferroelectric nature of these transitions.

the sample from 70K ($T_2 \leq T_1$) reveals a single peak in the pyrocurrent at 60 K. On the other hand, poling the sample from $T_{pi} = 85\text{K}$ to $T_{pf} = 65\text{K}$ reveals a pyrocurrent peak at 80K. The polarization calculated after integrating the measured pyrocurrent is depicted in Fig. 5.11(b). Moreover, the sign of the observed polarization in both the measurements were reversed by reversing the direction of electric field, indicating the presence of two independent ferroelectric states at T_1 and T_2 .

5.3.6.2 Rate dependent pyroelectric measurements

The possibility of thermally trapped charge carriers giving rise to a pyrocurrent peak near a magnetic phase transition, mimicking a ferroelectric-like has to be experimentally ruled out. This could be resolved by performing the measurement at different warming rates for a fixed poling electric field [165, 166, 167]. As is shown in Fig. 5.12, the fact that we see no change in T_{peak} , in measurements where the heating rates vary from 5 K/min to 10 K/min conclusively proves that the pyrocurrent in our case does not arise from thermally stimulated currents. Hence, the observed magnetic states are also associated with true ferroelectric states.

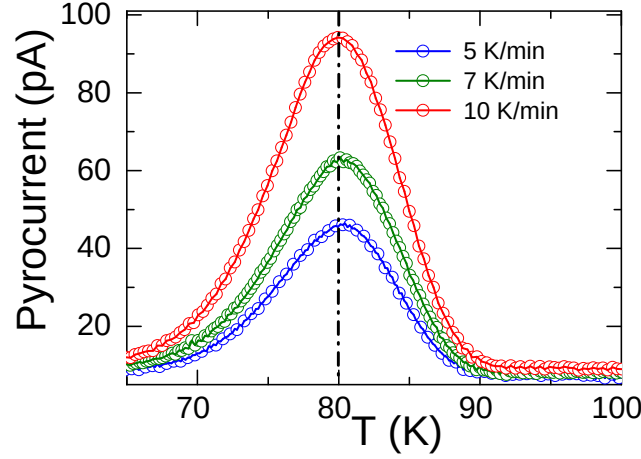


Figure 5.12: Pyrocurrent measurement performed under different warming rate after poling under a fixed electric field. The pyrocurrent peak is independent of warming rate reaffirms the occurrence of ferroelectric state.

5.3.6.3 Pyroelectric measurements in the presence of a magnetic field

Pyroelectric measurement performed under magnetic field exhibit a pyrocurrent peak concomitant with the anomaly as observed in dielectric and magnetic measurement in presence of a magnetic field. The specimen was polled with applied electric and magnetic

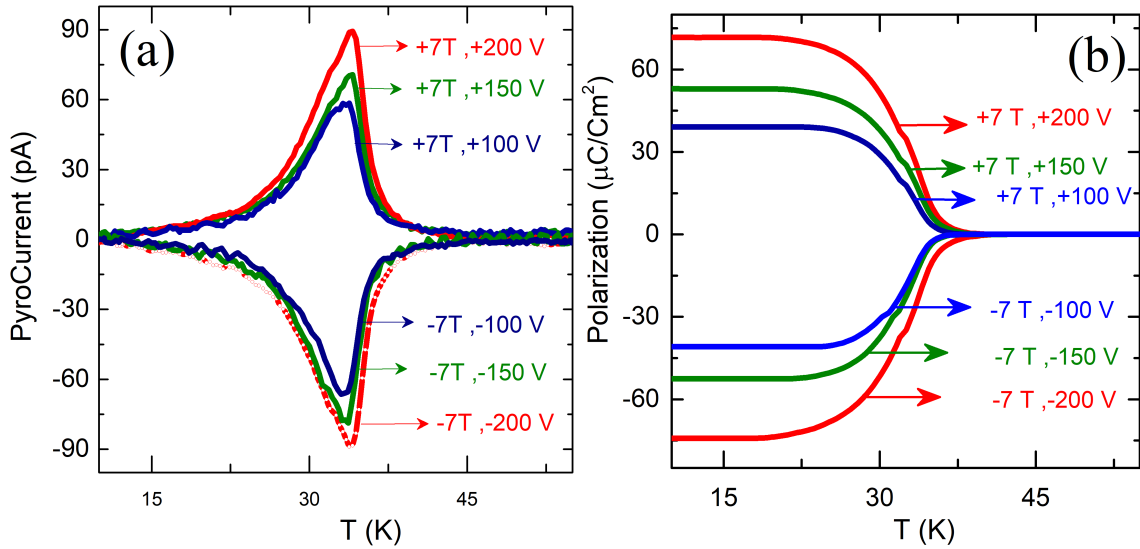


Figure 5.13: (a) Pyrocurrent measurement performed after electromagnetic poling across the magnetic field induced transition ($T_3(H)$) for a fixed magnetic field of 7 Tesla. (b) Polarization obtained after integrating the measured pyrocurrent under different electromagnetic poling conditions.

field ($E \perp H$), called electromagnetic poling from 50K. At low temperature, the electric field was removed and standard pyroelectric measurements were performed in the pres-

ence of a magnetic field. For poling with fixed magnetic field (7 Tesla) and varying the electric field shows a sharp peak at the temperature as observed in magnetic and dielectric measurement, as depicted in Fig.5.13(a). The polarization associated with this magnetic field induced transitions can be fully flipped by reversing the direction of the electric and magnetic fields, as shown in Fig.5.13(b).

On the other hand, the pyroelectric measurement performed by electromagnetic poling

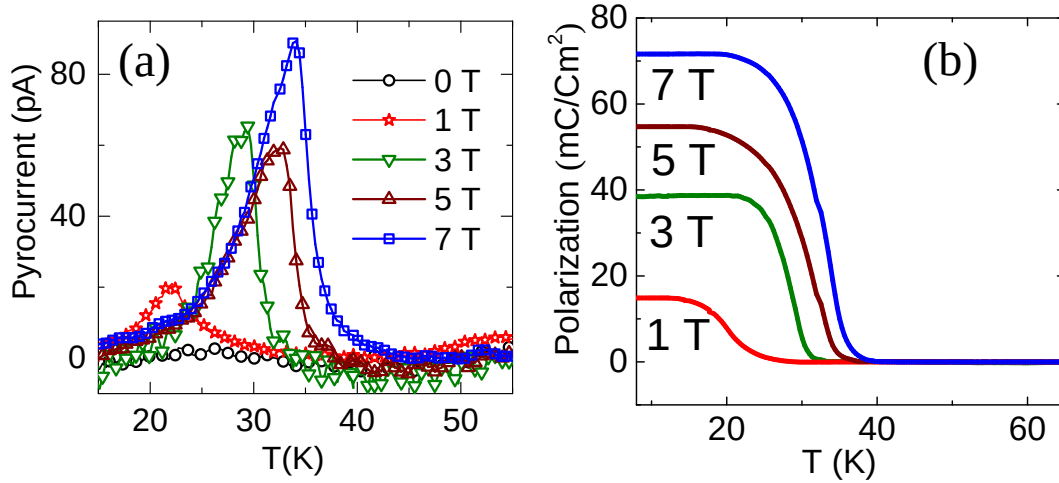


Figure 5.14: (a) Temperature evolution of pyrocurrent measured under different values of applied magnetic field. Appearance of pyrocurrent peaks are concomitant with the anomalies observed in both dielectric and DC magnetic measurements performed under same values of applied magnetic field. (b) Polarization obtained after integrating the measured pyrocurrent under different electromagnetic poling conditions.

keeping the electric field constant and varying the magnetic field exhibits the pyrocurrent shifts towards high temperature as depicted in Fig.5.14(a). The value of this magnetic field induced polarization increases with increasing the strength of magnetic field as shown in Fig.5.14(b). A similar signature was also observed in our magnetic and dielectric measurements.

Pyroelectric measurements across the transition $T_4=5\text{K}$ after poling the specimen from 15K does not exhibit a peak in the pyrocurrent and rules out the possibility of a new ferroelectric phase at this temperature. Interestingly, on poling from temperature above 35K in the presence of magnetic field, we observed that the field induced ferroelectric state sustain well below 5K. Hence, the field induced ferroelectric state is not affected by the transition at T_4 .

5.3.7 Low-temperature X-Ray diffraction

Low temperature X-Ray diffraction measurements performed at low temperature indicates that the crystallographic symmetry of $\text{Fe}_4\text{Ta}_2\text{O}_9$ remains invariant down to 15 K. The Rietveld refinement of x-ray diffraction data reveals that both the unit cell parameters a and c decreases and below the onset of ferroelectric state it again increases as is illustrated in Fig. 5.15(a). Both the in-plane Fe1-O2, Fe2-O1 bond lengths exhibit an

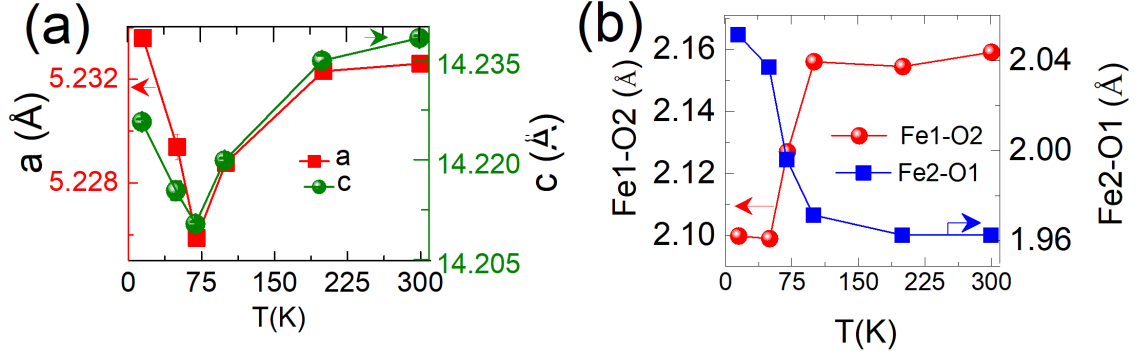


Figure 5.15: (a) Variation of Lattice parameter a and c as obtained from Rietveld refinement of temperature dependent X-ray diffraction data. (b) Variation of the Fe1-O and Fe2-O bond lengths as a function of temperature.

abrupt change at the onset of ferroelectric state, with the former decreasing and the latter increasing across this transition, as is shown in Fig. 5.15(b). Such bond distortion associated with the occurrence of ferroelectric state results in a distortion of the polyhedral cage along the ab plane in the fashion as shown in Fig. 5.16. However, the X-ray diffraction profile down to 15 K could be fitted with the space group Trigonal $P - 3c1$. This confirms that the observed structural distortion does not lead to change in crystallographic symmetry within the resolution of our measurements.

5.3.8 Possible reduction in the dimensionality of magnetic lattice

It is interesting to note that $\text{Fe}_4\text{Ta}_2\text{O}_9$ is the only member which exhibits true polar order instead of linear magneto-electricity the $A_4\text{Ta}_2\text{O}_9$ family. We postulate that this could emerge from an effective reduction in the dimensionality of the magnetic lattice in this system. Our analysis of ZFC magnetization data clearly indicates that approximately half of the Fe^{2+} ions in $\text{Fe}_4\text{Ta}_2\text{O}_9$ stabilize in the nonmagnetic ($S=0$) state. The Fe^{2+} ions occupy two distinct crystallographic sites Fe1 ($1/3, 1/3, 0.517$) and Fe2 ($1/3, 2/3, 0.307$),

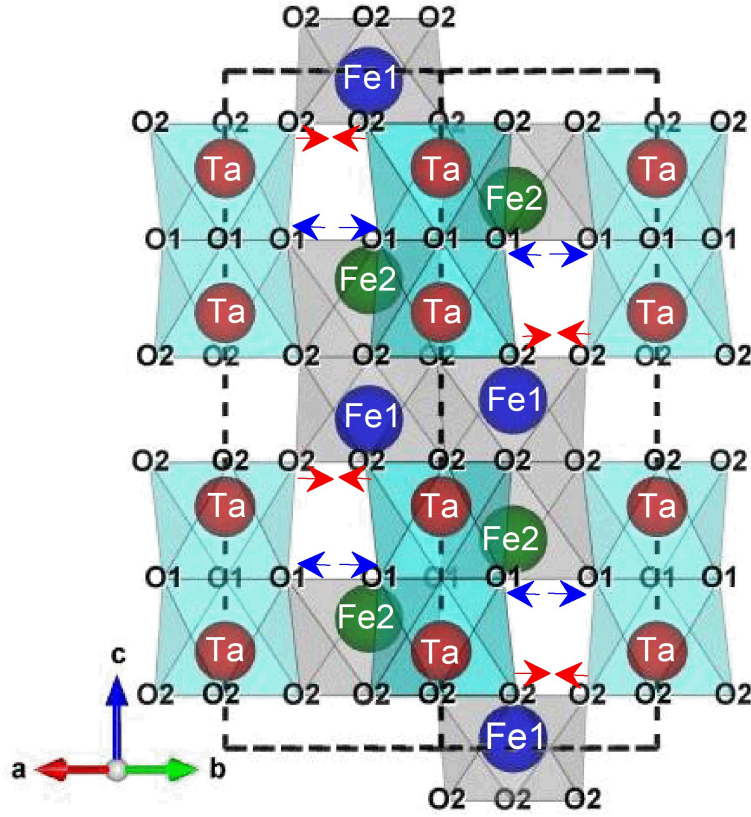


Figure 5.16: Crystal structure of $\text{Fe}_4\text{Ta}_2\text{O}_9$ below the magnetic transition where the buckling of FeO_6 polyhedra is clearly observed.

which reside in different planes stacked along the crystallographic c axis. These two distinct lattice sites form separate distorted hexagonal sub-lattices along the ab plane, as depicted in Fig. 5.17. The Fe1 sub-lattice is slightly buckled in nature [Fig. 5.17(a)] and the Fe2 sub-lattice forms a zig-zag like chain along the b axis [Fig. 5.17(b)]. In an octahedral environment, a Fe^{2+} ($3d^6$) ion would be expected to have a $t_{2g}^4 e_g^2$ and $t_{2g}^6 e_g^0$ electronic configuration in the high spin and low spin states respectively. If the different ($S=2$ and $S=0$) spin species of Fe^{2+} *preferentially* occupy the two possible crystallographic sites, we would expect to see this being subtly reflected in the local octahedral environment of each of these FeO_6 sub-units. For e_g orbital the electrons clouds being along the direction of the oxygen $2p$ orbitals, the resultant Coulomb interaction would be expected to result in a slight elongation of the resultant bond, as depicted in Fig. 5.18. On the other hand, the t_{2g} orbitals being directed along the bisector of the O-Fe-O angle would be expected to have a smaller effect. Fe^{2+} in the low spin state is Jahn-Teller inactive within an octahedral environment and would thus not be a contributing factor. However, in its high-spin state, the t_{2g} orbitals of Fe^{2+} are Jahn-Teller active and could also possibly contribute to the observed octahedral distortion.

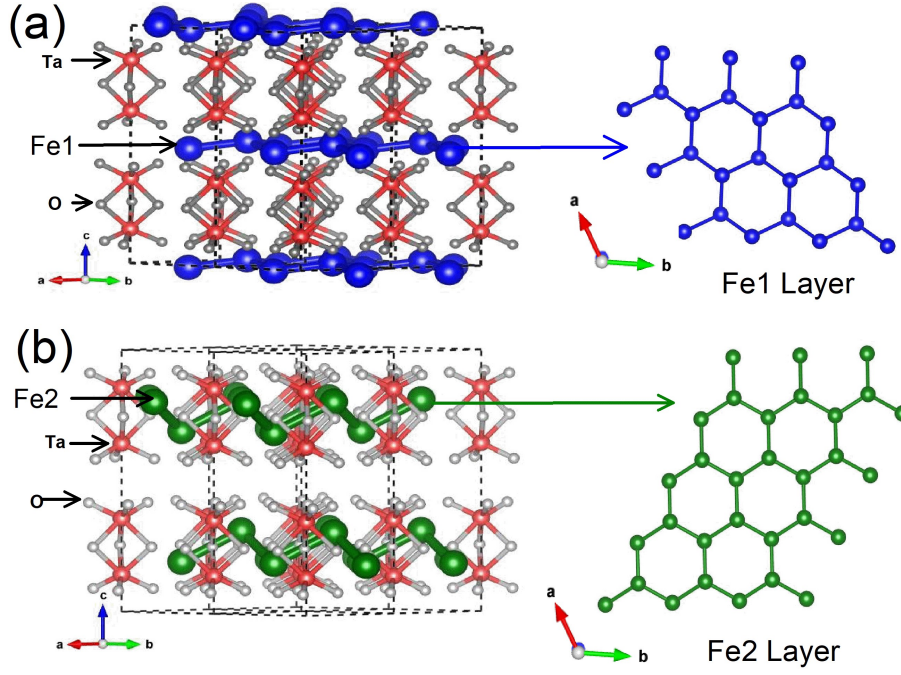


Figure 5.17: (a) The buckled honeycomb lattice formed by the magnetic Fe1 and non magnetic TaO₆ octahedra. (b) The zig-zag chain formed by the nonmagnetic Fe2 ions.

