STRUCTURE-PROPERTY CORRELATIONS IN Ni BASED PEROVSKITE AND Fe-Mo BASED DOUBLE PEROVSKITE

THIN FILMS

Ph.D. THESIS

By EKTA YADAV



DEPARTMENT OF PHYSICS INDIAN INSTITUTE OF TECHNOLOGY INDORE

JULY 2023

STRUCTURE-PROPERTY CORRELATIONS IN Ni BASED PEROVSKITE AND Fe-Mo BASED DOUBLE PEROVSKITE THIN FILMS

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by EKTA YADAV



DEPARTMENT OF PHYSICS INDIAN INSTITUTE OF TECHNOLOGY INDORE

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INDIAN INSTITUTE OF TECHNOLOGY INDORE

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled "STRUCTURE-PROPERTY CORRELATIONS IN Ni BASED PEROVSKITE AND Fe-Mo BASED DOUBLE PEROVSKITE THIN FILMS" in the partial fulfilment of the requirements for the award of the degree of DOCTOR OF PHILOSOPHY and submitted in the DEPARTMENT OF PHYSICS, INDIAN INSTITUTE OF TECHNOLOGY INDORE, is an authentic record of my own work carried out during the time period from July 2018 to July 2023 under the supervision of Prof. Krushna R. Mavani, Professor, Department of Physics, Indian Institute of Technology Indore.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

Egadar

31.07.23

Signature of the student with date (Ekta Yadav)

This is to certify that the above statement made by the candidate is correct to the best of my/our knowledge.

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(Prof. Krushna R. Mavani)

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- 2 GIAN course on "Computationally Aided Materials Designing for Material Genomeduring" during January 04 - 08, 2018, IIT Indore.
- **3** Attended national conference **"Emerging Interfaces of Physical Sciences and TechnologyEIPT- 2019**" in Vikram University, Ujjain.
- 4 Attended one week Short Term Course on "Advanced Energy Materials" during October 12-16, 2020 organized by Dr. B. R. Ambedkar national Institute of technology, Jalandhar.
- Attended "International Conference on Sculptured Thin Films (GLAD-2021)" from 6-7 May 2021 organized by IIT Delhi.
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ACRONYMS

XRD	X-Ray Diffraction
RNiO ₃	Rare earth nickelates
AFMO	A ₂ FeMoO ₆
CMR	Colossal magnetoresistance
LFMR	low-field magnetoresistance
MIT	metal-insulator transition
PLD	Pulsed Laser Deposition
QCP	Quantum critical point
T _{MI}	Metal-insulator transition temperature
NFL	Non-Fermi liquid
T _C	Curie temperature
TEM	Transmission Electron Microscopy
SFMO	Sr ₂ FeMoO ₆
RT	Room Temperature
Ms	Saturation Magnetization
APB	Antiphase Boundaries
ASD	Anti-site disorder
DFT	Density Functional Theory
DOS	Density of States
RSM	Reciprocal Space Mapping
XRR	X-Ray Reflectivity
AFM	Atomic Force Microscopy
XAS	X-Ray Absorption Spectroscopy
XPS	X-Ray Photoelectron Spectroscopy
THz-TDS	Terahertz time-domain spectroscopy
PVD	Physical Vapour Deposition

EXAFS	Extended X-Ray Absorption Fine Structure
XANES	X-Ray Absorption Near Edge Structure
CCD	Charge Coupled Device
LAO	LaAlO ₃
FWHM	Full Width at Half Maxima
CFMO	Ca ₂ FeMoO ₆
BFMO	Ba ₂ FeMoO ₆

Chapter 1 Introduction

This chapter provides a general introduction to the perovskite-type oxides and their applications. This chapter describes the previously made investigations and associated phenomena on $RNiO_3$ (R=Pr) and A₂FeMoO₆ (A= Sr and Ca) oxides. The basic theories behind the charge transfer nature in $RNiO_3$ and half-metallic transport in A₂FeMoO₆ materials are also discussed in detail.

1.1 Introduction to Perovskites:

Perovskites belong to an important class of oxides which have gained a plethora of attention from the scientific community due to their interesting fundamental properties of technological significance [1-2]. These materials have a potential to replace the conventional silicon-based semiconducting devices [3]. Due to the mutual coupling between charge, spin, lattice, and orbital degrees of freedom, these oxides exhibit rich physics with fundamental importance [4-6]. In this regard, a lot of the research activities in past years have been focused on high T_C superconductivity in Cuprates (RCuO₃), Colossal magnetoresistance (CMR) in manganites (RMnO₃), multiferroicity in ferrites (RFeO₃), metal-insulator transition in nickelates (RNiO₃) and low-field magnetoresistance (LFMR) in half-metallic oxides [7].

Perovskite oxides are characterized by the general formula ABO3 where A and B are cations. A-site cation is usually larger in size and consists of rare earth, alkali, or alkaline earth metal ions. B-site consists of 3d/4d/5d transition metal ions which are generally smaller in size. In the perovskite geometry, B-site cations are six-fold coordinated with Oxygen to form BO₆ octahedra which are three-dimensionally connected in a corner-shared network across the lattice and A ion is present in the center (Fig.1.1). These BO₆ octahedra are the basic building blocks of the perovskite structure and decide the structural and transport properties of the system [8, 9]. In an ideal case, the perovskite structure is cubic, and the B-O-B bond angle is 180° . However, the real perovskite systems show some deviation from the ideal cubic structure to gain structural stability. The degree of distortion of perovskites can be quantified by Goldschmidt's tolerance factor *t*, defined as:

$$t = \frac{r_A + r_0}{\sqrt{2} (r_B + r_0)}$$

where r_A , r_B and r_O are the ionic radii of A, B and O ions, respectively. For the ideal perovskite structure, the value of t is 1. With slight distortion, the cubic perovskite structure is stable for 0.9 < t < 1, where some compounds



Fig. 1.1 Ideal perovskite ABO₃ structure [from ref 9].

relax to rhombohedral geometry. With an increase in structural distortion, the structure tends to acquire orthorhombic or monoclinic symmetries for t < 0.9. Due to the small ionic radii of the A-site cation, the corner-sharing BO₆ octahedra undergo distortion to fill the empty space in the structure by changing the B-O-B bond lengths and bond angles. This changes the effective overlap between metal 3*d* and Oxygen 2*p* orbitals, thereby influencing the structural, electronic, and magnetic properties of the system [10-12].