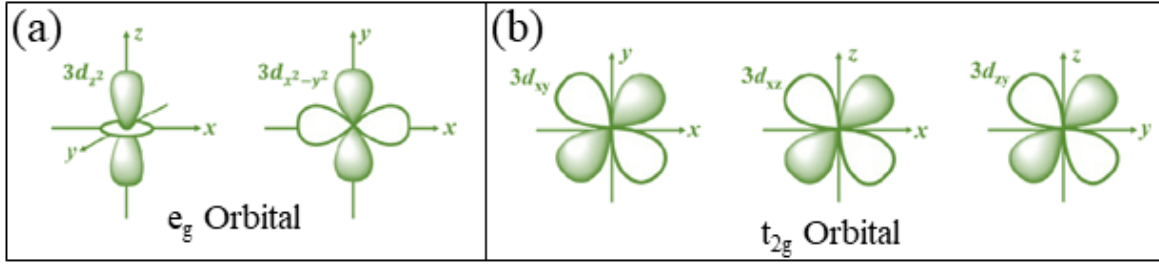


Figure 5.18: Electron density of crystal field split e_g and t_{2g} orbitals. The electron density of e_g orbitals is maximum along the hybridization of oxygen $2p$ orbitals whereas for t_{2g} orbitals it is along the bisector of the O-Fe-O angle. This results an elongation of the Fe-O bond with an occupied e_g orbitals.

Analysis of our x-ray diffraction data indicate that the average Fe1-O bond length (2.16) exceeds that of the Fe2-O bond length (2.05) by 5%. For instance, in the case of $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ molecule, with Fe^{2+} in an octahedral environment, it has been shown that the average Fe^{2+} -N bond length in the high spin ($S=2$) and low spin ($S=0$) states could differ by up to 9% [168]. This leads us to speculate that the magnetic ($S = 2$) Fe^{2+} ions exclusively occupy the buckled honeycomb sub-lattice, with the nonmagnetic ($S = 0$) Fe^{2+} ions occupying the alternating zig-zag one. This basically reduces the dimensionality of the magnetic lattice from a 3D to a quasi-2D one. It is well known that short range magnetic fluctuations can persist in a wide temperature window above the magnetic transition in 2D magnets [169], signatures of which we have also observed in

our magnetization measurements.

5.4 H - T Phase Diagram

The H - T phase diagram of $\text{Fe}_4\text{Ta}_2\text{O}_9$ as determined using the magnetic, thermodynamic, dielectric and pyroelectric data at our disposal is depicted in Fig. 5.19. The anomaly

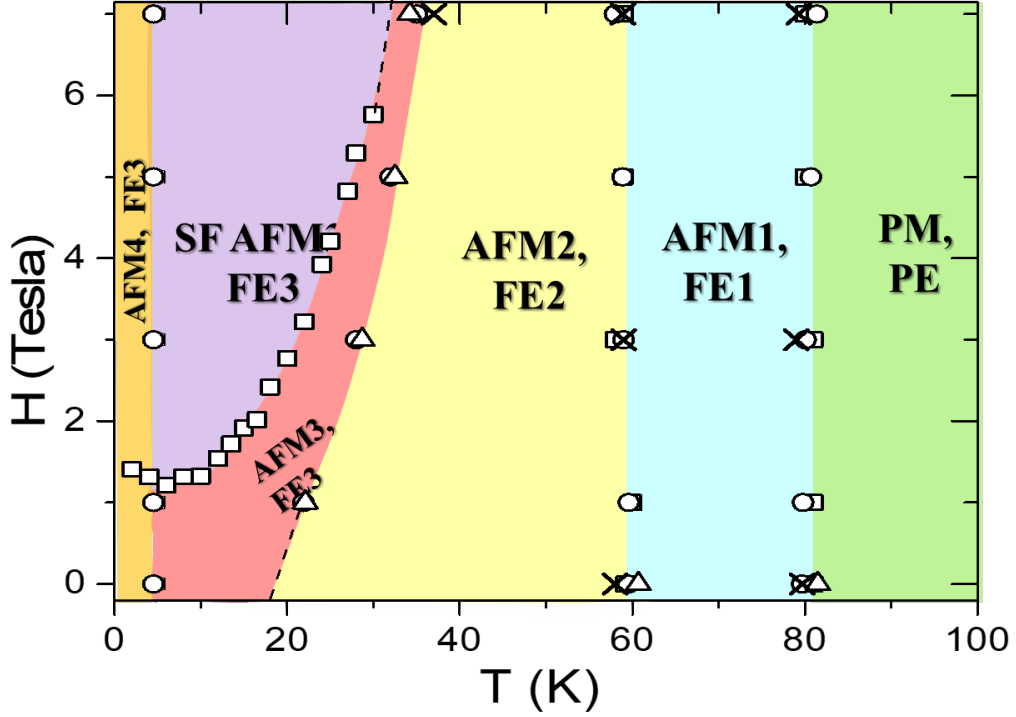


Figure 5.19: The H - T phase diagram of $\text{Fe}_4\text{Ta}_2\text{O}_9$ as determined from magnetic ($\square$), specific-heat ($\times$), dielectric ($\circ$), and pyroelectric ($\triangle$) investigations. The dotted lines do not represent experimentally determined phase boundaries and are only meant as a guide to the eye.

observed in low field ZFC magnetic measurement as a function of decreasing temperature are also being identified in dielectric and pyroelectric measurements performed under zero field. This reveals two distinct multiferroic states of $\text{Fe}_4\text{Ta}_2\text{O}_9$ labeled as AFM1 FE1, and AFM2 FE2 with onsets at $T_1=80\text{K}$ and $T_2= 60\text{K}$ respectively. On cooling further, and in the presence of magnetic fields in excess of 1 Tesla, we observe a field induced multiferroic state denoted as AFM3 FE3. Within this state, we also observe the presence of a metamagnetic (spin-flop) transition which appears to have no discernible influence on the polar state (SF-AFM3 FE3). We further observe the onset of possibly a different kind of antiferromagnetic order at temperatures of the order of 5K, (AFM4 FE3) as is evidenced by magnetic and dielectric measurements.

5.5 Conclusions

It is remarkable that $\text{Fe}_4\text{Ta}_2\text{O}_9$ exhibits such a complex phase diagram, which is in stark contrast to the other members of the extended $A_4\text{Ta}_2\text{O}_9$ family. We note that the phase diagram of this system has some parallels to that observed in the $\text{Ni}_3\text{V}_2\text{O}_8$ [170, 171] and $\text{KCu}_3\text{As}_2\text{O}_7(\text{OD})_3$ [172] systems, stabilizing in distorted variants of the Kagome structure, where a series of low temperature magnetic phases coupled with polar order have been observed. A common factor here appears to be the presence of 2 dimensional honeycomb layers which are buckled in and out of plane, with competing nearest and next-nearest neighbor interactions giving rise to a complex magnetic and polar phase diagram. Needless to say, in-field neutron diffraction measurements would be imperative to further reconfirm these phase boundaries, and to identify the changes in the magnetic structure across these different phases.

Chapter 6

Anisotropy in the magnetization and magneto-electric response of single crystalline $\text{Mn}_4\text{Ta}_2\text{O}_9$

6.1 Summary

The present chapter deals with the temperature dependent magnetization and electric field dependent magnetic measurements along the different crystallographic axes of the hitherto unexplored single crystal of $\text{Mn}_4\text{Ta}_2\text{O}_9$. The magnetic structure solved from high-resolution T.O.F powder neutron diffraction data reveals that the magnetic structure comprises of antiferromagnetically coupled ferromagnetic chains of Mn^{2+} spins aligned along the trigonal c axis, in sharp contrast to that reported in other isostructural members of this family. DC magnetic measurements performed with magnetic field parallel and perpendicular to the crystallographic c axis of the crystal reveals anisotropic behavior with the presence of Dzyloshinskii-Moriya interaction, making the magnetic phase diagram of $\text{Mn}_4\text{Ta}_2\text{O}_9$ far richer than the other members of this family. The magnetic isotherm measurement shows a metamagnetic transition along $H \parallel c$, which is absent with the field $H \perp c$. More importantly, magnetic measurements performed under a period electric field indicate that the magneto-electric response is also anisotropic, with this coupling along the trigonal c axis and that perpendicular to it having different signs.

6.2 Introduction

The corundum family of the form $A_4X_2O_9$ (with $A = \text{Mn, Co or Fe}$, and $X = \text{Ta or Nb}$) has attracted recent interest owing to its promising magneto-electric properties [149, 154, 155, 150, 151, 173]. Based on structural considerations, S. C. Abrahams had earlier predicted that $\text{Mn}_4\text{Ta}_2\text{O}_9$ crystallizing in the $R\bar{3}c$ space group could host a potential ferroelectric state [148]. However, subsequent investigations have established that the manganese and cobalt ($A=\text{Mn, Co}$) members of this family are predominantly linear magneto-electrics crystallizing in the trigonal $P\bar{3}c1$ symmetry, whereas $\text{Fe}_4\text{Ta}_2\text{O}_9$ is now known to be a genuine multiferroic with multiple coupled magnetic and ferroelectric states [174, 175].

The linear magneto-electric effect is expressed as $P_i = \alpha_{ij} M_j$ or $M_i = \alpha_{ij} P_j$, where P is the polarization, M is the magnetization and the proportionality constant α_{ij} ($\frac{\partial M_i}{\partial E_j} / \frac{\partial P_i}{\partial H_j}$) quantifies the linear magneto-electric coupling. The magneto-electric susceptibility α_{ij} is a reducible second rank tensor with possible diagonal and off-diagonal elements as obtained from the coupling response parallel and perpendicular to a given crystallographic orientation. For a crystal, magneto-electric susceptibility (α) is finite only when

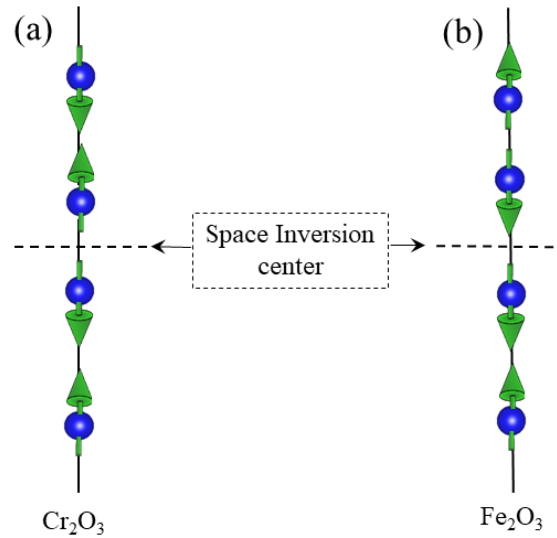


Figure 6.1: Role of magnetic symmetry in establishing a magneto-electric state. Spin configuration of prototype linear magnetoelectrics (a) Cr_2O_3 where both the space and time reversal symmetry is broken. (b) The space inversion is not broken in the case of Fe_2O_3 as shown by dotted line as a reference to the space inversion center and consequences in absence of magneto-electric effect.

space and time reversal symmetry are broken simultaneously. Hence, both the crystallographic and magnetic space groups often predetermine the existence of magneto-

electric coupling. Because of such severe symmetry restrictions, there are very few materials which are linear magneto-electrics. Prominent examples include Cr_2O_3 [176], MnTiO_3 [177], NdCrTiO_5 [178], LiFePO_4 [179] and $\text{Co}_4\text{Nb}_2\text{O}_9$ [152]. Below T_N , Cr_2O_3 (magnetic point group: $\bar{3}'m'$) shows collinear spin ordering along the trigonal $\mathbf{z}$ axis and breaks both the time and space inversion symmetry (Fig.6.1(a)). On the other hand, the spin orientation of Fe_2O_3 (magnetic point group: $\bar{3}m$) remains invariant under space inversion symmetry, as is illustrated in Fig.6.1 (b)[180]. Hence although the time reversal symmetry is broken by magnetic ordering, the space inversion symmetry is not broken and results in absence of the magneto-electric effect. Hence the magnetic symmetry plays a crucial role in inducing a magneto-electric effect. In this context, the $\text{A}_4\text{X}_2\text{O}_9$ family of compounds crystallizes in the same point group ($\bar{3}'m'$) as the prototype linear magneto-electric Cr_2O_3 with possible magneto-electric tensor [181] as:

$$\begin{pmatrix} \alpha_{xx} & 0 & 0 \\ 0 & \alpha_{yy} & 0 \\ 0 & 0 & \alpha_{zz} \end{pmatrix}$$

The magneto-electric effect in this family has been proposed to arise from two non equivalent A sites and could have possibly resulted in a giant linear magneto-electric effect if they had contributed additively [156]. The absence of ferroelectric polarization without a magnetic field is due to the balance of two different AFM domains with equal and opposite ME coefficients. In the presence of an external magnetic field, one of the domains is preferred, and results in the appearance of a finite electric polarization.

The magnetic structures of $\text{Co}_4\text{Nb}_2\text{O}_9$ were studied by N.D. Khanh *et.al* [152] and G.Deng *et. al* [182], and their inferences were contradictory to each other. The former reported that the Co^{2+} spins at two crystallographic sites are aligned in the ab plane with a canting angle of 20° along the c axis, while the latter suggested that canting is within the ab plane. Canting of Mn^{2+} spins has been proposed as the possible origin of the observed anisotropy and Dzyaloshinskii-Moriya interaction. A electric polarization induced in the presence of an external magnetic field has been reported in polycrystalline $\text{Mn}_4\text{Ta}_2\text{O}_9$, whereas its magnetic structure remains to be reported [183]. Moreover, investigations of single crystalline specimens remain unexplored due to the unavailability of high quality single crystals.

6.3 Results and Discussions

6.3.1 Synthesis of single phase polycrystalline $\text{Mn}_4\text{Ta}_2\text{O}_9$

Polycrystalline $\text{Mn}_4\text{Ta}_2\text{O}_9$ was synthesized by the standard solid state reaction route. High purity Mn_2O_3 and Ta_2O_5 precursors were mixed stoichiometrically and ground using a ball mill for 24 hrs at 120 rpm. This mixture was sintered under argon atmosphere at 900 °C followed by treatments at 1050 °C and 1200 °C respectively. In order to ensure a homogeneous particle size of the powder, the final treatment was repeated thrice with intermediate grinding.

6.3.2 Structural investigation

Rietveld refinement of room temperature X-Ray diffraction data of polycrystalline $\text{Mn}_4\text{Ta}_2\text{O}_9$ is shown in Fig 6.2 (a) [77]. $\text{Mn}_4\text{Ta}_2\text{O}_9$ is known to crystallize in both the $R\bar{3}c$ [184] and

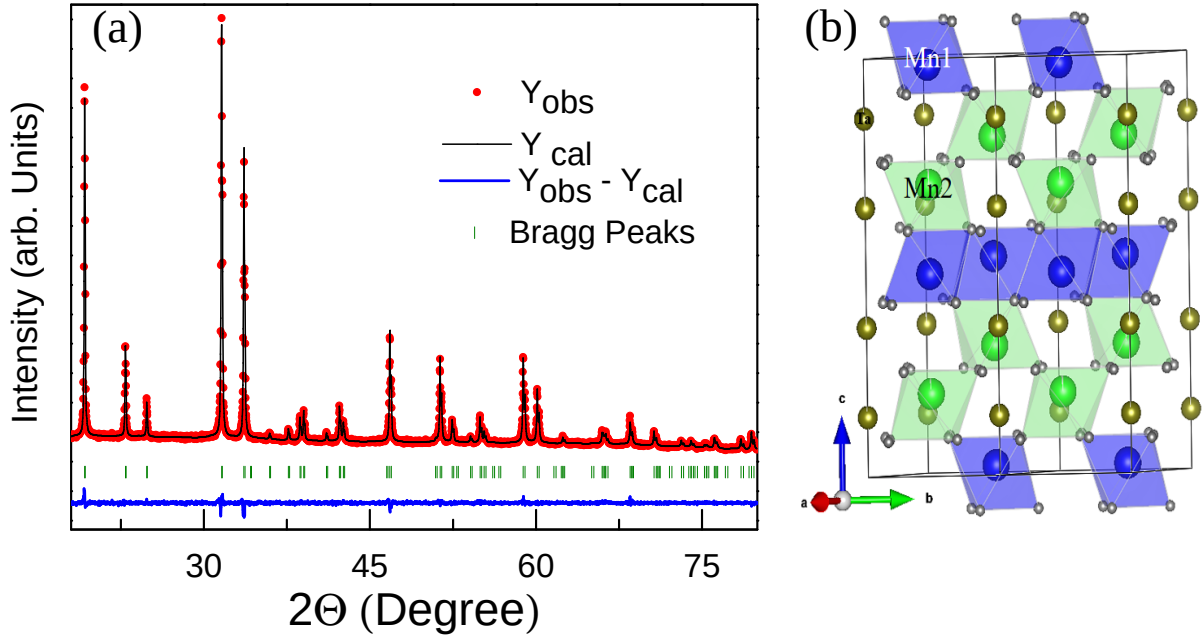


Figure 6.2: (a) Rietveld refinement of room temperature X-ray diffraction data of powder $\text{Mn}_4\text{Ta}_2\text{O}_9$ specimen, which corresponds to a fit with R parameters of $R_{wp} = 12.3$, $R_e = 9.34$, and $\chi^2 = 1.72$. (b) Crystal structure as obtained from the Rietveld the refinement of room temperature powder diffraction data. The manganese (Mn^{2+}) ion occupies in two distinct crystallographic site in octahedral environment.

the $P\bar{3}c1$ [185] space groups. We have found that this system crystallizes in the centrosymmetric Trigonal $P\bar{3}c1$ space group which is similar to the other members of the

$\text{A}_4\text{X}_2\text{O}_9$ family [154, 155, 150, 151, 173]. The obtained crystallographic parameters are summarized in Table.6.1. A representation of the structure of $\text{Mn}_4\text{Ta}_2\text{O}_9$ is shown in

Table 6.1: Structural Parameters of $\text{Mn}_4\text{Ta}_2\text{O}_9$ as determined from the Rietveld analysis of room temperature X-ray diffraction data.

$\text{Mn}_4\text{Ta}_2\text{O}_9$					
Temperature = 298 K ; Space Group : $P - 3c1$					
Crystal system: Trigonal					
$a = 5.31(32)$, $b = 5.31(32)$, $c = 14.29(33)$					
$\alpha = \beta = 90^\circ, \gamma = 120^\circ$					
Atom	Wyckoff	x/a	y/b	z/c	occupation
Mn ¹	4d	0.3333	0.6667	0.01876	0.3333
Mn ²	4d	0.3333	0.6667	0.3053	0.3333
Ta	4c	0	0	0.35(69)	0.3333
O1	6f	0.27(73)	0	0.2500	0.4999
O2	12g	0.33(49)	0.30(79)	0.08(63)	1

Fig.6.2(b). The manganese ions in octahedral configuration occupy two different crystallographic sites denoted by Mn1 and Mn2.

6.3.3 Single crystal growth of $\text{Mn}_4\text{Ta}_2\text{O}_9$ and its characterization

Polycrystalline feed and seed rods were prepared by packing the fine powder inside a rubber tube and applying a hydrostatic pressure of ≈ 700 bar. These compact rods were then sintered at 1200°C under argon atmosphere. The crystal growth was performed using a four mirror optical floating zone furnace (Crystal System Corporation Japan) with each lamp of 500 watt. In the presence of Ar atmosphere at ambient pressure, an inhomogeneous melting of the feed rod was observed and the growth was unstable. This was possibly due to the evaporation of Mn from the system, which was further confirmed by the deposition of materials at the wall of quartz enclosure. A stable growth was optimized under an Ar atmosphere of 0.19 MPa. The molten zone was moved vertically down at a rate of 5 mm/h and an axially symmetric counter rotation of both the feed and seed rods at 16 rpm was set in order to maintain temperature and phase homogeneity at the molten zone. Powder diffraction patterns of the frozen melted zone exhibit similar pattern as that of the specimen prepared by solid state reaction, indicating that the melting behavior of $\text{Mn}_4\text{Ta}_2\text{O}_9$ is congruent.

Crystal pieces were obtained by cleaving the grown crystal rod. Several crystal pieces were

polished using a polishing machine. A representative of which is shown in Fig.6.3(a). The X-ray diffraction pattern obtained from θ - 2θ scan of a representative crystal is depicted in Fig.6.3 (b). All the Bragg peaks were solely indexed by $[00\ 2l]$ planes (with $l=2,3,4,5$). The crystallographic orientations of the crystal were then determined by back reflection Laue X-Ray photography. The absence of any additional spots in the Laue patterns indicate

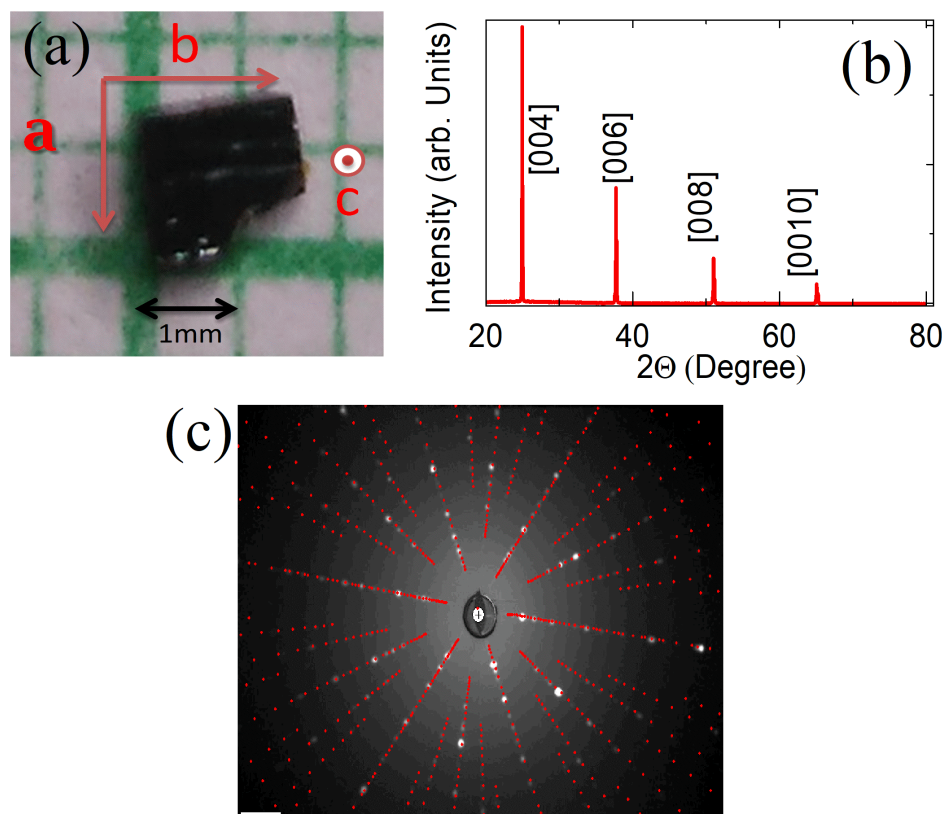


Figure 6.3: (a) Image of a cleaved crystal piece denoting the respective crystallographic orientations. (b) The Inset shows θ - 2θ scan of single crystal piece. The observed Bragg peaks were exclusively indexed by $[0, 0, 2l]$ ($l= 2,3,4,5$) (c) The fitting of Laue pattern with the simulated pattern of the crystal piece performed using Orient Express software [83].

that the $\text{Mn}_4\text{Ta}_2\text{O}_9$ single crystal is of high quality. The crystallographic orientations were determined by an exact matching of the simulated and observed patterns using the Orient Express software [83], as depicted in Fig.6.3(c). A number of crystallites were characterized using a similar procedure and we found all of them were cleaved along the ab plane. Energy dispersive x-ray analysis (EDX) confirms that the Mn:Ta atomic percentage is in the ratio 2:1.

6.3.4 DC Magnetization

DC magnetic measurements were performed in the standard Zero Field Cooled (ZFC) and Field Cooled (FC) protocols at 100 Oe magnetic field. Measurements were performed along both the crystallographic directions $H \parallel c$ and $H \perp c$, designated as longitudinal susceptibility ($\chi_{\parallel}$) and the transverse susceptibility ($\chi_{\perp}$), as is shown in Fig.6.4. A

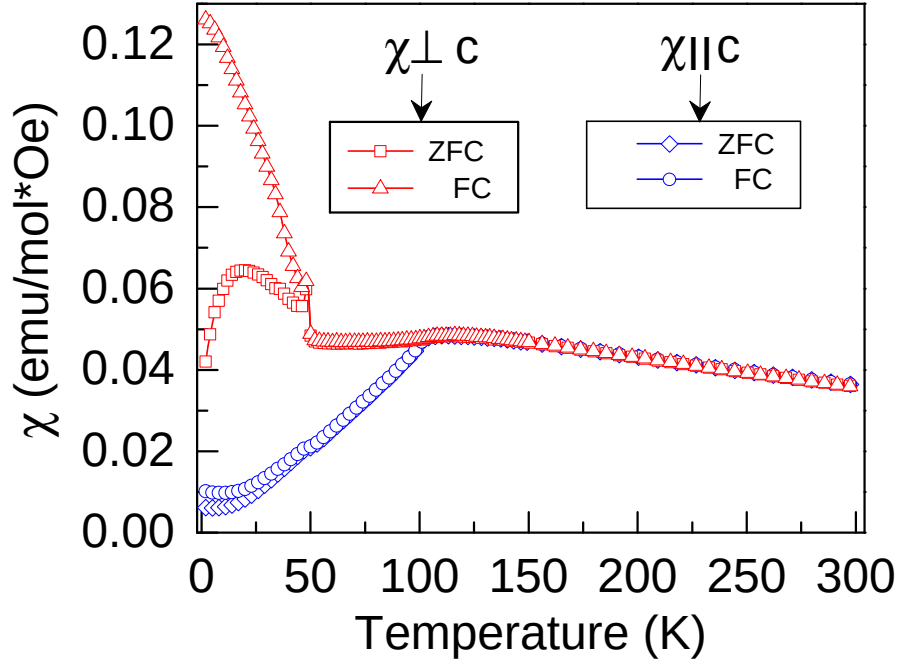


Figure 6.4: The main panel depicts temperature dependent DC magnetic measurement performed in ZFC and FC protocol at 100 Oe magnetic field along different orientations of the crystal.

broad anomaly is observed at $T_N \approx 110\text{K}$, which is associated with the onset of anti-ferromagnetic order and in agreement with earlier report for polycrystalline specimens of $\text{Mn}_4\text{Ta}_2\text{O}_9$ [183]. Upon further cooling, the magnetization along the ab plane is relatively temperature independent, whereas that along the crystallographic c axis drops rapidly just below the anti-ferromagnetic transition. This implies that the Mn^{2+} moments are aligned along the crystallographic c axis. Recent measurements on single crystal specimens of $\text{Mn}_4\text{Nb}_2\text{O}_9$ have exhibited similar signatures [186].

Interestingly, on further reducing the temperature, an additional transition appears in the transverse susceptibility $\chi_{\perp}$ at $\approx 48\text{ K}$ as depicted in Fig. 6.4. This feature is absent in the longitudinal susceptibility $\chi_{\parallel}$ and possibly corresponds to a weak-ferromagnetic phase arising from the well known antisymmetric Dzyaloshinskii-Moriya interaction [187, 188]. Upon further cooling, the transverse susceptibility increases till 19 K and then exhibits

a downturn. On the other hand, the longitudinal susceptibility decreases monotonically until 19 K below which it remains relatively temperature independent. This anomalous low temperature behavior of $\chi_\perp$ and $\chi_\parallel$ below 19K is reminiscent of that observed in single crystals of the brownmillerite $\text{Ca}_2\text{Fe}_2\text{O}_5$ [189], where a regime of anisotropic weak ferromagnetism (below 150K) was observed within the antiferromagnetic regime ($T_N = 750\text{K}$). Hence, the magnetic measurements performed along the different crystallographic axes exhibits highly anisotropic behavior and a richer magnetic phase diagram of $\text{Mn}_4\text{Ta}_2\text{O}_9$ comparable to the other members of this family.

Magnetic isotherms measured along the two different crystallographic orientations as a function of temperature reveals the presence of a metamagnetic transition. $M - H$

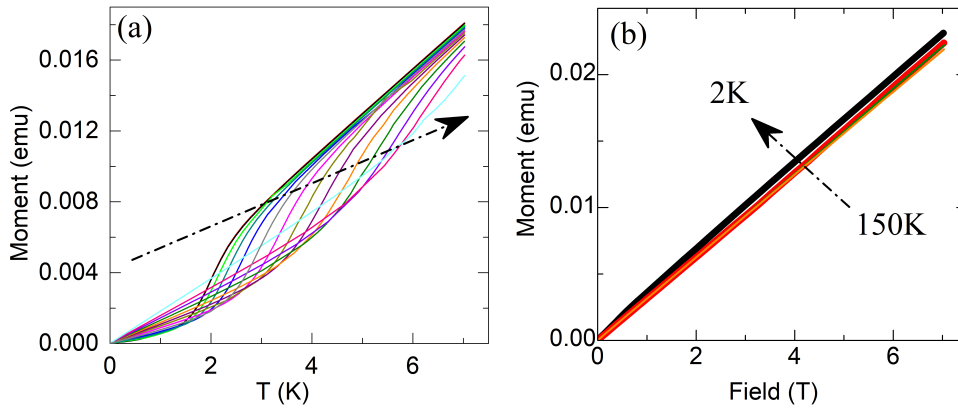


Figure 6.5: (a) $M-H$ isotherm measured along $H \parallel c$ and (b) $H \perp c$. A field induced transition is evidenced from the slope change in the measured magnetization along c axis, which is absent along perpendicular to c axis.

isotherms measured with $H \parallel c$ shows a field induced transition as evidenced by a change of slope [Fig.6.5(a)], whereas this feature is absent in the $H \perp c$ isotherms [Fig.6.5(b)]. The spin flop transition is clearly observed in the form of a peak [Fig.6.6(a)] in dM/dH vs H . The evolution of the critical field (H_c) of this field induced transition with temperature was observed to as T^2 [Fig.6.6(b)]. This was also observed in the closely related $\text{Fe}_4\text{Ta}_2\text{O}_9$ system and ascribed to a spin flop transition within the AFM where after a critical magnetic field, the magnetization rotates perpendicular to the magnetic easy axis provided the magneto crystalline anisotropy is weak enough [190, 191]. The observed T^2 dependence of H_c is in broad agreement with Yamada's theory [163], which was formulated to explain field driven phenomena in itinerant metamagnets. However, the applicability of this theory is restricted in the case of $\text{Fe}_4\text{Ta}_2\text{O}_9$ and other insulating antiferromagnetic specimens.