1.1.1 Rare Earth Nickelates:

Rare earth nickelates, with generic formula $RNiO_3$, are an important class of perovskite oxides that show strong correlations among structural electronic, and magnetic properties. Here, R is a rare earth ion ranging from La to Lu in the Lanthanide series, which is three-dimensionally surrounded by 8 NiO₆ octahedra in the perovskite structure. One of the interesting features of $RNiO_3$ is a sharp metal-insulator phase transition (MIT) as a function of temperature, which makes them suitable candidates for potential applications in thermal switches, temperature sensors, memory devices, thermochromic coating, photovoltaic cells, *etc.* [13, 14]. Furthermore, there are some theoretical predictions of topological insulating phases, bad-metallic conductivity, and quantum criticality which have stimulated research activities in the RNiO₃ system.



Fig. 1.2 Schematic showing the applications of RNiO₃ thin films [from ref 13].

The very first synthesis of nickelates in bulk form was carried out in 1971. It is worth noting that the synthesis of nickelates is a challenging process due to the stabilization of the Ni³⁺ state, which requires high temperatures and pressures, particularly when the R-site ion is in a smaller size. As a result, bulk single crystals of these compounds were not been synthesized, with the largest reported crystals being smaller than 100 μ m [15, 16]. Consequently, the initial research on nickelates was focused on powdered polycrystalline samples. However, the advent of Pulsed Laser Deposition (PLD) has opened new avenues for research in perovskite oxides, especially nickelates, by enabling the synthesis of thin films (nanometer range) and heterostructures. Epitaxial thin films of nickelates are a feasible system to explore the intrinsic properties of the system [17-19].

1.1.2 Metal-Insulator Transition

Metal-Insulator transition (MIT) is a complex, extensively researched but not fully comprehended phenomenon of condensed matter physics. MIT is an intermediate state where two elementary excitations of different statistics come together, leading to conceptual difficulties and theoretical challenges in analyzing this problem [20]. The study of MIT is helpful to get further insight into Quantum critical point (QCP) [20, 21].

RNiO₃ (R \neq La) systems exhibit the first-order MIT as a function of temperature, whereas LaNiO₃ remains metallic throughout the temperature range (Fig. 1.3). The transition temperature (T_{MI}) of nickelates shifts towards higher temperatures as the R cation size decreases, due to the distortions in NiO₆ octahedra which changes the Ni-O-Ni bond angles and lengths. These changes determine the overlapping of Ni 3d and O 2p orbitals, and hence the electronic properties [13]. More detailed information is dictated by the rich phase diagram of RNiO₃ which indicates the metal-insulator and Néel transition temperatures (T_N) as a function of the tolerance factor t and Ni–O– Ni bond angle (Fig. 1.4). Here, LaNiO₃ exhibits the highest tolerance factor *i.e.*, 0.94 in the entire series due to the large ionic radius of La^{3+} (1.36 Å). This larger ionic radius favors a cubic perovskite structure with less octahedral tilting, as compared to other nickelates. LaNiO₃ also has a Ni-O-Ni bond angle of approximately 165.2°, which enables significant overlapping between Ni 3d and O 2p orbitals, resulting in a steady-state metallicity throughout the temperature range [15].



Fig. 1.3 *The electrical resistance of* LaNiO₃, *PrNiO*₃, *NdNiO*₃ *and SmNiO*₃ *showing their metal–insulator transitions* [*from ref* 15].

In contrast, the smaller ionic radii of Pr^{3+} (1.32 Å) and Nd^{3+} (1.27 Å) ions give rise to tolerance factors of 0.93 and 0.92 for $PrNiO_3$ and $NdNiO_3$, respectively. The transition temperature of $PrNiO_3$ and $NdNiO_3$ are 130 and 200K, respectively. At high temperatures, $RNiO_3$ compounds exhibit metallic behavior with a paramagnetic state. As the temperature decreases, they undergo a transition to insulating state, accompanied by an antiferromagnetic ground state. The phase diagram indicates that the transition temperatures, T_N and T_{MI} are the same for both $PrNiO_3$ and $NdNiO_3$ compounds [13]. Additionally, these compounds undergo a structural transition from orthorhombic to monoclinic symmetry at the same temperature. These observations make $PrNiO_3$ and $NdNiO_3$ potential candidates for studying the correlated magnetic, electronic, and structural degrees of freedom. For other members of the RNiO₃ series with lower R-ion radii, there appears to be a significant difference in the electronic and magnetic transition temperatures.



Fig.1.4 The phase diagram of RNiO₃ compounds, indicating T_{MI} and T_N as a function of the tolerance factor t (bottom x-axis) and the Ni–O–Ni- angle (top x-axis) [from ref 13]

One of the probable reasons of MIT in nickelates is the charge disproportion of Ni³⁺ ions which gives rise to Ni^{3+δ} and Ni^{3-δ} states [14]. For a perfectly stoichiometric RNiO₃, Ni ion is in 3+ valence state and it has one electron in the two-fold degenerate e_g orbitals (low-spin $3d^7$ ($t_{2g}{}^6e_g{}^1$) configuration. However, the charge disproportion leads to two different Nickel sites in the monoclinic P2₁/*n* ground state. As a result of this, one NiO₆ octahedra has compressed Ni-O bonds, while the other has elongated Ni-O bonds.

The MIT in nickelates depends on various parameters such as doping, temperature, pressure, strain, oxygen non-stoichiometry, and external field [13]. Any change in these parameters can cause a shift from a metallic phase to an insulating state. These parameters affect the Coulomb interactions, bandwidth or 3d band filling, thereby influencing the effective overlap between Nickel 3*d* and Oxygen 2*p* orbitals. For example, by modifying the doping level, MIT can be tuned due to the associated band-filling effect. The physical properties of RNiO₃ are also dramatically influenced by altering these external parameters [15].

1.1.3 The mechanisms driving Metal-Insulator Transitions

In the field of solid-state physics, a variety of models have been proposed to explain the change the electronic transport properties as a function of temperature. One class of materials that has received particular attention in this context is the *R*NiO₃ family of compounds, which exhibit a complex interplay between metallic and insulating behavior that can be influenced by various external factors, including temperature, strain, and oxygen content. Despite numerous experiments conducted on the RNiO₃ system, a comprehensive theoretical understanding of the precise mechanisms underlying the metal-insulator transitions (MITs) and the properties of the insulating and magnetic ground states is yet to be explored.

1.1.3.1 RNiO₃ band-structure

The band structure of RNiO₃ consists of oxygen 2p and nickel 3d bands. The electronic transport in these compounds is influenced by the hybridization of these O 2p and Ni 3d orbitals. This orbital overlap depends on the rare earth element's size, which affects the structure of the unit cell and the Ni-O-Ni bond angle.

The insulating state in a few metallic oxides like NiO was not properly explained by the conventional band theory of solids. N.F. Mott proposed an explanation for the insulating behavior of metal oxides, attributing it to the Coulomb repulsion resulting from electron-electron interactions [22]. This theory was further developed by P.W. Anderson and J. Hubbard, who formulated the concept using the Hubbard Hamiltonian, H described as:

$$H = T\Sigma_i^i c_i^{\dagger} c_j + U\Sigma_i^i n_{i\uparrow} n_{j\downarrow}$$

.

where T is hopping integral denoting a matrix, U is on-site Coulomb interaction, c_i^{\dagger} and c_j are creation and annihilation operators which indicate the hopping of electrons from the ith to the jth site. The first term in the Hamiltonian, representing electrons hopping, is responsible for the metallicity in RNiO₃. In the second term, *n* is the quantum number for the spin-up and spin-down states, obeying the Pauli exclusion principle. In the presence of considerable Coulomb repulsion, the *d* band splits into two bands due to the difference in energy between the ground-state electron system and the uncompensated electron system. These two bands are called the lower Hubbard band and the upper Hubbard band, and the resulting splitting drives the system towards an insulating state [22].

The metallic or insulating behavior of the system can be quantified in terms of the U/T ratio, where U is the Coulomb term and T is the hopping term. If U/T <1, the system favors metallicity, whereas U/T >1 favors insulating state [22-23]. In certain conditions, the lower p band may be energetically above the lower Hubbard band, resulting in the formation of a gap between the cation upper Hubbard band and the anion oxygen p band.

This gap is called the charge transfer gap Δ , leading to an insulating state. Such insulators are known as charge transfer insulators [23]. PrNiO₃ and NdNiO₃ lie in the category of charge-transfer insulators.



Fig. 1.5 Schematic representation of Mott-Hubbard and Charge transfer type of insulators [from ref 23].

1.1.3.2 Electrical Conduction in RNiO₃

The electrical conductivity of solids is known to be strongly affected by temperature. The temperature dependence of the resistivity of a material depends on whether the material is a metal, semiconductor, or insulator. According to the classical theory, the resistivity of a metal at a given temperature can be attributed to two factors: *i*) resistance resulting from interactions between electrons and phonons (ρ_{ph}), and *ii*) resistance resulting from impurities or disorder in the material (ρ_{de}) [24]. Therefore, the resistivity of a material in the classical picture can be expressed as:

$$\rho = \rho_{ph} + \rho_{de}$$

Here, the contribution to resistivity arising from defects or impurities depends on the intrinsic property of the material and remains independent of temperature. However, the temperature dependence of resistivity arising from phonon scattering can be described as

$$\rho_{ph} = \frac{\hbar^2 \Pi}{kM} \frac{T}{\theta^2}$$
where k is the Boltzmann constant, M is the mass of ions and θ is the Debye frequency. According to this picture, at high temperatures, the resistivity is primarily influenced by electron-phonon scattering and is linearly dependent on temperature. However, at low temperatures, the resistivity is mostly affected by defects in the lattice structure. This classical model explains the metallic behavior of materials, but it does not consider the interactions between electrons. In 1956, Soviet physicist Lev Landau modified this model to incorporate the interactions between fermions, which show a quadratic dependency on temperature. This modified model is known as the classical Landau picture or Fermi liquid behavior [25]. According to Fermi Liquid behavior, the temperature dependence of resistivity can be given as:

$$\rho = \rho_0 + AT + BT^2$$

Here, ρ_0 denotes the residual resistivity caused by various factors, such as grain boundary, lattice imperfections, dislocations, and defects. The linear dependence of resistivity on temperature in a material is attributed to the electron-phonon interaction. On the other hand, the quadratic relationship between resistivity and temperature arises due to electron-electron interaction, which is a signature of Fermi liquid behavior. However, certain metal oxides don't obey this quadratic dependence, and instead exhibit a power-law exponent relation with n < 2 [26]. This abnormal behavior in the material's electrical transport is referred as Non-Fermi liquid (NFL) behavior. Various literature studies on *R*NiO₃ suggest that these materials exhibit NFL behavior in metallic states.

1.2 Double Perovskites:

As discussed earlier, perovskite oxides have a capability to modify their electronic structure and physical properties by choosing suitable combinations of A and B-site cations, which also enhances the applicability of perovskites. In addition to this, the partial substitution of A or B cations in ABO₃ perovskites has also been explored to achieve tunability in properties. In this context, half doped perovskites, where exactly half of the B site ions are replaced by other cation, are of particular interest of the scientific community. This kind of substitution gives rise to $A_2BB'O_6$ double perovskite oxides, where half of the BO₆ octahedra are exactly replaced by B'O₆ octahedra in the crystal. The crystal structure of double perovskites is an expanded unit cell of perovskite type structure. Here, both the BO₆ and B'O₆ octahedra are three-dimensionally arranged in an alternate manner throughout the crystal as shown in Fig.1.6.



Fig. 1.6 Schematic representation of (a) perovskite structure, (b) double perovskite structure with Fm3m space group derived from simple perovskite structure [from ref 27].

In double perovskites, the A-site ions are coordinated with 12 surrounding oxygen atoms, similar to simple perovskites, and are typically occupied by divalent or trivalent cations, such as alkaline earth metals or lanthanides. The B-sites, which are generally 3d/4d/5d transition metals, are

octahedrally coordinated with six oxygen atoms. The most common example of double perovskite is a highly symmetrical cubic structure with Fm3m space group. Similar to simple perovskites, a mismatch in the size of B and B' cations gives rise to symmetry lowering via cooperative tilting and distortion of oxygen octahedra. In the case of double perovskites, the modified tolerance factor can be defined as

$$t = \frac{r_A + r_0}{\sqrt{2} \left(\frac{r_B + r_{B'}}{2} + r_0\right)}$$

where the ionic radii of A, B, B' and O ions are given by r_A , r_B , $r_{B'}$ and r_O , respectively. When *t* is close to unity, double perovskites typically adopt a stable cubic structure with Fm3m space group. For 0.97 < t < 1, a tetragonal space group (I4/m) is commonly observed. With t < 0.97, double perovskites tend to have a monoclinic structure with a P2₁/n space group.

Double perovskites have gained tremendous attention of the scientific community due to the flexibility of using various elemental compositions of A, B and B' ions, thereby modifying the fundamental properties as well as technological importance. Over the years, several studies have been conducted on more complex and potentially rich double perovskites [28-29]. Fig. 1.7 shows the applications of double perovskites in various fields.



Fig. 1.7 Schematic representing applications of double perovskites [from ref 28].

In 1960, Longo and Ward revealed that Rhenium-based double perovskites have the potential for room temperature magnetism [28]. Later in 1998, Kobayashi *et al.* reported half-metallicity in Sr_2FeMoO_6 double perovskites, which has attracted significant attention due to its high FM Curie temperature (T_C) ~400 K, and potential for spintronic applications [29]. Ba₂YMoO₆ is a promising candidate for high-temperature solid oxide fuel cells due to high oxygen ion conductivity [30]. Sr₂MgMoO₆ is known to show high bandgap and high absorption coefficient, and therefore can be used for photovoltaic applications [31]. Vasala et al. have estimated that there are nearly 20,000 double perovskites within their structural limits, while only 1000 compounds having been experimentally reported so far [32]. Therefore, double perovskites present an exciting field of investigation as functional oxides.