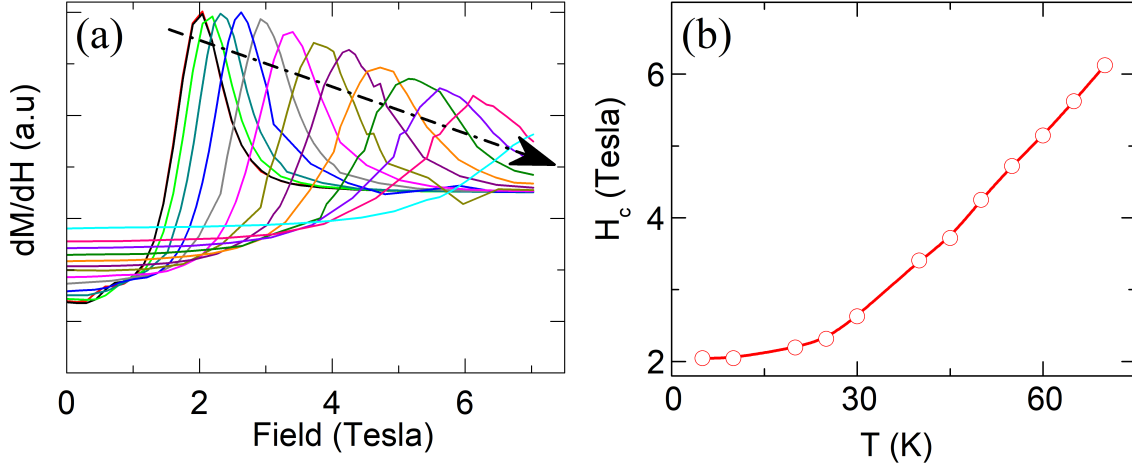


Figure 6.6: (a) dM/dH (first derivative magnetization with respect to magnetic field) of the isotherm measured along $H \parallel c$. The spin flop transitions were clearly seen in the form a sharp peak. (b) The evolution of critical field of metamagnetic transition with temperature (T) exhibit a T^2 dependence.

6.3.5 Solving magnetic structure from powder neutron diffraction

Comparison of the neutron diffraction patterns recorded in the paramagnetic (135 K) and the magnetically ordered states (1K) confirm that the magnetic Bragg contributions are restricted to the nuclear peak positions only. A pronounced enhancement of intensity is

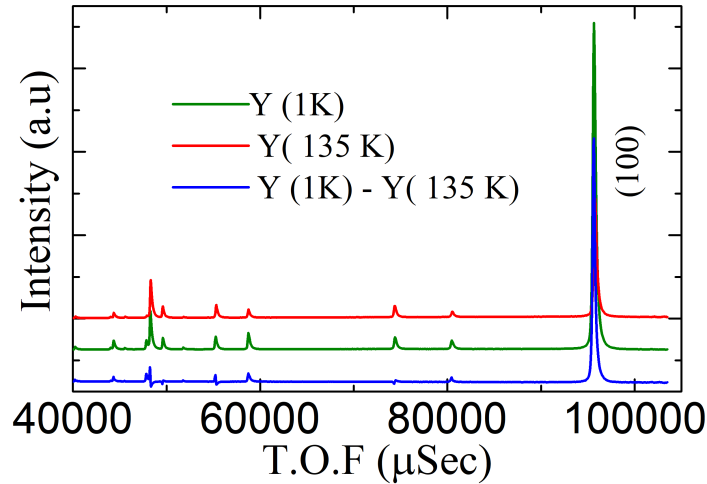


Figure 6.7: The Time of Flight (T.O.F) neutron diffraction data in paramagnetic state (135 K) and magnetically ordered state at 1K exhibit the magnetic bragg contribution appear only in the nuclear peak position with a sharp enhancement to $[100]$ Bragg reflection.

observed for the (100) reflections within the magnetically ordered state, which is evident

from the subtraction of the diffraction pattern in the paramagnetic state (135 K) from magnetically ordered state (1K) as shown in Fig.6.7. Temperature dependence of the magnetic intensity of (100) Bragg peak has been fit (Fig.6.8(a)) by the equation 6.1.

$$I = I_0 \left(1 - \frac{T}{T_N}\right)^{2\beta} \quad (6.1)$$

From the fitting, we obtain Neel temperature $T_N = 97.41$ K and critical exponent $\beta = 0.182$. The value of the critical exponents for a two-dimensional (2D) and three-dimensional (3D) Ising models are $\beta = 0.125$ and 0.32 respectively. Hence, the nature of magnetic interactions in $\text{Mn}_4\text{Ta}_2\text{O}_9$ is intermediate to that described by the 2D and 3D Ising models. This observation is analogous to that reported for the magneto-electrics LiCoPO_4 and $\text{Co}_4\text{Nb}_2\text{O}_9$ [179, 152].

The K search program in FULLPROF suggested that the most possible propagation

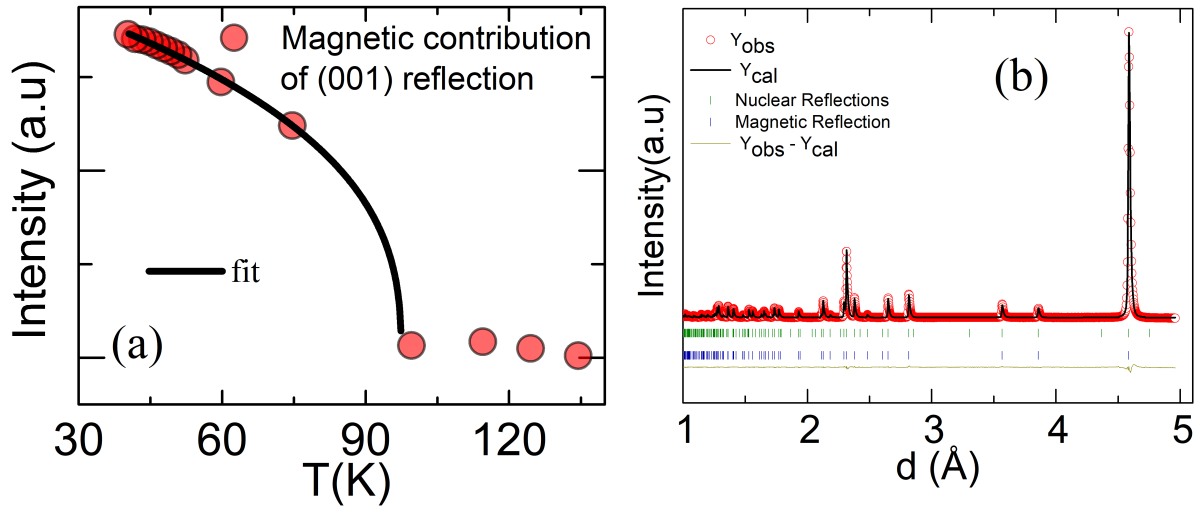


Figure 6.8: (a) Temperature dependence of magnetic contribution to the intensity of (001) reflection and solid line represent the fit using equation.4.1 (b) A Rietveld refinement including magnetic phase with Irep Γ_2 of T.O.F neutron diffraction at 1K.

vector ($\vec{K}$) down to the lowest measured temperature is (000). For symmetry analysis, a combination of axial vectors localized on 4d (for Mn1 and Mn2) have been considered and the basis functions of the irreducible representations of the wave vector group $k = (0 \ 0 \ 0)$ were tested for symmetry. The decomposition of the magnetic structure contained six possible irreducible representations (Ireps)

$$\Gamma_{mag} = \Gamma_1 \oplus \Gamma_2 \oplus \Gamma_3 \oplus \Gamma_4 \oplus 2\Gamma_5 \oplus 2\Gamma_6$$

Out of the six possible Ireps, $\Gamma_1 - \Gamma_4$ represents Mn^{2+} moments aligned along the crystallographic c axis, and Γ_5, Γ_6 represents the Mn^{2+} aligned along the ab plane. The basis vector for each Ireps are listed in Table. 6.2

Table 6.2: Basis vector of irreducible representation of Mn^{2+} with the space group $P - 3c1$, $\vec{k} = (000)$ as obtained from Basireps program of FullProf suite.

IR_S	Mn1	Mn2	Mn3	Mn4
Γ_1	$(0, 0, 1)$	$(0, 0, -1)$	$(0, 0, 1)$	$(0, 0, -1)$
Γ_2	$(0, 0, 1)$	$(0, 0, -1)$	$(0, 0, -1)$	$(0, 0, 1)$
Γ_3	$(0, 0, 1)$	$(0, 0, 1)$	$(0, 0, 1)$	$(0, 0, 1)$
Γ_4	$(0, 0, 1)$	$(0, 0, 1)$	$(0, 0, -1)$	$(0, 0, -1)$
Γ_5	$\begin{pmatrix} 1, 0, 0 \\ -0.58, -1.15, 0 \end{pmatrix}$	$\begin{pmatrix} 0, 0, 0 \\ 0, 0, 0 \end{pmatrix}$	$\begin{pmatrix} -1, 0, 0 \\ 0.58, 1.15, 0 \end{pmatrix}$	$\begin{pmatrix} 0, 0, 0 \\ 0, 0, 0 \end{pmatrix}$
	$\begin{pmatrix} 0, 0, 0 \\ 0, 0, 0 \end{pmatrix}$	$\begin{pmatrix} 0, 1, 0 \\ 1.15, 0.58, 0 \end{pmatrix}$	$\begin{pmatrix} 0, 0, 0 \\ 0, 0, 0 \end{pmatrix}$	$\begin{pmatrix} 0, -1, 0 \\ -1.15, -0.58, 0 \end{pmatrix}$
	$\begin{pmatrix} 0, 0, 0 \\ 0, 0, 0 \end{pmatrix}$	$\begin{pmatrix} 0, 1, 0 \\ -1.15, -0.58, 0 \end{pmatrix}$	$\begin{pmatrix} 0, 0, 0 \\ 0, 0, 0 \end{pmatrix}$	$\begin{pmatrix} -0, -1, 0 \\ 1.15, 0.58, 0 \end{pmatrix}$
	$\begin{pmatrix} 1, 0, 0 \\ 0.58, 1.15, 0 \end{pmatrix}$	$\begin{pmatrix} 0, 0, 0 \\ 0, 0, 0 \end{pmatrix}$	$\begin{pmatrix} -1, 0, 0 \\ -0.58, -1.15, 0 \end{pmatrix}$	$\begin{pmatrix} 0, 0, 0 \\ 0, 0, 0 \end{pmatrix}$
Γ_6	$\begin{pmatrix} 1, 0, 0 \\ -0.58, -1.15, 0 \end{pmatrix}$	$\begin{pmatrix} 0, 0, 0 \\ 0, 0, 0 \end{pmatrix}$	$\begin{pmatrix} 1, 0, 0 \\ -0.58, -1.15, 0 \end{pmatrix}$	$\begin{pmatrix} 0, 0, 0 \\ 0, 0, 0 \end{pmatrix}$
	$\begin{pmatrix} 0, 0, 0 \\ 0, 0, 0 \end{pmatrix}$	$\begin{pmatrix} 0, 1, 0 \\ 1.15, 0.58, 0 \end{pmatrix}$	$\begin{pmatrix} 0, 0, 0 \\ 0, 0, 0 \end{pmatrix}$	$\begin{pmatrix} 0, 1, 0 \\ 1.15, 0.58, 0 \end{pmatrix}$
	$\begin{pmatrix} 0, 0, 0 \\ 0, 0, 0 \end{pmatrix}$	$\begin{pmatrix} 0, 1, 0 \\ -1.15, 0 - 0.58, 0 \end{pmatrix}$	$\begin{pmatrix} 0, 0, 0 \\ 0, 0, 0 \end{pmatrix}$	$\begin{pmatrix} 0, 1, 0 \\ -1.15, -0.58, 0 \end{pmatrix}$
	$\begin{pmatrix} 1, 0, 0 \\ 0.58, 1.15, 0 \end{pmatrix}$	$\begin{pmatrix} 0, 0, 0 \\ 0, 0, 0 \end{pmatrix}$	$\begin{pmatrix} 1, 0, 0 \\ 0.58, 1.15, 0 \end{pmatrix}$	$\begin{pmatrix} 0, 0, 0 \\ 0, 0, 0 \end{pmatrix}$

Refinement with Γ_2 gave the best fit to the magnetic contribution of our diffraction data. Rietveld refinement of the diffraction data at 1K with Ireps Γ_2 is depicted in Fig.6.8(b), and represents a ferromagnetic chain of Mn spins coupled antiferromagnetically along the c axis as shown in Fig.6.9 (a). A detailed description of the determination of magnetic structure of $\text{Mn}_4\text{Ta}_2\text{O}_9$ from the TOF Neutron data is presented in APPENDIX-I of this thesis. The magnetic structure which we have inferred is in sharp contrast to that described earlier for the isostructural member $\text{Co}_4\text{Nb}_2\text{O}_9$ where the spins are aligned within the ab plane with a canting either along the c axis [152] or in the ab plane [182]. However,

the weak ferromagnetic component observed in our bulk magnetic measurement perpendicular to the crystallographic c axis is not clearly discernible from the powder neutron diffraction data.

Assuming the spin only moment value with the orbital moment (L) fully quenched, the calculated value of effective moment of (Mn^{2+} , d^5) are tabulated in Table 6.3. The mag-

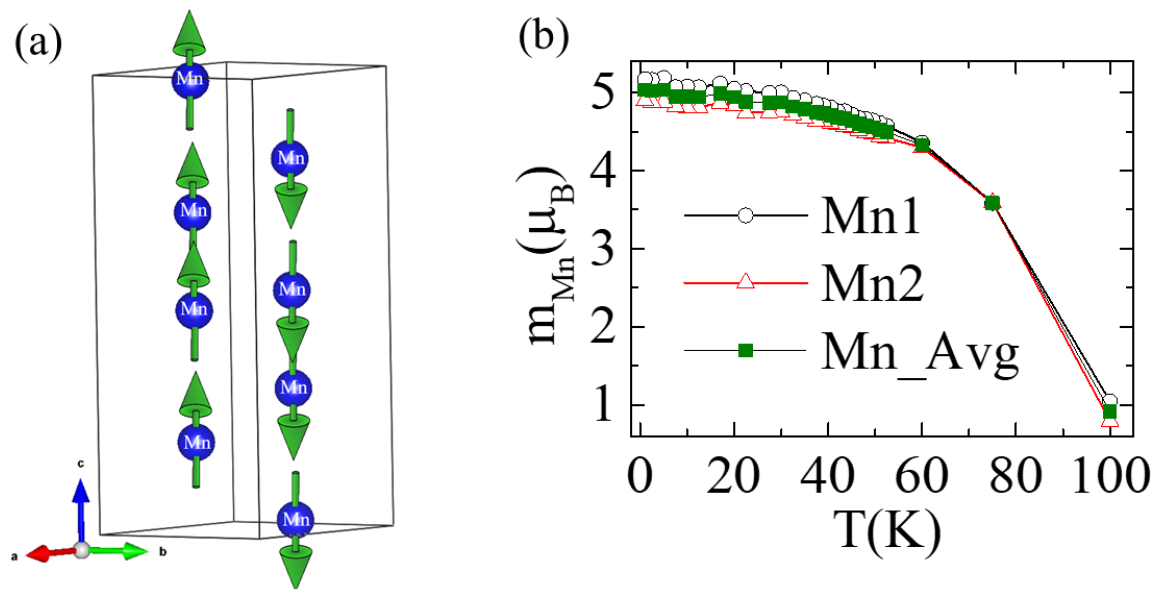


Figure 6.9: (a) Magnetic structure of $\text{Mn}_4\text{Ta}_2\text{O}_9$ at 1K as obtained from the Rietveld refinement of T.O.F diffraction data with Ireps Γ_2 . The structure comprises of ferromagnetic chains of Mn^{2+} ions aligned along the trigonal c axis, coupled antiferromagnetically (b) The refined magnetic moments of Mn^{2+} for Mn1 and Mn2 sites.

Table 6.3: Spin only moment of Fe^{3+} ($3d^5$) in high and low spin states under an octahedral crystal field.

	Spin state	Electronic configuration	Calculated Spin only moment (S _μ / Fe ²⁺)						
Mn ²⁺ (3d ⁵)	Low Spin	<table><tr><td></td><td></td><td><i>e_g</i></td></tr><tr><td>↑↓</td><td>↑↓</td><td>↑</td></tr></table> <i>t_{2g}</i>			<i>e_g</i>	↑↓	↑↓	↑	1.73
			<i>e_g</i>						
↑↓	↑↓	↑							
	High Spin	<table><tr><td>↑</td><td>↑</td><td><i>e_g</i></td></tr><tr><td>↑</td><td>↑</td><td>↑</td></tr></table> <i>t_{2g}</i>	↑	↑	<i>e_g</i>	↑	↑	↑	5.91
↑	↑	<i>e_g</i>							
↑	↑	↑							

netic moments of Mn^{2+} for Mn1 and Mn2 as obtained from the Reitveld veld refinement are $5.1(6) \mu_B$ and $4.8(8) \mu_B$ respectively as depicted in Fig. 6.9(b), and they are close to the high-spin $S = 5/2$ state for Mn^{2+} .

6.3.6 Electric field dependent magnetic measurements

Magnetic field dependent dielectric and pyroelectric measurements were typically used to identify the presence of magneto-electric coupling. The cross coupling between magnetic and polar orders can also be dictated by relatively underutilized electric field (E) dependent magnetization (M) measurement. We have performed time dependent magnetic measurements under a square wave electric field (of 20.8kV/cm) in the $E \parallel c$ and the $E \perp c$ crystallographic orientations. Here, the sample was first electromagnetically poled ($H \parallel E$, with $H = 2\text{T}$ and $E = 20.8\text{kV/cm}$) down to 40K, after which the electric and magnetic fields were switched off. The magnetization was then measured at a constant magnetic field of 500 Oe in the presence of a periodic square wave electric field of 20.8 kV/cm to monitor the change in magnetization as a function of the applied electric field. The influence of periodic electric field on the magnetization along both the crystallographic axes is depicted in Fig.6.10.(a) and (b). The magnetization is modulated

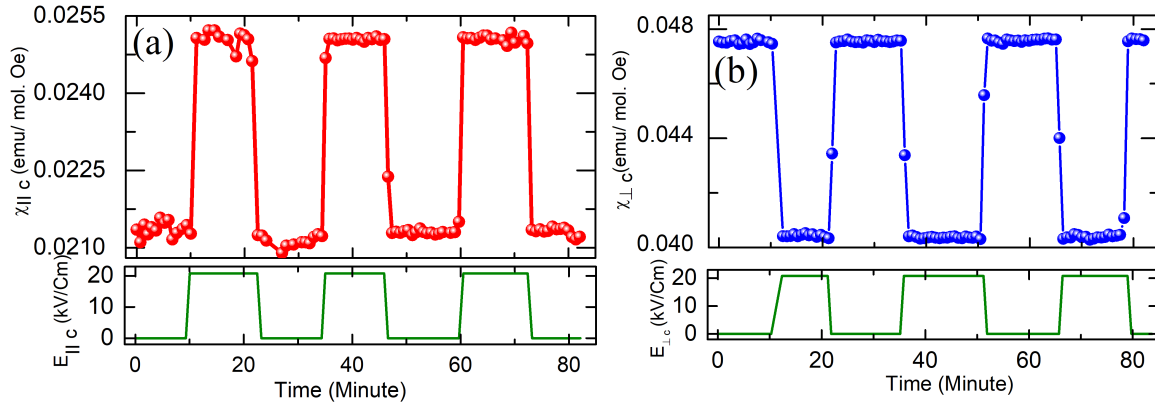


Figure 6.10: Time dependent magnetic measurement performed after electromagnetic poling at 40K under periodic square electric pulse with (a) $H \parallel c$ and (b) $H \perp c$. Measured moment along parallel to c axis is enhanced in presence of electric field, which is suppressed perpendicular to c axis. Such manipulation of magnetization by electric field identify a telltale signature of magnetoelectric coupling in single crystal $\text{Mn}_4\text{Ta}_2\text{O}_9$.

as a function of the applied electric field, clearly reinforcing the presence of strong magnetoelectric coupling in $\text{Mn}_4\text{Ta}_2\text{O}_9$. Interestingly, this magnetoelectric coupling is also observed to be highly anisotropic, with the magnetization increasing on the application of the electric field along the c axis, whereas it decreases when the electric field is applied perpendicular to it. The absence of experimental artifacts were confirmed by performing the same measurement on a slab of the insulating paramagnet Er_2O_3 , where no such change in magnetization was observed on the application of an electric field.

The magnetoelectric effect in the prototypical magnetoelectric Cr_2O_3 is known to be highly anisotropic [14]. The coupling along the trigonal c axis ($\alpha_{\parallel}$) and that perpendicular to it ($\alpha_{\perp}$) is reported to exhibit different temperature dependencies, with $\alpha_{\parallel}$ also exhibiting a change of sign at $\approx 100\text{K}$. The magnetoelectric response in an antiferromagnet with two sublattices can be ascribed to a combination of effects arising from the single ion anisotropy, the Lande g factor, and the symmetric and antisymmetric magnetic exchange interactions [199]. The effect on magnetization due to the application of an electric field may occur due to one or more of these contributory factors which are then reflected in the form of a change (magnitude/ direction) in magnetization. For instance, in the case of Cr_2O_3 , the temperature dependence of $\alpha_{\parallel}$ has been suggested to arise as a result of the modification of the intrasublattice magnetic exchange due to an applied electric field at higher temperatures, whereas the low temperature behavior is primarily governed by the electric field induced shift in g factor. On the other hand, the temperature dependence of $\alpha_{\perp}$ was attributed to the effect of electric field on the single ion anisotropy term [200, 201]. Prior report of magnetoelectric response of the Co based members of this family exhibit a number of distinctive features. For instance, in the honeycomb $\text{Co}_4\text{Nb}_2\text{O}_9$, the sweeping of magnetic field by an angle ϕ consequences in rotation of the electric polarization by an angle -2ϕ due to a magnetic field driven rotation of the spins [202, 203]. It has also been suggested that the electric polarization is a vector addition of the effective magnetoelectric contributions from two nonequivalent magnetic sublattices in $\text{Co}_4\text{X}_2\text{O}_9$ ($\text{X}=\text{Ta}, \text{Nb}$). The anisotropic and a smaller value of the magnetic field induced electric polarization has been suggested to arise due to a partial compensation of these two contribution [156]. However, the case of $\text{Mn}_4\text{Ta}_2\text{O}_9$ is slightly different, since our data indicates that its magnetic structure (comprised of antiferromagnetically coupled ferromagnetic chains along the c axis) is different from that of Cr_2O_3 as well as the Co based members of this family of honeycomb magnets. An added complication is the presence of a weak ferromagnetic phase below 50K which has not been observed in the other members of this family till date. The fact that we observe an electric field induced decrease in magnetization in the $H \perp c$ direction where this weak ferromagnetic component is observed, leads us to speculate that the our observations could be a consequence of the anisotropic response of the antisymmetric Dzyaloshinskii-Moriya interaction on the application of an electric field. However, more comprehensive experiments, monitoring the temperature evolution of $\alpha_{\parallel}$ and $\alpha_{\perp}$, as well as the effect of electric fields on the crystallographic and magnetic structures would be required to

understand the microscopic mechanisms responsible for the magnetoelectric response in $\text{Mn}_4\text{Ta}_2\text{O}_9$.

6.4 Conclusions

We report on the temperature dependent DC magnetization as measured on a single crystal of the magneto electric $\text{Mn}_4\text{Ta}_2\text{O}_9$, which reveals that the magnetic susceptibility parallel and perpendicular to the trigonal c axis is anisotropic. Our magnetic susceptibility data indicate that the magnetic moments are aligned along the crystallographic c axis. This is also confirmed by the magnetic structure obtained from the Rietveld refinement of T.O.F neutron diffraction data, which indicates that the magnetic structure comprises of ferromagnetic chains of Mn^{2+} spins aligned along the $[001]$ axis and is in contrast to that observed in the closely related isostructural $\text{Co}_4\text{Nb}_2\text{O}_9$ system. A feature in the magnetic susceptibility with magnetic field perpendicular to the c axis is observed at ≈ 48 K and this is absent when the magnetic field is parallel to c axis. Rotation of the easy axis of magnetization is also observed below 19K, a case similar to that observed in brownmillerite candidate $\text{Ca}_2\text{Fe}_2\text{O}_5$. Time dependent magnetic measurements performed under a square electric pulse indicate that the magnetoelectric response parallel and perpendicular to the trigonal c axis have different signs. Our observations unveil $\text{Mn}_4\text{Ta}_2\text{O}_9$ system as a valuable addition in the quest for understanding the interplay between magnetism and electric polarization in magnetoelectric honeycomb lattices.

Chapter 7

Conclusions and scope of future work

In this chapter conclusions of the complete work presented in this thesis are summarized. Possible methods and avenues for future work are also highlighted.

- Dielectric and pyroelectric measurement setups in a Closed Cycle Refrigerator (CCR) have been developed. A sample holder for dielectric measurements in parallel plate configuration was designed and fabricated. Several features like use of a spring to take care of the mechanical vibration originating from the refrigerator of CCR and a lesser weight of the sample holder to attain lowest possible temperature at the sample position were incorporated. Both the measurements were automated using the LabVIEW program.
- Dielectric and Pyroelectric measurements in the presence of a magnetic field (upto ± 7 Tesla) were performed in the MPMS-XL (Quantum Design) using a Manual Insertion Utility Probe (MIUP).
- Using MPMS-XL Manual Insertion Utility Probe, electric field dependent magnetic measurement were performed on a single crystal specimen of $\text{Mn}_4\text{Ta}_2\text{O}_9$ to study magnetoelectric coupling.
- The polycrystalline specimens of the Swedenborgite $\text{Dy}_{1-x}\text{Ca}_x\text{BaCo}_4\text{O}_7$ ($x= 0$ to 1) series were investigated using X-ray diffraction, magnetization and dielectric measurements. Rietveld refinement of the powder X-ray diffraction pattern has shown that $\text{DyBaCo}_4\text{O}_7$ crystallizes in the Trigonal $P31c$ space group. Systematic doping causes a structural transition from a high symmetry trigonal $P31c$ to a low

symmetry orthorhombic $Pbn\bar{2}_1$ structure at the doping concentration $x=0.4$. Interestingly, all the specimens crystallizing in the orthorhombic structure exhibit a structural transition to high symmetry Trigonal $P\bar{3}1c$ at elevated temperatures. One of the distinguishing features in the RBaCo_4O_7 ($\text{R}=\text{Rare earth ions, Ca}^{2+}$) is that temperature at which this structural transition occurs is observed to scale linearly with the mean ionic radius of the R site ion. However, such a quasilinear relationship is violated for $\text{R}=\text{Ca}^{2+}$ comprising an equal number of Co^{2+} and Co^{3+} , indicating that charge ordering could possibly influence the structural transition. The ZFC-FC magnetization exhibits a large paramagnetic background arising from Dy^{3+} ions that apparently masks the magnetic transition appearing from the cobalt sublattice. Using Thermo-remanent Magnetization (TRM) measurements, we have identified the magnetic ordering temperatures of the solid solution of the series $\text{Dy}_{1-x}\text{Ca}_x\text{BaCo}_4\text{O}_7$. Finally, we chart out the phase diagram of the $\text{Dy}_{1-x}\text{Ca}_x\text{BaCo}_4\text{O}_7$ series. $\text{SrBaCo}_4\text{O}_7$, a new member of Swdenborgite family has been synthesized successfully by the solid state reaction route. We have solved its structure using DICVOL06 and LeBail profile refinement of powder X-ray diffraction data. This system stabilizes in the orthorhombic $pbam$ space group. Detailed magnetic and thermodynamic study reveals multiple phase transitions as a function of temperature.

- Polycrystalline specimen of $\gamma\text{-Fe}_2\text{WO}_6$ has been prepared using the solid state ceramic route. Crystallizing in the centrosymmetric $Pbcn$ space group, this particular polymorph exhibits a number of different magnetic transitions, all of which are seen to exhibit a finite magneto-dielectric coupling. DC resistivity measurements performed across the observed transitions conclusively rules out the possible contribution of magneto-resistance and implies that the observed magneto-dielectricity is intrinsic to the system. The presence of a low temperature magnetic glass like state is also inferred from aging and magnetic viscosity measurements. Also reflected in the frequency dependent dielectric measurements, these signatures possibly arises as a consequence of the oxygen non-stoichiometry, which promotes an inhomogeneous magnetic and electronic ground state.
- We revealed the corundum member $\text{Fe}_4\text{Ta}_2\text{O}_9$ as a new type-II multiferroic with coupled magnetic and ferroelectric states. Polycrystalline specimen of $\text{Fe}_4\text{Ta}_2\text{O}_9$ were prepared using encapsulation synthesis technique, employing a sealed quartz ampoule. This system crystallized in the Trigonal $P - 3c1$ symmetry and was

seen to exhibit a series of magnetic transitions, many of which are associated with the emergence of ferroelectric order. Pyroelectric measurements performed under zero magnetic field exhibits the appearance of spontaneous polarization at $T_1=80\text{K}$ (AFM1 FE1) and $T_2=60\text{K}$ (AFM2 FE2) concomitant with the observed magnetic transitions. On cooling further, a field induced multiferroic state is observed (AFM3 FE3) and within this state, a metamagnetic (spin-flop) transition appears with no discernible influence on this polar state (SF- AFM3 FE3). The dielectric and magnetic measurement further evidenced a transition $\approx 5\text{K}$, which remains robust under an applied magnetic field. We suggest that the observed properties arise due to an effective reduction in the dimensionality of the magnetic lattice, with the magnetically active Fe^{2+} ions preferentially occupying a quasi 2D buckled honeycomb structure. The low temperature H - T phase diagram of $\text{Fe}_4\text{Ta}_2\text{O}_9$ reveals a rich variety of coupled magnetic and ferroelectric phases, in similarity with that observed in the distorted Kagome systems.

- We report on the temperature dependent DC magnetization as measured on a single crystal of the magneto electric $\text{Mn}_4\text{Ta}_2\text{O}_9$, which reveals that the magnetic susceptibility parallel and perpendicular to the trigonal c axis is anisotropic. Our magnetic susceptibility data indicate that the magnetic moments are aligned along the crystallographic c axis. This is also confirmed by the magnetic structure obtained from the Rietveld refinement of T.O.F neutron diffraction data, which indicates that the magnetic structure comprises of ferromagnetic chains of Mn^{2+} spins aligned along the $[001]$ axis and is in contrast to that observed in the closely related isostructural $\text{Co}_4\text{Nb}_2\text{O}_9$ system. A feature in the magnetic susceptibility with magnetic field perpendicular to the c axis is observed at $\approx 48\text{K}$ and this is absent when the magnetic field is parallel to c axis. Rotation of the easy axis of magnetization is also observed below 19K , a case similar to that observed in the brownmillerite $\text{Ca}_2\text{Fe}_2\text{O}_5$. Time dependent magnetic measurements performed under a square electric pulse indicate that the magnetoelectric response parallel and perpendicular to the trigonal c axis have different signs. Our observations unveil $\text{Mn}_4\text{Ta}_2\text{O}_9$ system as a valuable addition in the quest for understanding the interplay between magnetism and electric polarization in magnetoelectric honeycomb lattices.
- Transition metal ions residing in geometrically frustrated structural motifs are promising avenue for exploring magnetoelectric coupling. Investigation of the magnetic structure of several specimens presented in this thesis would be useful in

better understanding of these systems. Dielectric setup designed during the course of work could be extended for nonlinear dielectric measurement where higher harmonics of the response signal is measured. Such measurement would be useful for investigating magnetoelectric coupling in glassy systems, known as multiglass where the influence of disorder, geometrical frustration and other contributory factors could lead to the stabilization of a frozen polar and magnetic state. Study on single crystalline specimens of the reported phase pure polycrystalline samples in this thesis would be educative. We have demonstrated the use of electric field dependent magnetic measurements for exploring magnetoelectric coupling on a single crystal specimen of $\text{Mn}_4\text{Ta}_2\text{O}_9$ and the same could be extended for other reported specimens. The study of magnetoelectric coupling in the other members of the geometrically frustrated Swedenborgite members and the corundum family $\text{A}_4\text{X}_2\text{O}_9$ ($\text{A}=\text{Fe}, \text{Co}, \text{Mn}, \text{Ni}, \text{Cu}$ and $\text{X}=\text{Ta}, \text{Nb}$) would be interesting. Often such frustrated system manifests in a highly degenerate ground state instead of a single stable ground state. The study of these specimens under high magnetic field ($> 7 \text{ T}$) would shed light on new field induced phases and reveal the role of symmetry in tailoring the magnetoelectric interaction.