1.2.1 Cation ordering:

In case of double perovskites, a well-ordered crystal structure dictates the fundamental and practical importance of these systems. Ideally, the B and B' cations should be alternatively arranged for a perfectly ordered structure. The arrangement of B-site cations in $A_2BB'O_6$ is greatly influenced by a disparity in *i*) ionic radii, and *ii*) ionic valence of B and B' cations. When the difference in ionic radii of both B-site cations is negligible, it provides an ease to these cations to readily exchange their position in the crystal. This gives rise to a disordered/random arrangement of B-site cations in the system. Similarly, when the difference in ionic valence of B and B' cations is two or more, such as in Sr₂Fe²⁺W⁶⁺O₆, double perovskites, a high degree of cation ordering are observed [33]. On the other hand, when the ionic valence difference is less than 2, as in La₂Ni^{3+/2+}Mn^{3+/4+}O⁶, the cation ordering in double perovskites is disturbed.

Anderson et al. proposed three possible ways of ordering B and B' cations in double perovskites: rock salt, columnar, and layered, as illustrated in Figure 1.8 [34]. Rock salt ordering is the most commonly observed ordering in double perovskite systems, in which B and B' cations are arranged

alternately along all the three axes. This is also referred as 0D ordering because each BO_6 octahedra is completely detached from all other BO_6 octahedra, and all the neighboring octahedra are $B'O_6$ type.



Fig. 1.8 *Cation ordering scheme in* $A_2BB'O_6$ *double perovskites: Rock salt ordering* (0D), *Columnar ordering* (1D), *and layered ordering* (2D) [from ref 34].

Columnar ordering, on the other hand, involves the connectivity of same octahedra, like BO_6 to BO_6 or vice versa, along a column only in one dimension, making it a 1D type ordering [35, 36]. Layered ordering allows connectivity of BO_6 or $B'O_6$ octahedra in two dimensions, making it a 2D type ordering [35, 36]. It should be noted that columnar and layered orderings are relatively less observed ordering between B and B' cations. For this thesis, only rock salt ordering will be considered.

1.2.2 Anti-site disorder

Ideally, a double perovskite structure should exhibit B-site rock salt ordering with distinct crystallographic sites, as shown in Fig. 1.9(a). However, experimental observations have revealed some deviations from the ideal ordered state, often due to the presence of cationic defects in partially ordered rock salt compounds. These defects occur when B and B' cations are misplaced, resulting in some of the B-sites being occupied by B' cations, or vice versa, as depicted in Figure 1.9(b). Such defects are commonly referred to as anti-site disorder (ASD) [32]. Vasala et al. have confirmed that small amount of anti-site disorders are intrinsically present in a double perovskite due to the forces responsible for the change of entropy [37].



Fig. 1.9 (a) Perfectly ordered, (b) Anti-site disordered $A_2BB'O_6$ double perovskites [from ref 36].

The synthesis techniques play a crucial role in controlling the level of anti-site defects. In the case of bulk double perovskites, X-Ray Diffraction (XRD) can be used to investigate anti-site disorder. A superstructure peak is observed in the XRD patterns of ordered double perovskites due to the doubling of unit cell [38]. Apart from XRD, transmission electron microscopy (TEM) can also provide ideas about anti-site defects. Anti-site defects also affect the magnetic exchange interactions between B and B' cations; therefore, a signature of these disorders can be given by magnetization measurements also.

1.2.3 A₂FeMoO₆ (AFMO) Double Perovskites:

 A_2FeMoO_6 (A= Ca, Sr, Ba) type of double perovskites have gained considerable interest in past years owing to the fascinating magnetic and electronic properties. The striking discovery of low field magnetoresistance (LFMR) in Sr₂FeMoO₆ (SFMO) by Kobayashi in 1998 opened up new avenues for progressive research in these materials [30]. The ground state of these materials is half-metallic, meaning one spin channel is metallic with a finite density of states at the Fermi level, whereas the other spin channel is semiconducting with a bandgap as shown in Fig. 1.10 [41]. Half-metallicity gives rise to 100% spin-polarization of charge carriers at Fermi level, which gives rise to spin current and enhances the spintronic functionality of the materials [39]. Moreover, the Curie temperature of these AFMO materials is well above room temperature (RT) *i.e.*, 360K, 415K, and 380K for A= Ca, Sr, and Ba, respectively [40].



Fig 1.10 Schematic representation of (a) conventional ferromagnet and (b) halfmetallic ferromagnet [from ref 41].

The high T_C , high intrinsic magnetoresistance (MR), fully spinpolarized electron transport, and high saturation magnetization (M_S) of AFMO double perovskites make them better spintronic candidates as compared to low T_C doped magnanites such as La_{1-x}Ca_xMnO₃ [30]. The AFMO-based magneto-electronic devices provide us an opportunity to realize devices functioning at room temperature.

1.2.3.1 Crystal Structure:

The crystal structure of AFMO is comprised of alternating FeO₆ and MoO₆ octahedra arranged in rock salt type network, and A ion is present in the center. At room temperature, BFMO crystallizes in Cubic unit cell with Fm3m space group where lattice parameter, a = 8.0697 Å. With slight decrease in the ionic radii from Ba²⁺ (1.38 Å) to Sr²⁺ ion (1.21 Å), the crystal structure of SFMO is tetragonal with 14/mmm space group [42]. The unit cell dimensions are a = b = 5.5724 Å, c = 7.9006 Å, indicating slight distortion

from ideal cubic structure. With a further decrease in ionic radius of Ca²⁺ ion (1.06 Å), a monoclinic structure with P2₁/n space group is favored. In CFMO, the unit cell parameters are a = 5.4131 Å, b = 5.5209 Å, c = 7.7065 Å, $\beta = 89.95^{\circ}$. This indicates significant octahedral distortions and tilting in the double perovskite structure due to the lower size of Ca²⁺ cation. The tolerance factor, *t* of these AFMO compounds is 1.026, 0.976, and 0.942 for A= Ba, Sr and Ca ions respectively, which indicates decreased structural symmetry as shown in Fig. 1.11.



Fig. 1.11 Schematic representation of crystal structures of $A_2BB'O_6$ (A = Ba, Sr, Ca) double perovskites [from ref 43].