Chapter 8

APPENDIX-I

Solving the magnetic structure of $\text{Mn}_4\text{Ta}_2\text{O}_9$

8.1 Summary

Here, the details of the steps involved in solving the magnetic structure from Neutron powder diffraction pattern using Fullprof Suite toolbar are explained. The important steps in determining the magnetic structure are summarized in the flowchart as shown in Fig.8.1 and will be discussed explicitly in the subsequent sections.

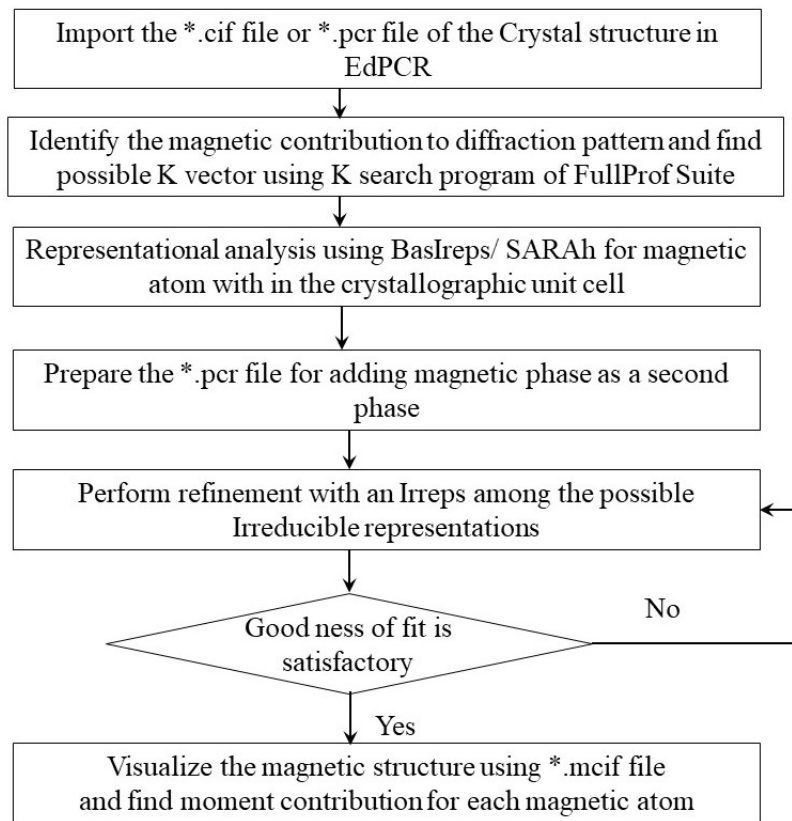


Figure 8.1: Flowchart of solving magnetic structure using FullProf suite toolbar.

8.2 Introduction

The magnetic structure of materials could vary from being as simple as a ferromagnetic/ antiferromagnet [204] (8.1(a) and (b)) ordering to a complex spin configuration with multiple propagation (k) vectors, e.g. a Skyrmion lattice of MnSi with 4-k structure (8.1(c)) [205]. The intensity of a Bragg reflection for an unpolarized neutron is:

$$I_h = N_h N_h^* + M_{\perp h} \cdot M_{\perp h}^* \quad (8.1)$$

The magnetic structure factor M_h is expressed as:

$$M_{\perp h} = e \times (M(H) \times e) = M(h) - e(e \cdot M(h)) \quad (8.2)$$

e is the unit vector along the scattering vector $h=H+k$, where H is reciprocal lattice vector and k is the propagation vector. The basis of the elastic magnetic scattering by neutron and its relation with magnetic structure explained in details in this references [206, 207, 208]. Here the aim is to describe the treatment of the T.O.F powder neutron

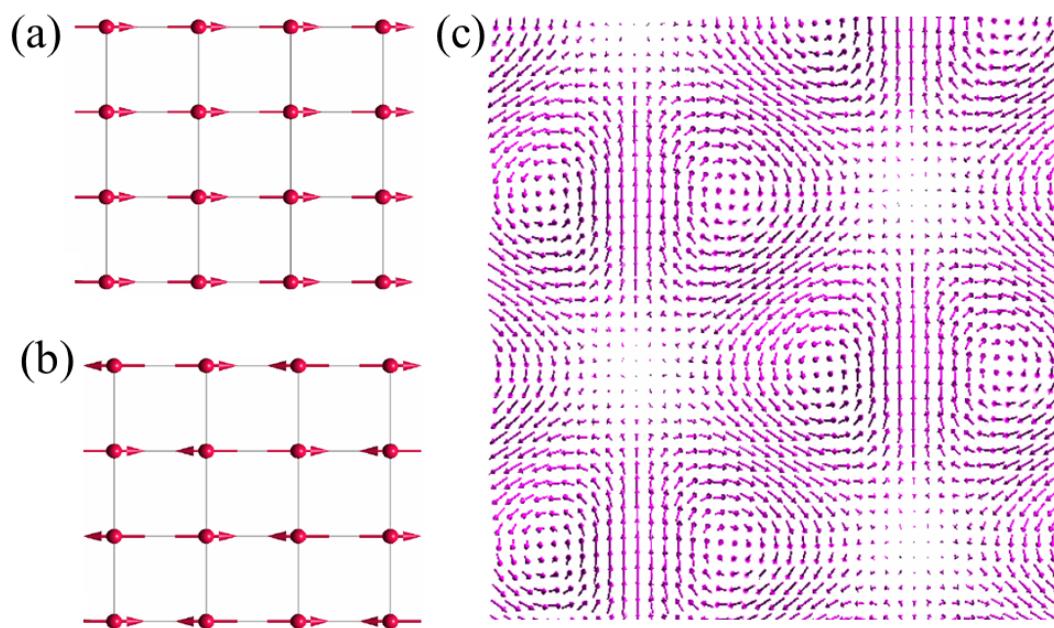


Figure 8.2: Magnetic moments/ spin of a ferro and antiferromagnetic materials in a periodic (a) parallel and (b) Antiparallel fashion (c) A nontrivial magnetic structure of Skyrmion lattice in MnSi, where multiple combinations of propagation vectors describe the magnetic structure.

data for exploring the magnetic structure of $\text{Mn}_4\text{Ta}_2\text{O}_9$ using FullProf Suite toolbar. The early development of magnetic structure determination based on conventional Shubnikov groups [209] and representation analysis [146] was an essential step in the middle of the seventies for solving the magnetic structure. The steps described here is applicable in general for treating any powder neutron diffraction data, except the instrumental and profile parameters (peak shape/FWHM) which will vary depending upon the diffraction configuration of the collected data. For instance, in the case of treating our T.O.F data a *"T.O.F. Convolution pseudo-Voigt with back-to-back exponential functions."* profile functions was used whereas for diffraction profile collected as a function of 2θ , typically a *"Pseudo-Voigt/ Thompson-Cox-Hastings pseudo-Voigt convoluted with axial divergence asymmetry function"* profile functions are typically used. The method adopted for solving magnetic structure of $\text{Mn}_4\text{Ta}_2\text{O}_9$ is by the analysis of the irreducible representations of the propagation vector group and their associated basis functions [146, 210, 211, 212, 213]. The theoretical background of describing a magnetic structure is discussed in the section 2.12 of chapter 2 of the thesis.

Prerequisite knowledge of the structural refinement is necessary before analysis of the neutron data. The crystal structure in the paramagnetic state is determined by performing a Rietveld refinement either on X-ray diffraction pattern or Neutron diffraction data

collected above the magnetic ordering temperature ($T > T_N$ or T_C) and the atomic positions of the magnetic atom, relevant structural parameters were determined. A detailed description of the several functions/parameters used during a structural or magnetic refinement and their corresponding flag value in the PCR file (input control file for running the FULLPROF program) could be found in the manual of Fullprof program [214]. However, a bad input in the respective refined parameter value would either end up in a divergence in the refinement or ambiguity in the refined parameter values.

8.3 Steps for determining the magnetic structure

A Rietveld method for magnetic structure determination would be successful only when a starting model is good. A magnetic structure is completely described by:

1. Propagation vector $\mathbf{k}$
2. Fourier components S_{kj} (is a complex vector) of each j th magnetic atom with the wave vector $\mathbf{k}$.

The magnetic moment can be expressed as:

$$m_{lj} = \sum_k S_{kj} \exp(-2\pi i \mathbf{k} \cdot \mathbf{R}_l) \quad (8.3)$$

where, l is index corresponding to a direct lattice point and j denotes the Wyckoff site of

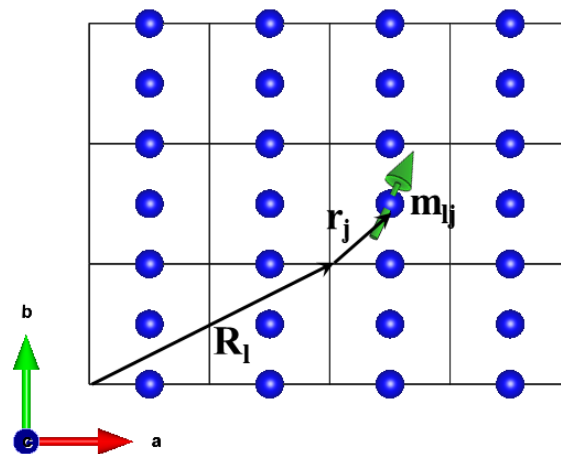


Figure 8.3: Describing the moment m_{lj} at the l th point in periodic direct lattice of the j th atom.

the atom at $\mathbf{r}_j$ expressed as $\mathbf{R}_{lj} = \mathbf{R}_l + \mathbf{r}_j$, as illustrated in Fig.8.3

However, since the magnetic moment is a real quantity, the complex Fourier components must satisfy the relation $S_{kj} = -S_{jk}^*$. The steps for solving magnetic structure using the FullProf Suite program (version May, 2016) are described in the following sections.

8.3.1 Identifying the k vector

The K_SEARCH program from FullProf Suite toolbar (FP_s) was used for calculating k vector. The k vector from a diffraction profile is calculated in this program by assigning the satellite peak of the magnetic contribution to the diffraction pattern. $\text{Mn}_4\text{Ta}_2\text{O}_9$ exhibits magnetic ordering at (T_N) 105K as determined from bulk DC magnetization measurement. Time of flight (T.O.F) Neutron diffraction data were collected both below

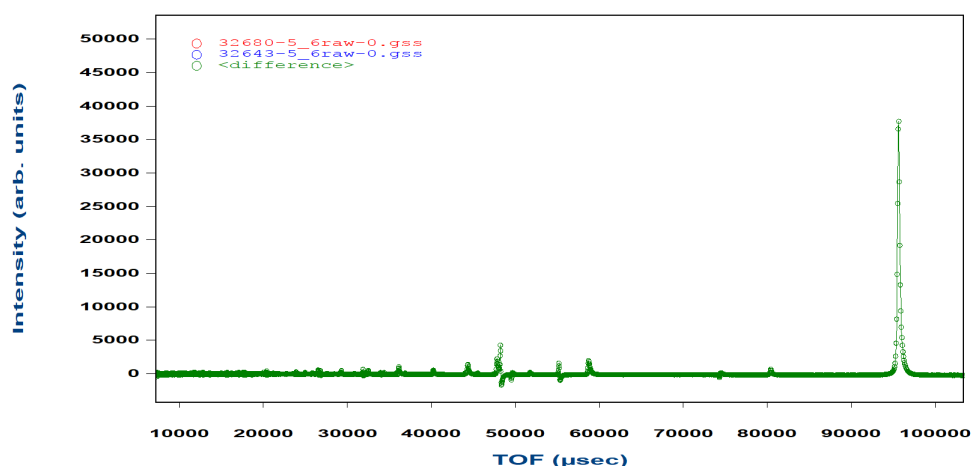


Figure 8.4: Magnetic contribution to the Neutron diffraction profile at 1K in $\text{Mn}_4\text{Ta}_2\text{O}_9$. The magnetic contribution to the diffraction pattern is obtained by subtracting the diffraction profile collected at paramagnetic state (135K) from the same in magnetically ordered state (1K)

and above the magnetic ordering temperature (T_N). The diffraction profile above T_N was subtracted from that below T_N (This can be done either in WinPLOTR-2006 [215] or Origin: Data Analysis and Graphic software [216]) for calculating the magnetic contribution to the diffraction. The difference can be calculated using WinPLOTR-2006 from the FP_s menu as $\rightarrow$ Calculation > difference after importing both the diffraction profile. The magnetic contribution to the diffraction pattern was determined by subtracting the diffraction profile at 135K from the diffraction at 1K, as shown in Fig.8.4.

However, diffraction profile collected at several temperatures has a zero shift depending upon the instrumental error and such manual subtraction is not recommended for calculating k vector. Instead, the following route was adopted for identifying k vector. First,

the PCR file in the paramagnetic state was used to refine the diffraction pattern in the magnetically ordered state. For $\text{Mn}_4\text{Ta}_2\text{O}_9$, the PCR file of the refinement performed at 135 K was used for the refinement of the diffraction profile collected at 1K, as is shown in Fig.8.5. The background parameter, zero shift and lattice parameter were refined

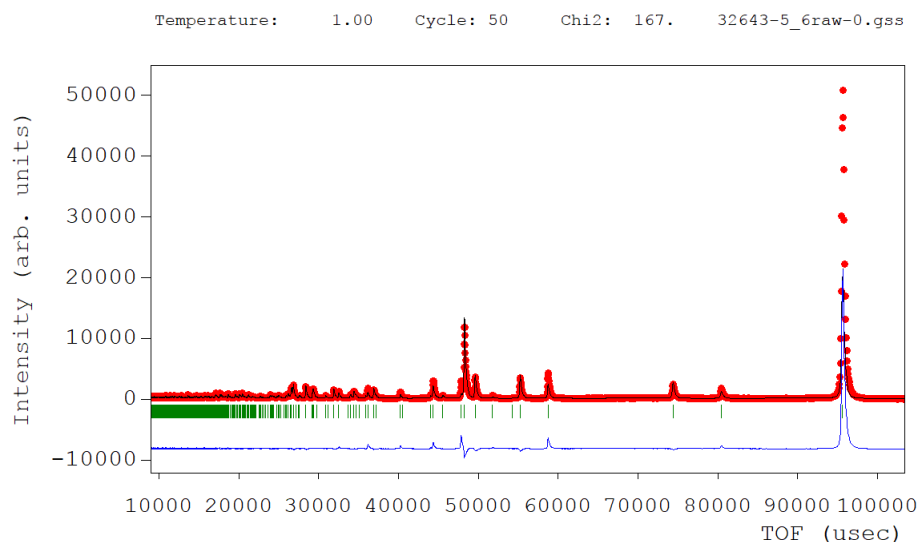


Figure 8.5: Refinement of the diffraction profile at 1K using the structural model only for designating the magnetic contribution. Instead of manual subtraction, a refinement with structural model take care of the zero shift and other instrumental parameters.

for achieving the best fit. However, a complete fit between the observed and calculated pattern cannot be achieved in this refinement due to the magnetic contribution to the intensity. In Fig.8.5, the pattern corresponding to blue curve represents the magnetic contribution. As is clearly seen, magnetic contributions are present only at the nuclear Bragg peak position (represented by Green bar in Fig.8.5) and no additional magnetic Bragg peaks are observed.

The refinement process would generate *.prf (PICS Rule file) and this was viewed with WinPLOTTR-2006 for assigning magnetic peaks (satellite) and searching for the K vector. The satellites detection in WinPLOTTR is made active from the FP_s tool bar dialog as $\rightarrow$ **peak detection** > **enable** and followed by, **calculations** > **peak detection** > **satellite detection**. This will give rise to a tool bar as shown in Fig.8.6(a). Providing specific value of peak threshold, shoulder threshold, background threshold and iteration parameters in this toolbar, the peak corresponding to magnetic contribution are assigned. For instance, a value of peak threshold= 0.1 , shoulder threshold=2.0, background threshold= 0.5 and iteration=3 select only 2 peaks, as shown in Fig.8.5.