Like any other double perovskite, AFMO compounds also exhibit anti-site disorder, where Fe and Mo atoms are misplaced in the crystal. This disorder leads to the formation of antiphase boundaries (APB) which hinder the current flow by creating domain walls [44]. Fig. 1.12 (a-c) schematically illustrates the difference between the ordered AFMO structure and the structures with ASD or APB. Here, small arrows represent the magnetic moments of the atoms, and the larger arrows represent the total magnetization. The impact of ASD on the electronic and magnetic properties of AFMO has been experimentally and theoretically demonstrated by various research groups. ASD affects the magnetic exchange interactions between Fe and Mo ions, thereby deteriorating the transport properties of Fe-Mo-based double perovskites. Numerous theoretical studies have also shown that these defects reduce the half-metallic characteristic of AFMO [45].



Fig.1.12 Schematic picture of AFMO with gray (Mo) and blue (Fe) circles. (a) The optimal ordering of the AFMO, (b) Anti-site disorder in AFMO, (c) antiphase boundary formed by the misplaced Fe atoms [from ref 46].

1.2.3.2 Band structure of AFMO

Previous band structure calculations suggest that AFMO compounds exhibit half-metallic ferrimagnetism at room temperature. For the very first time, Kobayashi *et al* studied the electronic structure of Sr₂FeMoO₆ using Density Functional Theory (DFT) in 1998 [30]. Fig. 1.13 shows the Density of States (DOS) plots of SFMO, indicating the half-metallic nature. This halfmetallicity is characterized by a gap of ~0.8eV at the Fermi level in the majority spin-up channel, and 100% spin-polarization of charge carriers in the minority spin-band. In the minority spin-down channel, both Fe and Mo t_{2g} levels are partially filled, whereas e_g levels are empty. These bands lying at the Fermi level exhibit full spin polarization of (P = -1), are predominantly from Mo and Fe t_{2g} states with a small contribution from O 2p states [30].

Many research groups have studied the half-metallicity and electronic structure of AFMO double perovskites using various computational techniques such as DFT, Monte Carlo simulations *etc.* [30, 47, 48].



Fig.1.13 The density of state (DOS) of SFMO calculated by Kobayashi et al [from ref 30].

1.2.3.3 Magnetic Properties of AFMO

AFMO exhibits ferrimagnetic ordering as a result of the antiferromagnetic coupling between magnetic Fe³⁺ (S=5/2) and Mo⁵⁺ (S= ¹/₂) ions [49]. Here, the spin counting formula gives the total saturation magnetization: $g_J\mu_B(5/2-1/2) = 4 \mu_B/f.u.$, where g_J is the Lande g factor when only the spin contributes to the angular momentum. Here, the total ferromagnetic contribution is split into localized and itinerant parts [44]. For the localized electrons, Fe core spin contributes 5 $\mu_B/f.u.$, and itinerant Mo t_{2g} down-spin polarized electrons contribute $-1 \mu_B/f.u.$, to a total saturation magnetization of 4 $\mu_B/f.u.$ Fig. 1.14 shows the super-exchange interactions in Fe³⁺Mo⁵⁺ configuration [51].



Figure 1.14. Schematic showing the super-exchange type interactions in the $Fe^{3+}Mo^{5+}$ configurations in AFMO [from ref 46].

The experimentally observed value of saturation magnetization in AFMO is always found to be lower that the ideally calculated value of 4 μ_B /f.u., owing to the presence of anti-site disorders [39]. As a result of antisite disorder, the Fe³⁺ and Mo⁵⁺ ions replace their positions in the crystal due to small difference in the ionic radii. It destroys the spin arrangements at Fe and Mo sublattices, without affecting the individual magnetic moments at these sites. Originally in a perfectly ordered AFMO system, the Fe-O-Mo interactions are ferrimagnetic in nature; however, in the presence of anti-site disorder, the Fe-O-Fe or Mo-O-Mo superexchange interaction gives rise to antiferromagnetic and paramagnetic coupling, respectively. Additionally, anti-site disorder changes the chemical environment of each ion, which also decreases the magnetic moment at each site. However, extensive *ab initio* band structure calculations suggest the decrease in M_S in the presence of antisite defects in AFMO. Several research groups have quantified the fraction of anti-site disorder present in these AFMO systems as [52]:

$M_S = (4 - 8\chi)\mu_B$

where χ is the concentration of anti-site disorder and M_S is the saturation magnetization. These experimental investigations on anti-site disorder in AFMO are in good agreement with theoretical Monte Carlo simulations [39].

The ferro-paramagnetic transition temperature of AFMO compounds is exceptionally high among half-metals. According to the theoretical calculations, the Curie temperature (T_C) of SFMO is around 450 K [45]. However, the experimental investigations show large variation in T_C values depending on the sample type, or degree of B-site ordering. In polycrystalline and single crystal samples, T_C values around 420 K have been reported [17, 47, 48], but the T_C of thin films have not reached as high values. An example of a typical temperature dependence of magnetization for polycrystalline SFMO is shown in the inset of Fig. 1.15. The T_C value for CFMO and SFMO compounds is 350 and 380K, respectively. The highest T_C of SFMO amongst all the AFMO compounds makes it the most applicable spintronic half-metal. As a result, most of the research is carried out on SFMO only, either bulk or thin film, since past many years.



Figure 1.15. Magnetic hysteresis loop of SFMO at 300 K. Inset shows temperature dependence of magnetization of SFMO for H = 1 kOe [from ref 53].

1.2.3.4 Magnetoresistance in AFMO

Another noteworthy property of AFMO towards spintronic applications is its large magnetoresistance (MR). This implies a substantial decrease in resistance when in the presence of applied magnetic field. The MR can be expressed as:

$$MR(\%) = \frac{R(H) - R(0)}{R(0)} \times 100$$

where R(H) is the resistance in presence of field, and R(0) is the resistance when magnetic field is not present. The maximum value of magnetoresistance generated theoretically for SFMO at 0K is -50%. Experimental investigations also approach this value at high fields. The reported value of MR is -10% at room temperature, and -25% at liquid Nitrogen temperature as shown in Fig. 1.16.



Figure 1.16. Magnetoresistance (MR) plots for SFMO at 300K and 77K shown by N Kumar et al [54].

In the case of polycrystalline samples, the magnetoresistance is primarily governed by the tunneling of spin-polarized charge carriers through the grain boundaries. The behavior of inter-grain tunneling magnetoresistance at low magnetic fields depends greatly on factors such as grain size, oxygen content at grain boundaries, and the formation of antiphase boundaries. On the other hand, the response at high magnetic fields is more influenced by the antiferromagnetic spin disorder (ASD), and the low field magnetoresistance is insignificant in highly disordered samples [55]. Single crystals and epitaxial thin films also exhibit negative magnetoresistance, although the magnitude is approximately one order of magnitude smaller compared to polycrystalline samples. Experimental results and theoretical studies suggest that magnetoresistance in thin films originates from the suppression of antiferromagnetically ordered ASD domains and is highly dependent on the amount of ASD present.