Whereas, a value corresponding to peak threshold= 0.02 , shoulder threshold=2.5, back-

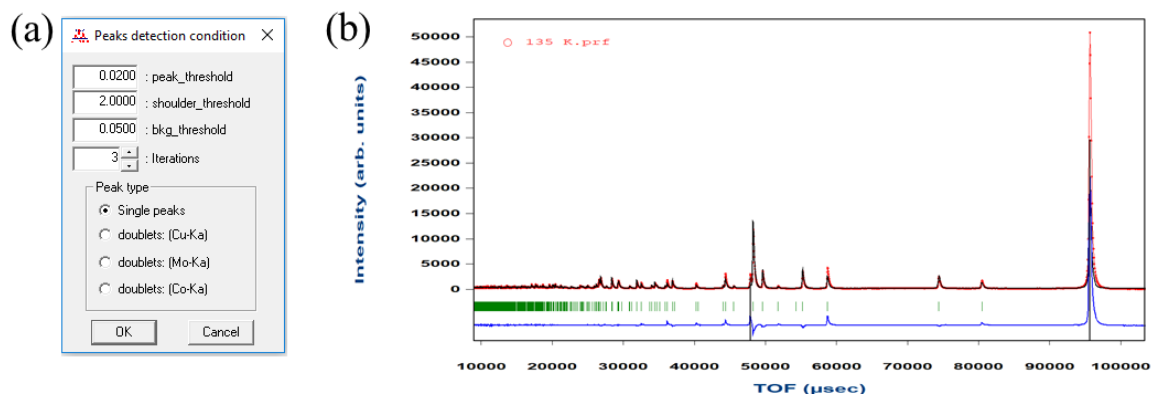


Figure 8.6: (a) The toolbar for selecting the peak solely arising from the magnetic scattering. All the peak has to be assigned carefully by selecting specific values of different input parameters in this tool bar. (b) A satellite detection for calculating K vector search of $\text{Mn}_4\text{Ta}_2\text{O}_9$. Value with Peak threshold= 0.02, shoulder threshold= 2.5, background threshold=0.01 and iteration=3 detects only 2 peaks in the diffraction pattern, as shown by two vertical line from the bottom.

ground threshold= 0.01 and iteration=3 detects 7 peaks. The same could be performed automatically following from the menu bar `calculations > peak detection > Auto detection`. However, an auto detection often includes/excludes a satellite peak. Satellite peaks could be added/removed manually using the `calculation> peak> detection> insert peak/delete peak` function.

Once all the satellite peaks corresponding to magnetic reflections are assigned, it is saved in the k-Search programme format (*.sat) from winPLOTTR dialog as `Calculation> peak detection > save peaks> K Search format`. This leads to following dialog box, as shown in Fig. 8.7 (a) for saving the data in *.sat format.

The K_Search program in FullProf runs in a console rather than a GUI. In the console, the input path for the *.sat file is provided (e.g C:\Panja \Mn4Ta2O9 \MnTaO1K.sat) and also the name of the output file also provided asked for. Running the program will generate a possible list of K vectors and corresponding R factor value, as shown in Fig.8.7 (b). For our case, the most possible K vector (lowest R value) is (000). This process is repeated multiple time with a different selection of magnetic peaks and a stable solution of K vector was found. The k vector was examined for all the diffraction patterns collected at several temperature below the magnetic ordering of $\text{Mn}_4\text{Ta}_2\text{O}_9$ and the k vector remains invariant down to the lowest temperature.

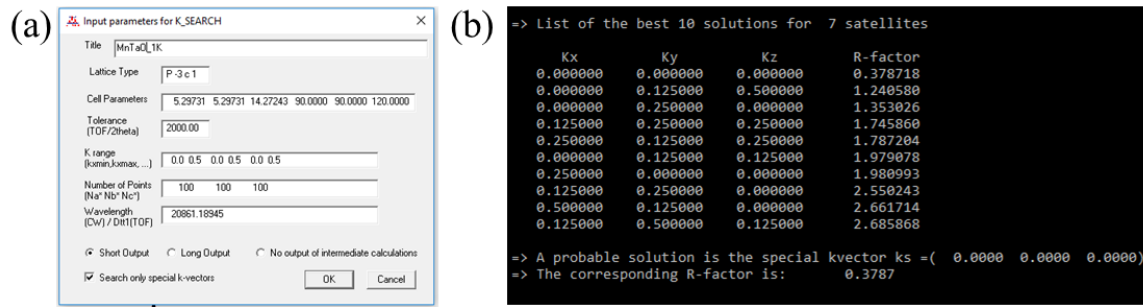


Figure 8.7: (a) Toolbar for calculating the k vector from K_serach program (b) Output of the K_search program as obtained for the diffraction pattern of $\text{Mn}_4\text{Ta}_2\text{O}_9$ at 1K. The most possible K vector is (0,0,0)

8.3.2 Representational analysis for solving magnetic structure

The Irreducible representation (Irreps) of the little group G_k and basis vector for Irreps, called representational analysis, were performed using either BasIreps from FP_s [77] or SARAh[81]. The necessary inputs for the BasIreps program are explained in Fig.8.8. The

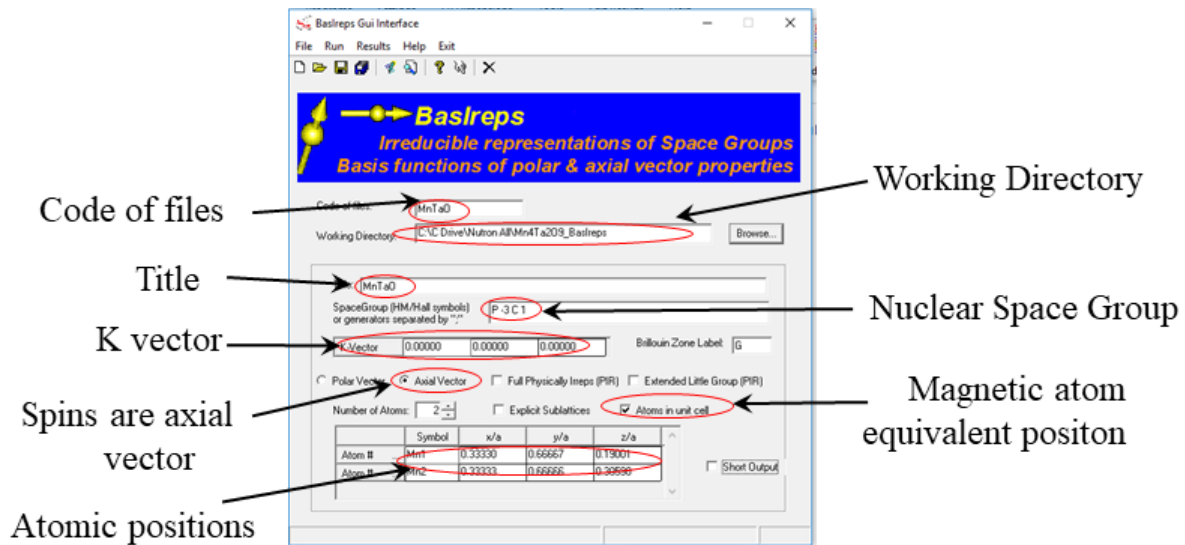


Figure 8.8: The BasIreps GUI interface for representational analysis in determining the magnetic structure. The nuclear space group, K vector and atomic position of the magnetic atom are required for performing a representational analysis.

necessary input for running the program are the crystallographic space group, k vector and the atomic positions of the magnetic atom. Selecting the "Atom in unit cell" in the program require only the first representative of the Wyckoff site of the unit cell. Once the required inputs are provided correctly, running the program will generate the result of the representational analysis in the *.bsr and *.fp output file. The *.bsr file contains detailed information of the symmetry elements of Γ_{mag} , Γ_{perm} and Γ_{axial} and also the basis vectors

of each irreducible representation when the short output box is unchecked, as shown in Fig.8.8.

8.3.2.1 Understanding the output file of the BasIreps program

The different parameters calculated from the representational analysis in BasIrep program are listed below.

- **The irreducible representation of the little G_k :**

As is already explained in section 2.12 of chapter 2, the little group G_k is a set of symmetry elements that leaves the k vector invariant. The irreducible representation of the little group G_k , as calculated from the BasIreps program, is tabulated in Table.8.1. An irreducible representation (Irreps) consists of characters which cannot be reduced further and is the simplest representation of symmetry operations. Each space group constitutes

Effect of symmetry operator on the permutation of atomic position

Character of the representation Γ_{axial}

Sym.Op.	Atoms Numbers, phases and returning Vectors	Character(U)	Character(Perm)(r,i)	ChM	
SYMM_K(1): x,y,z	Atoms: 1 2 3 4 Phase: + + + + Vector: 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 Vector Representation: (Mx, My, Mz) Ch(U): 3.0 Chr(P): 4.0 Chr(T): 12.0	1	2	3	4
SYMM_K(2): -y,x-y,z	Atoms: 1 2 3 4 Phase: + + + + Vector: 1.0 1.0 0.0 1.0-0.0 0.0 1.0-0.0 0.0 1.0 1.0 0.0 Vector Representation: (-My, Mx-My, Mz) Ch(U): 0.0 Chr(P): 4.0 Chr(T): 0.0	1	2	3	4
SYMM_K(3): -x+y,-x,z	Atoms: 1 2 3 4 Phase: + + + + Vector: -0.0 1.0 0.0 1.0 1.0 0.0 1.0 1.0 0.0 -0.0 1.0 0.0 Vector Representation: (-Mx+My, -Mx, Mz) Ch(U): 0.0 Chr(P): 4.0 Chr(T): 0.0	1	2	3	4

Character of the representation Γ_{perm}

Transformation of the axial components of the moment under Different symmetry operation

Figure 8.9: Part of the *bsr file as obtained from the representational analysis perform in BasIreps program for $\text{Mn}_4\text{Ta}_2\text{O}_9$. The elements, character of the permutation (Γ_{perm}) and axial (Γ_{axial}) representations are indicated by a arrow.

a combination of several symmetry operators/ generators (g_i) and can be represented in terms of the matrix. The space group $P-3c1$ has 12 generators as tabulated in the Table.8.2 and all of them contribute to the little group G_k .

The effect of a symmetry element on each magnetic atom is to change the position of an atom, and reorient the magnetic moment. The combination of these two results are described by the magnetic representation Γ_{mag} . The Effect of symmetry element on atomic

positions is represented by the permutation representation Γ_{perm} and character of this matrix is χ_{perm} . The character of Γ_{perm} for a generators refer to the number of position labels that are unchanged under the symmetry operation. On the other hand, the effect of symmetry element on moment vectors is expressed by the axial vector representation Γ_{axial} and the character of this matrix is χ_V . The operation of the 12 generators for $\text{Mn}_4\text{Ta}_2\text{O}_9$ on the magnetic site (Γ_{perm} and Γ_{axial}) are tabulated in Table.8.3. The elements and character of both Γ_{perm} and Γ_{axial} in the *bsr output file were schematically shown in Fig.8.9

• **Decomposition of the magnetic representation Γ_{mag} :**

A symmetry operator $g=[h|\tau]$ operate on both the position r_j and also on the several components of the axial vectors that describe the moment. The magnetic representation ($\Gamma_{mag} = \Gamma_{perm} \otimes \Gamma_{axial}$) can be decomposed in terms of Irreps of the little group G_k . The number of irreducible representations for a given magnetic site is calculated and also

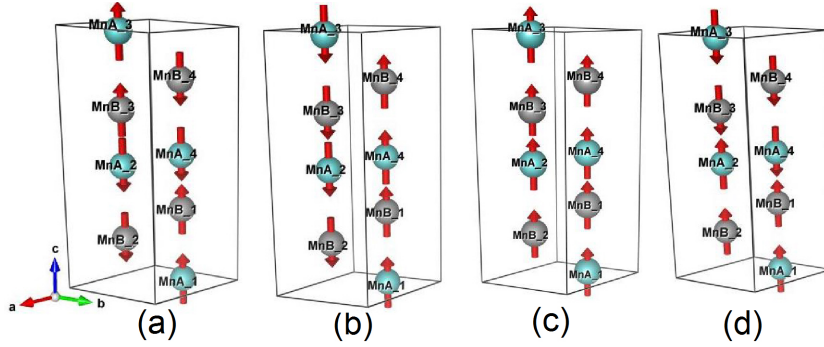


Figure 8.10: Schematic of the possible magnetic structure represented by first four Irreducible representation ((a) Γ_1 to (d) Γ_4)

the number of times each irreducible representation appears are also calculated by the BasIrep program. In the case of $\text{Mn}_4\text{Ta}_2\text{O}_9$, there are six possible irreducible representations for each magnetic site, and the first four real one dimensional representations (Γ_1 to Γ_4) appear once whereas the last two complex two dimensional (Γ_5 and Γ_6) appear twice in the decomposition of the magnetic representation and expressed as:

$$\Gamma_{mag} = \Gamma_1 \oplus \Gamma_2 \oplus \Gamma_3 \oplus \Gamma_4 \oplus 2\Gamma_5 \oplus 2\Gamma_6$$

Each Irreps are a possible description of the magnetic structure. The magnetic structure corresponding to first four real Irreps are shown in Fig.8.10

• **Basis vector of each Irreps:**

The basis vector for each irreducible representation of G_k are also calculated by the BasIreps. The calculation of basis vector is done based on the projection operator technique[217]. This involves choosing a test function and projecting from it the part

which transforms according to each of the Irreps. If Ψ_α is a basis vector and D_ν is the matrix representative of the Irreps Γ_μ^ν with index ν , μ dimensional representation, then the projection operator formula is:

$$\Psi_{\alpha\nu}^\lambda = \sum_{g \in G_k} u D_\nu^\lambda(g) \sum_i \delta_{i,gi} R_g \phi_\alpha \det(R_g) \quad (8.4)$$

The basis vector of each Irreps as described in the *.bsr file will be discussed in the next section. The basis vector for each Irreps of $\text{Mn}_4\text{Ta}_2\text{O}_9$ were tabulated in Table. 1.3 of Chapter-6 of this thesis.

8.3.3 Constructing the PCR input file

The final important step is to create the *.pcr file including the k vector, basis vectors for incorporating the calculation of magnetic contribution and test the different representations to find the correct magnetic model. A right description of the magnetic structure is obtained with the best fit for an Irreps among the all possible Irreps with the agreement between the observed and calculated pattern. The magnetic phase is added as a second phase with only the magnetic atoms within the crystallographic unit cell. For starting point, the second magnetic phase (designated as phase 2) is added by making a copy of the crystallographic phase (designated as phase 1) in existing PCR file of paramagnetic phase and removing the nonmagnetic atoms.

However, following parameter with their respective flag values has to take care of in

```
NPATT      1      1 <- Flags for patterns (1:refined, 0: excluded)
W_PAT      1.000
!Nph Dum Ias Nre Cry Opt Aut
  2   1   1   0   0   0   1
!Job Npr Nba Nex Nsc Nor Iwg Ilo Res Ste Uni Cor Ann Int
-1  13  27   2   0   1   0   0   0   0   1   0   0   0   0 ?-> Patt#: 1
?
!File names of data(patterns) files
32643-5_grow-0.gss
?
!Mat Pcr NLI Rpa Sym Sho
  0   1   0  -1   0   0
!Ipr Pp1 Ioc Ls1 Ls2 Ls3 Prf Ins Hkl Fou Ana
  0   2   1   0   4   0   3  14   0   0   0   0 ?-> Patt#: 1
,
```

Figure 8.11: Part of the PCR file for refining the nuclear contribution (phase 1) to the diffraction pattern of Time of flight data.

both the Phase 1 and 2 during creating the PCR file, are as listed below:

1. Nph=2 imply that the calculation were executed including two phases, namely nuclear and magnetic phase.

2. Job=1 (for data recorded in constant wavelength mode) or Jbt=-1 (for data recorded in T.O.F mode) in phase 1
3. Jtyp=-1 in the phase 2, for specifying that the calculation has to be performed purely based on magnetic structure factor.
4. Jbt=1 (components of moments along the unitary vectors along the crystallographic basis a, b, c) we can use spherical components by putting Jbt=-1.
5. Irf=-1 is necessary to instruct the program to generate only the magnetic satellites for the magnetic contribution
6. Isy=-1 or Isy=-2 for telling the program that the program will read either from symmetry instructions (Isy=-1) or directly the component of the basis vectors of the irreps (Isy=-2). The input for Isy=-1/-2 are shown in Fig.8.12 and 8.13.
7. The symbol of the space group that we need to provide in the magnetic phase is not used for generating atoms. It is only used for generating magnetic reflections, so, in the absence of the knowledge of the magnetic symmetry, it is safe to use the symbol "L -1" where L is the lattice symbol: P, A, B, C, I, F or R.