1.2.3.5 Electrical Properties of AFMO

The temperature dependence of resistivity of AFMO compounds is highly influenced by the degree of cation ordering and the synthesis techniques used. These compounds can exhibit either metallic, or semiconducting, or insulating behavior accordingly [56]. The temperature dependence of resistivity of a perfectly ordered AFMO compound is metallic, but this is not observed in real samples. Instead, in polycrystalline AFMO samples, the resistance is too high to be considered metallic, and the temperature dependence shows semiconductive behavior. This suggests that the resistance is primarily influenced by the scattering of carriers at the grain boundaries while the individual grains themselves may exhibit metallic properties. Single crystals and epitaxial thin films of AFMO, on the other hand, have been found to have metallic resistivity, accompanied by a lowtemperature increase in temperature dependence. However, the underlying cause of this complex resistivity behavior remains unexplained.

A small upturn in dc electrical resistivity at low temperatures has been observed for A₂FeMoO₆ compounds and mixed manganites. As discussed earlier, AFMOs are half-metallic systems where the band structure has a gap in the majority spin band and a density of states in the minority spin band, and these two spin channels act parallel to each other [30]. Here, the spin-up channel, having a band-gap, acts like a semiconductor while the spindown channel behaves like a metal. In the metallic state, the resistivity as a function of temperature in the spin-down channel can be described as [57]:

$$\rho_m(T) = \rho_0 + \rho_n T^n$$

where ρ_0 is residual resistivity which is the temperature-independent term, existing due to lattice imperfections, impurities, grain boundary contributions *etc.*, and *n* is an adjustable parameter which governs the collective strength of electron-electron and electron-magnon interaction. This model describes the

electrical conduction mechanism in spin-down metallic state only. On the other hand, the resistivity of spin-up semiconducting band can be described as [57]:

$$\rho_{SC}(T) = \rho_0 + \rho_d^{SC} e^{\frac{E_g}{KT}}$$

where ρ_0 is a temperature-independent term, ρ_d^{SC} is a constant governing electrical charge density and E_g is the bandgap in spin-up channel. Also, the band gap in this double perovskite system is enough to excite the charge carriers to the conduction band. In this context, the total resistivity for AFMO system, which takes into account the resistivity from spin-up semiconducting band (ρ_{SC}), spin-down metallic band (ρ_m) and the temperature-independent term (ρ_0), can be described by parallel spin channel given as [56, 58]:

$$\frac{1}{\rho} = \frac{1}{\rho_m} + \frac{1}{\rho_{SC}}$$

This parallel spin-channel model has been known to explain the total resistivity of half-metallic AFMO systems.

1.2.3.6 Challenges in synthesizing A₂FeMoO₆ thin films:

In earlier sections, we have discussed that due to unique fundamental properties, A_2FeMoO_6 compounds have gained potential applications in solidoxide fuel cells, anode materials, orbitronic devices, and memory devices *etc* [28]. However, fabrication of a single phase, chemically homogeneous and B-site-ordered AFMO film is required in order to realize these device functioning. It is worth noting that synthesis of AFMO compounds, either in bulk or in thin film form, has always been a challenging task for researchers.

Amongst various thin film deposition techniques, Pulsed Laser Deposition (PLD) method has been extensively used for synthesizing AFMO films at high deposition rates [59]. However, there are various obstacles in synthesizing high quality stoichiometric AFMO thin films by PLD due to many constraints in the deposition parameters [60]. Synthesis of high quality AFMO films require a high substrate temperature since the atomic mobility seems to be insufficient to achieve a perfectly ordered double perovskite system at low substrate temperature [61]. In addition to this, a very narrow window of oxygen pressure ($<10^{-4}$ mbar) is required for AFMO phase stabilization. A little oversupply of oxygen gives rise to undesirable phases such as AMoO₄ and AFeO₃ which are more stable at higher oxygen pressures. Few reports suggest that vacuum and reducing environment (N₂ or H₂+Ar) can also be used to prepare phase pure AFMO thin films. In addition to this, the choice of underlying substrate, imparting lattice-mismatch induced strain, also affects the growth and physical properties of AFMO thin films [61].

In addition to single-phase synthesis, improving cation ordering in AFMO thin films has also been a long-standing problem. Synthesis of B-site ordered AFMO films requires absurd growth parameters which are not accessible for every growth chamber. This also causes an issue in the reproducibility of AFMO films which is the main reason for still-missing wide applications of AFMO.

1.3 Motivation and Objectives:

Researchers have faced challenges in synthesizing single-phase $RNiO_3$ compounds with balanced stoichiometry due to the requirement of high temperatures and pressures for phase stabilization. However, the advanced deposition techniques such as pulsed laser deposition (PLD), polymerassisted deposition, and magnetron sputtering have overcome these difficulties. In PLD, the accompanying epitaxial strain in thin films has proven to be an effective alternative to high-pressure conditions for stabilizing the structure. In thin films, researchers have observed systematic variations in the metal-insulator transition temperature (T_{MI}) by altering various parameters, including dimensionality (bulk to 2D and 1D), doping, oxygen content variation, application of electric fields or voltage, strain, and thickness variations. Chemical modifications, particularly charge carrier injection via chemical doping, offer significant control over the electronic properties. Doping can occur at the *R*-site or the Ni-site. However, 3*d* metal ion doping at the Ni-site has a more precise and direct impact on the electronic bands. Previous studies on thin films have predominantly focused on *R*-site doping and limited investigations on Ni-site doping have been conducted. Based on the aforementioned considerations, we have conducted a study to explore the effects of Cu-doping at Ni-site in $PrNiO_3$ thin films. Tuning epitaxial strain by thickness variation in *R*NiO₃ thin films is another key parameter in modifying the physical properties.

Anti-site disorder, appearing intrinsically in double perovskites including AFMO, hampers the spintronic applicability of the system by reducing the Curie temperature and saturation magnetization, *etc.* Therefore, it becomes essential to control the degree of anti-site disorder which is very sensitive to the synthesis conditions in this half-metallic system. A lot of efforts have been carried out, theoretically as well as experimentally, to improve the cation ordering in the AFMO system. In the case of thin films, improving and preserving B-site ordering, which is a much-needed attribute, is more challenging due to the requirement of absurd growth parameters such as very high deposition temperature and very low pressure. Chemically homogeneous and B-site-ordered AFMO thin films have potential applications in solid-oxide fuel cells, anode materials, orbitronic devices, and memory devices. Despite several efforts carried out so far, improving B-site ordering in double perovskite thin films at ambient conditions is still under research.

Earlier studies suggest that cation ordering can be enhanced by synthesizing thin films using Pulsed Laser Deposition (PLD) method at high substrate temperature (>1000 °C) and low oxygen pressure (10^{-4} mbar) [62-64]. However, there appears a difficulty in achieving such absurd growth parameters, and these parameters are not so suitable for all double perovskites including AFMO. We have tried to improve the cation ordering in AFMO (A= Ca, Sr) thin films by depositing thin films in different growth conditions such as in vacuum, or under nitrogen or oxygen atmospheres. In addition to this, the deposition of these thin films on different orientation of underlying substrates also helps in improving B-site ordering.

Based on the above-mentioned ideas, the objectives of this work are as follows:

- 1. To study the effects of doping at Ni-site and epitaxial strain on the structural, electrical and vibrational properties of RNiO₃ thin films.
- 2. To suppress anti-site disorder by varying deposition conditions, substrate orientation and epitaxial strain and study the effects on the physical properties of A_2 FeMoO₆ (A= Sr, Ca) double perovskite thin films.
- To explore the effects of strain on spin-phonon coupling in thin films of double perovskites A₂FeMoO₆ (A= Sr, Ca).

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Chapter 2

Experimental and Characterization Techniques

This chapter encompasses the basic overview of the synthesis methods and characterization techniques used for the present thesis. The synthesis methods involve bulk target preparation using the solid-state reaction method, followed by thin film synthesis using Pulsed Laser Deposition (PLD) technique.

The thin films were characterized for phase formation and structure using X-Ray Diffraction (XRD) and Reciprocal Space Mapping (RSM), thickness estimation using X-Ray Reflectivity (XRR), surface morphology using Atomic Force Microscopy (AFM), oxidation states of elements using X-Ray Absorption Spectroscopy (XAS) and X-Ray Photoelectron Spectroscopy (XPS), and vibrational properties using Raman spectroscopy. In the later sections, the transport properties have been investigated by temperature-dependent resistivity and magnetization measurements, followed by optical conductivity measurements using Terahertz time-domain spectroscopy (THz-TDS).

2.1 Synthesis Techniques

The bulk polycrystalline pellets of $PrNi_{1-x}Cu_xO_3$ ($0 \le x \le 0.1$), LaNiO₃, Sr₂FeMoO₆, and Ca₂FeMoO₆ have been prepared using solid-state reaction route. Then these pellets have been used as targets for the synthesis of thin films using the Pulsed Laser Deposition (PLD) method. A more detailed explanation of the synthesis procedure is given below.

2.1.1 Solid-state reaction method for bulk synthesis

Although there are various methods available for the preparation of bulk material, the solid-state reaction is one of the most commonly used methods for the preparation of bulk oxides [1-3]. As the name suggests, it is a solvent-free process and requires proper mixing of constituent powders in exact stoichiometric amounts. This was acquired through intermittent grindings in pestle-mortar and using propanol as a mixing medium in order to ensure homogenous mixing. The grinding decreases the particle size and increases the surface area and therefore, a high reaction rate is achieved. After grinding, a certain temperature is required for the oxides to react properly. Therefore, the obtained mixture is heated in a furnace at a particular temperature (below the melting point of these oxides) for a few hours with a controlled heating and cooling rate. This process is called calcination and is generally used for the removal of some volatile gases like CO₂ and NO₂ etc. After the first calcination, some powder may remain unreacted, and further grinding is required. In order to maintain uniformity and homogenous mixing of the powders, several intermittent grindings and calcinations are carried out repeatedly. Finally, the grounded mixture is pressed in form of a pellet using a hardened steel made dieset of 15 mm diameter under 4 tons of pressure using a hydraulic press. Then, these pellets are sintered at a temperature higher than the calcination temperature for several hours. This sintering is used for the densification of the compound.

Synthesis of $PrNi_xCu_{1-x}O_3$ (x = 0-0.1) and targets:

Using the solid-state reaction method, we have prepared $PrNi_xCu_{1-x}O_3$ (*x*= 0-0.1) bulk targets. The basic steps involved in the process are presented in the block diagram:



Synthesis of A_2 FeMoO₆ (A= Sr, Ca) target:

The bulk polycrystalline pellets of A₂FeMoO₆ (A= Ca, Sr) have been prepared by conventional solid-state reaction route. The high-purity (~99.99%) powders of ACO₃ (A= Ca, Sr), Fe₂O₃, and MoO₃ powders were taken in proper stoichiometric amounts. These powders were mixed properly in pestle and mortar for 3 to 4 few hours. The mixture was calcinated at 1000°C for 10 hours for the removal of CO₂. Second grinding was carried out for 2 to 3 hours and again calcinated at 1000°C. The third grinding was done for 1 hour and then the resultant mixture was pressed into a pellet of 15mm diameter using stainless steel dia-set. Sintering of this pellet was done in a tubular furnace at 1150°C in presence of a reducing atmosphere *i.e.*, Ar+5% H_2 gas for 12 hours. The heating and cooling rate was kept 5°C/min for all the temperature ramps.

2.1.2 Pulsed Laser Deposition for Thin Film Synthesis

A thin film is a layer of a material with thickness ranging from several nanometers to few micrometers. Due to confinement in *z*-direction, thin films exhibit various interesting fundamental properties and applications as compared to its bulk counterparts. In addition to this, the growth of multilayers and heterostructures has opened a new avenue in the applicability of thin films. In order to meet the technological requirement, it is imperative to fabricate phase pure and stable thin film. As far as the synthesis is concerned, there are various physical and chemical vapor deposition methods available. The most commonly used methods are molecular beam epitaxy (MBE), magnetron and Radio Frequency (RF) sputtering, thermal evaporation, Chemical vapor deposition, and Pulsed Laser Deposition (PLD), *etc.* Out of the various methods stated above, PLD is one of the promising techniques which has been extensively used for the fabrication of oxide thin films and multilayers for years.

For the very first time, the Ruby laser was introduced in 1960 by Mariam which stimulated the growth of laser-assisted thin film deposition. Then in 1965, Smith and Turner used the ruby laser to deposit the first thin film by laser evaporation from a solid surface. But the qualities of these thin films were still inferior to that deposited by other methods such as molecular beam epitaxy etc. In 1987, T. Vanketesh and co-workers revolutionized the world of thin film technology by synthesizing high-quality thin film of very complex high T_C superconductor YBa₂Cu₃O₇ by PLD technique [4]. Despite the complex stoichiometry of YBa₂Cu₃O₇, the properties of the grown film were quite advanced as compared to that grown by other techniques. Soon after that, the PLD technique has been comprehensively used to grow highly crystalline thin films of oxides, nitrides, multilayers, superlattices, and heterostructures, *etc.* The advancement of new laser technology with short pulse durations and high repetition rates has opened new dimensions towards the growth of complex thin films using PLD.