After the symbol of the space group for generating reflections, we have to also specify the number (Nsym) of symmetry operators (SYMM), the Laue class number (Laue) , the magnetic structure is centrosymmetric (Cen=2) or not (Cen=1) , and the number (MagMat) of different sets of magnetic operators (MSYM). For transition metals the name identifying the magnetic form factor is given as symbol: MCSV, CS is the chemical symbol and V is a number corresponding to the valence of the magnetic ion. For rare earths the symbol is JCSV to instruct the program to use the dipolar approximation for the form factor.

Once the PCR file is prepared, refinement is started for a particular representation. The Fourier coefficients of a magnetic structure are linear combinations of the basis functions of the irreducible representation of the propagation vector G_k . The mixing coefficient C_i of the basis vectors are free parameters during the refinement of the magnetic structure. In this way, the basis vectors of different representation are examined and a best fit is obtained. In the case of $\text{Mn}_4\text{Ta}_2\text{O}_9$, best fit was obtained with the Irreps Γ_2 , as shown in Fig.6.8(b) of chapter 6. The goodness of fit (GOF) for the refinement with other representations was not satisfactory. Refinement of diffraction profile with the Γ_4 is shown in Fig.8.14, where a difference between the observed and calculated data was

```

!-----
! Data for PHASE number:  2 ==> Current R_Bragg for Pattern#  1:  0.00
!-----
MnTaO
!
!Nat Dis Mom Jbt Isy Str Furth      ATZ      Nuk More
  2  0  0  1 -2  0  0      44.8353 -1  0
!Contributions (0/1) of this phase to the 1 patterns
1
!Irf Npr Jtyp Nsp_Ref Ph_Shift for Pattern#  1
 -1  9  -1  0  0
! Pr1 Pr2 Pr3 Brind. Rmua Rmub Rmuc      for Pattern#  1
 0.000 0.000 1.000 1.000 0.000 0.000 0.000
!
!
P -1      <--Space group symbol for hkl generation
! Nsym Cen Laue Ireps N_Bas
  4  1  10 -1  3
! Real(0)-Imaginary(1) indicator for Ci
 0 0 0
!
SYMM x,y,z
BASR 0 0 0 0 0 0 0 0 1
BAS1 0 0 0 0 0 0 0 0 0
SYMM y,x,-z+1/2
BASR 0 0 0 0 0 0 0 0 -1
BAS1 0 0 0 0 0 0 0 0 0
SYMM -x+1,-y+1,-z+1
BASR 0 0 0 0 0 0 0 0 -1
BAS1 0 0 0 0 0 0 0 0 0
SYMM -y+1,-x+1,z+1/2
BASR 0 0 0 0 0 0 0 0 1
BAS1 0 0 0 0 0 0 0 0 0
!
!Atom Typ Mag Vek X Y Z Biso Occ C1 C2 C3
! C4 C5 C6 C7 C8 C9 MagPh
Mn1 MMN2 1 0 0.33330 0.66670 0.01876 0.42202 1.00000 0.000 0.000 5.171
      0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00
      0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00
Mn2 MMN2 1 0 0.33330 0.66670 0.30535 0.54137 1.00000 0.000 0.000 4.897
      0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00
      0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00

```

Figure 8.12: PCR file of phase 2 for incorporating magnetic contribution in the diffraction pattern. The basis vector used here is directly copied from *fp output file of BasIreps program with Isy=-2.

observed and hence is not the correct representation for describing the magnetic structure $\text{M}_4\text{Ta}_2\text{O}_9$.

8.4 Conclusions

Using the Fullprof Suite, it is possible to treat the Neutron diffraction data and explore magnetic structure in simpler way (even for the unspecialized researcher) by understanding the input and output of the program. However, understanding/mastering the magnetic symmetry and the mathematical model used for calculations often useful for troubleshooting during a refinement. The problem of a physically unreasonable model leading to a good fit could also be avoided. A continuous trial, error process and experience in treating different cases of Neutron diffraction data over a period of time would definitely improve the performance. As a beginner, working with the example provided within the FullProf program is a good starting point and last not but the least as the author Nouredine Zettili of the book "Quantum Mechanics Concepts and Applications "

```

*****
=> Basis Functions of Representation IRrep( 2) of dimension 1 contained 1 times in GAMMA
*****
SVHM  x,y,z  y,x,-z+1/2  -x+1,-y+1,-z+1  -y+1,-x+1,z+1/2
Atoms:  Mn1_1  Mn1_2  Mn1_3  Mn1_4
BsU( 1, 1: 4):Re ( 0 0 1) ( 0 0 -1) ( 0 0 -1) ( 0 0 1)

----- The Fourier coefficients are LINEAR COMBINATIONS of Basis Functions: coefficients u,v,w,p,q ....(may be complex!)
The general expressions of the Fourier coefficients Sk(j) of the atoms non-related
by lattice translations are the following:

SVHM  x,y,z  Atom: Mn1_1  0.3333  0.6667  0.1900
Sk(1): (0,0,u)

SVHM  y,x,-z+1/2  Atom: Mn1_2  0.6667  0.3333  0.3100
Sk(2): (0,0,-u)

SVHM  -x+1,-y+1,-z+1  Atom: Mn1_3  0.6667  0.3333  0.8100
Sk(3): (0,0,-u)

SVHM  -y+1,-x+1,z+1/2  Atom: Mn1_4  0.3333  0.6667  0.6900
Sk(4): (0,0,u)

```

Figure 8.13: The basis functions of representation were expressed in terms of symmetry for the flag Irf=-1.

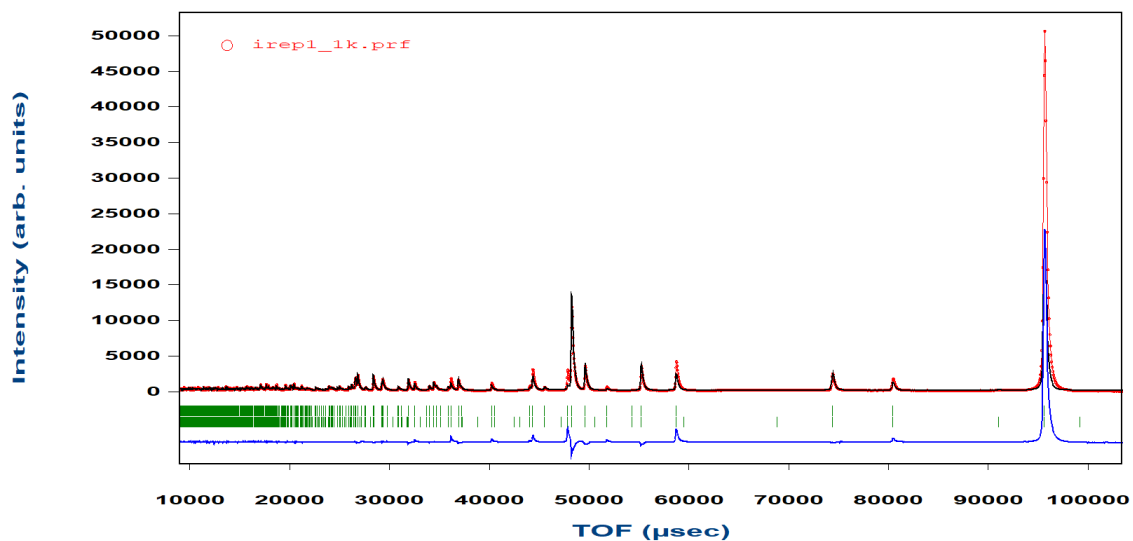


Figure 8.14: The Rietveld refinement of T.O.F diffraction pattern at 1K with the Irreps Γ_4 . The magnetic model does not yield a good fit between the observed and calculated pattern and thus concluded as wrong model for describing the magnetic structure.

has quoted[218] ,

"No one expects to learn swimming without getting wet. Nor does anyone expect to learn it by merely reading books or by watching others swim. Swimming cannot be learned without practice. There is absolutely no substitute for throwing yourself into water and training for weeks, or even months, till the exercise becomes a smooth reflex. "

List of Tables:

Table 8.1: Irreducible representation of the little group G_k of $\text{Mn}_4\text{Ta}_2\text{O}_9$.

Operator Ireps	g1		g2		g3		g4		g5		g6		g7		g8		g9		g10		g11		g12	
Γ_1	1		1		1		1		1		1		1		1		1		1		1		1	
Γ_2	1		1		1		1		1		1		1		-1		-1		-1		-1		-1	
Γ_3	1		1		1		-1		-1		-1		1		1		1		-1		-1		-1	
Γ_4	1		1		1		1		-1		-1		-1		-1		-1		1		1		1	
Γ_5	1	0	a	0	b	0	0	1	0	b	0	a	-1	0	-a	0	-b	0	0	-1	0	-b	0	-a
	0	1	0	b	0	a	1	0	a	0	b	0	0	-1	0	-b	0	-a	-1	0	-a	0	-b	0
Γ_6	1	0	a	0	b	0	0	1	0	b	0	a	1	0	a	0	b	0	0	1	0	b	0	a
	0	1	0	b	0	a	1	0	a	0	b	0	0	1	0	b	0	a	1	0	a	0	b	0

Phase factor: $a = \exp\{2\pi i \cdot 0.33333\} = (-0.50000, 0.86603)$

Phase factor: $b = \exp\{2\pi i \cdot 0.66667\} = (-0.50000, -0.86603)$

Table 8.2: Symmetry elements of the space group $P\bar{3}c1$. The notations used are of the International Tables, where the elements are separated into rotation and translation components, and the Jones faithful representations of the rotation parts. The latter corresponds to the vector formed from the operation of the rotation part of the element on position (x, y, z) .

Element Number	IT notations	Jones symbol	Rotation matrix (h)
g_1	$1(000)$	x,y,z	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$
g_2	$3^+(000)$	$-y, x-y, z$	$\begin{pmatrix} 0 & -1 & 0 \\ 1 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$
g_3	$3^-(000)$	$-x+y,-x,z$	$\begin{pmatrix} -1 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$
g_4	$2(0,0,1/2)$	$-y,-x,-z+1/2$	$\begin{pmatrix} 0 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$
g_5	$2(0\ 0\ 1/2)$	$-x+y,y,-z+1/2$	$\begin{pmatrix} -1 & 1 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$
g_6	$2\ (0\ 0\ 1/2)$	$x,x-y,-z+1/2$	$\begin{pmatrix} 1 & 0 & 0 \\ 1 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$
g_7	$-1(000)$	$-x,-y,-z$	$\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$
g_8	$-3^+(000)$	$y,-x+y,-z$	$\begin{pmatrix} 0 & 1 & 0 \\ -1 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$
g_9	$-3^-(000)$	$x-y,x,-z$	$\begin{pmatrix} 1 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$
g_{10}	$c(0\ 0\ 1/2)$	$y,x,z+1/2$	$\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$
g_{11}	$c(0\ 0\ 1/2)$	$x-y,-y,z+1/2$	$\begin{pmatrix} 1 & -1 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$
g_{12}	$c\ (0\ 0\ 1/2)$	$-x-x+y,z+1/2$	$\begin{pmatrix} -1 & 0 & 0 \\ -1 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$

Table 8.3: The permutation of Mn^{2+} atoms at position 4d and the transformation of the axial components of the moment under the different symmetry operators of the $P\text{-}3c1$ space group (point group D_{3d}^4) for $k = (000)$. The characters of the representations Γ_{perm} and Γ_{axial} is given by χ_{perm} and χ_V .

Element	$g=[h \tau]$	Atoms				χ_{perm}	Atoms			χ_V
		1	2	3	4		m_x	m_y	m_z	
g1	$[1 3]$	1	2	3	4	4	m_x	m_y	m_z	3
g2	$[3^+ 000]$	1	2	3	4	4	$-m_y$	m_x-m_y	m_z	0
g3	$[3^- 000]$	1	2	3	4	4	$-m_x+m_y$	$-m_x$	m_z	0
g4	$[2 001/2]$	2	1	4	3	0	m_y	m_x	$-m_z$	-1
g5	$[2 001/2]$	2	1	4	3	0	m_x-m_y	$-m_y$	$-m_z$	-1
g6	$[2 001/2]$	2	1	4	3	0	$-m_x$	$-m_x+m_y$	$-m_z$	-1
g7	$[-1 000]$	3	4	1	2	0	m_x	m_y	m_z	3
g8	$[-3^+ 000]$	3	4	1	2	0	$-m_y$	m_x-m_y	m_z	0
g9	$[-3^- 000]$	3	4	1	2	0	$-m_x+m_y$	$-m_x$	m_z	0
g10	$[c 001/2]$	4	3	2	1	0	m_y	m_x	$-m_z$	3
g11	$[c 001/2]$	4	3	2	1	0	m_x-m_y	$-m_y$	$-m_z$	-1
g12	$[c 001/2]$	4	3	2	1	0	$-m_x$	$-m_x+m_y$	$-m_z$	-1

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List of publications

•Publications included in this Thesis:

1. **Relieving geometrical frustration through doping in the $\text{Dy}_{1-x}\text{Ca}_x\text{BaCo}_4\text{O}_7$ swedenborgites**
Soumendra Nath Panja, Jitender Kumar, Shanu Dengre and Sunil Nair, J.Phys. Condens. Matter **28**, 486001 (2016)
2. **Coupled magnetic and ferroelectric states in the distorted honeycomb system $\text{Fe}_4\text{Ta}_2\text{O}_9$**
Soumendra Nath Panja, Luminita Harnagea, Jitender Kumar, P.K.Mukharjee, R.Nath, A.K.Nigam, Sunil Nair, Phys. Rev. B. **98**, 024410 (2018). Featured in PRB Kaleidoscopes: July 2018.
3. **γ - Fe_2WO_6 - a magnetodielectric with disordered magnetic and electronic ground states**
Soumendra Nath Panja, Jitender Kumar, Luminita Harnagea, A. K. Nigam, Sunil Nair, Journal of Magnetism & Magnetic Materials **466**, 354 (2018)
4. **Anisotropy in the magnetization and magnetoelectric response of single crystalline $\text{Mn}_4\text{Ta}_2\text{O}_9$**
Soumendra Nath Panja, Pascal Manuel, Sunil Nair, (to be submitted to Phys. Rev. B)
5. **$\text{SrBaCo}_4\text{O}_7$ -A new member of Swedenborgite family**
Soumendra Nath Panja, A.K.Nigam, Sunil Nair, (manuscript under preparation)

•Publications not included in this thesis:

1. **Identification of a Griffiths singularity in a geometrically frustrated antiferromagnet**
jitender Kumar, *Soumendra Nath Panja*, Shanu Dengre, and Sunil Nair, Phys. Rev. B **95**, 054401 (2017)

2. **Reentrant superspin glass state and magnetization steps in the oxyborate Co_2AlBO_5**

Jitender Kumar, *Soumendra Nath Panja*, Deepak John, Arpan Bhattacharyya, A. K. Nigam, and Sunil Nair, Phys. Rev. B **95**, 144409 (2017)

3. **Improper multiferroicity and colossal dielectric constants in Bi_2CuO_4**

Jitender Kumar, *Soumendra Nath Panja*, Amit Kumar Naiya, Sunil Nair, arXiv:1708.07703

4. **Possible Room-Temperature Ferromagnetism in Self-Assembled Ensembles of Paramagnetic and Diamagnetic Molecular Semiconductors**

Barun Dhara, Kartick Tarafder, Plawan K. Jha, *Soumendra Nath Panja*, Sunil Nair, Peter M. Oppeneer, and Nirmalya Ballav, J. Phys. Chem. Lett., **7**, 4988 (2016)

5. **Highly-stable COF Supported Co/Co(OH) Nanoparticles- Heterogeneous Catalyst for Reduction of Nitrile/Nitro Compounds under Mild Conditions**

Dinesh Mullangi, Debanjan Chakraborty, Anu Pradeep, Vijay Koshti, Chathakudath P. Vinod, *Soumendra Nath Panja*, Sunil Nair and Ramanathan Vaidhyanathan, Small **2018**, 1801233 (2018).