Operation and Growth mechanism of PLD:

PLD falls in the category of physical vapor deposition (PVD) technique where a high-energy laser beam is used to ablate the target material. The ablated material forms a plasma plume, which consists of atoms, ions, and molecules, and gets deposited on the substrate which is kept at a certain temperature [4-6]. The most used lasers in PLD are KrF, ArF and Nd-YaG. The idea of PLD is elementary, however, the experimental realization is a bit tricky. The basic steps involved in the synthesis of thin films by PLD are as follows:

- 1. Interaction of laser with the target material
- 2. Plasma Plume formation
- 3. Nucleation and thin film deposition under favourable conditions.

All these steps play a significant role in deciding the phase and properties of grown thin films. The description of these steps is given as:

Laser-Matter Interaction:

A high-energy beam of pulsed laser is focused on the target material which is to be deposited. This pulsed laser beam, being highly energetic in nature, increases the temperature of the target material slightly above the melting point. The laser penetrates the material surface, upto a few nanometers, depending on the laser energy and refractive index of the material. The ejection of atoms, ions, and molecules from bulk material is carried out by the vaporization of material surface in non-equilibrium [7]. This laser-matter interaction occurs inside a vacuum chamber in presence of background gas such as Oxygen, Nitrogen, Argon, *etc.* This is a very rapid process, and it takes about a few nanoseconds.

Plasma Plume Formation:

The ablated material consisting of atoms, ions, molecules, and chunks, forms a plasma plume which is elliptical in shape. The spatial distribution and shape of the plasma plume are decided the parameters like background gas pressure, laser energy, target-to-substrate distance, *etc*. The plume remains highly directed toward the substrate. In the case of vacuum, the plume remains very narrow due to the absence of scattering. However, in the case of a background gas, the shape of the plume expands in all directions. Background gases like oxygen compensate for the oxygen deficiency occurring in oxides, and sometimes influence the stoichiometry of the thin film to be deposited.

Nucleation and growth of thin films:

The highly energetic species from the target material are bombarded to the substrate. It starts nucleation on the surface of the substrate. Nucleation is the last step for thin film growth and is very crucial in determining the properties of the film. There are three major models describing the growth of thin films:

- a) Volmer-Weber growth model- This is also named as Island growth model. Here, small 3D islands start growing at the substrate surface as shown in the figure. The additional islands then grow on the top of old islands and remain more bounded to each other as compared to that to the substrate. This remains as 3D growth [8].
- b) Frenk-van der Merve growth model- This growth mode is also known as layer-by-layer growth. In this model, the atoms get deposited on the substrate in the form of monolayers, and then the other layer grows. This model is ideal for the deposition of highly epitaxial and crystalline films. This mode enables the lattice matching between the substrate and layer. The atoms remain more attracted to the substrate as compared to the layer itself, giving rise to 2D growth mechanism at initial stage [9].

c) **Stranski–Krastanov growth model-**This is a combination of both above described *i.e.*, 2D and 3D growth models, and is known as mixed growth model. In this process, firstly the monolayers get deposited on the substrate surface and then some islands start growing [10, 11].

As described earlier, the process of PLD is a bit complex and it requires various external parameters to be controlled precisely. These parameters play a crucial role in deciding phase purity, epitaxial growth, transport behavior, and many other physical properties of thin films. These parameters are listed below:

- 1. **Laser energy fluence**-It controls the kinetic energy of the ejected species and the growth rate of the material.
- 2. **Process gas partial pressure**-It helps in regulating the shape of the plasma plume.
- 3. **Substrate temperature**-It creates a favourable template for the growth of thin films.
- Target-to-substrate distance-It decides the annular spread of the plasma plume.
- 5. **Repetition rate**-It also decides the growth rate and epitaxial growth of thin films.

Like any other deposition technique, PLD also possesses a few advantages and disadvantages such as:

Advantages of PLD:

- a. PLD technique gives the flexibility to tune various synthesis parameters as mentioned above in order to grow desired phase pure thin films.
- b. PLD enables the complete transfer of target stoichiometry to the substrate [12].
- c. A single-phase film can be deposited using a multiphase target.

- d. PLD gives precise control of the thickness of thin films via controlling the number of laser shots.
- e. PLD is an efficient technique to grow multilayers.
- f. Heating and cooling rates of the substrate can be precisely controlled in PLD.

Disadvantages of PLD:

- a. PLD plume area is quite small, and the grown films can't be utilized commercially for industrial purposes, therefore, are limited to research purposes only.
- b. A high-energy pulse causes damage to the target surface, and the target surface needs to be cleaned every time after deposition in order to achieve a smooth target surface.
- c. It causes fast heating and cooling of target material and can cause the formation of lumps.

Experimental setup of PLD:

A typical PLD system consists of two main components *i.e.*, a pulsed laser (KrF Excimer Laser in the present case) and a vacuum chamber equipped with vacuum pumps. In addition to this, it also consists of a focusing lens, rotating target holder assembly, substrate holder with heater, gas inlets, *etc.* The schematic of the PLD system is shown in Fig. 2.1. And the real experimental setup of PLD at the thin-film laboratory, IIT Indore is shown in Fig. 2.2.



Fig. 2.1: Schematic representation of the experimental setup of a pulsed laser deposition system.

For the present work, we have deposited thin films of rare earth nickelates and double perovskites using the PLD system. The pulsed laser used here is a KrF excimer laser (Compex Pro 102F, Coherent, Germany) with a wavelength of 248 *nm*. A focusing lens, with a focal length of 30 *cm*, is used to focus the laser beam on the target material. The vacuum chamber is made up of stainless steel and is connected to a rotary and turbomolecular pump. The PLD chamber is initially evacuated by the rotary pump and then using the turbomolecular pump, the base pressure in the order of 10^{-4} Pa has been achieved.



Fig. 2.2: Actual experimental setup of pulsed laser deposition system at Thin Film Laboratory, IIT Indore.

The first step of deposition starts with chamber preparation. The required substrate is cut into the desired dimension using MTI made diamond cutter. Then the substrate is cleaned properly using acetone and propanol in an ultrasonicator. The cleaned substrate is then affixed on the substrate holder using silver paste. The target is also affixed using silver paste on the target holder, and the motion of the target (both raster and rotation) is monitored through a DC motor. The target is continuously rotated at 10rpm in order to ensure uniform ablation. The target-to-substrate distance is adjusted as per the optimization conditions. After chamber preparation, the chamber is evacuated for a few hours. After achieving the required base pressure, the substrate is heated to the deposition temperature in a controlled manner using the heater flange attached to the substrate holder. In the present setup, the heater can attain a maximum temperature of 830°C. The process gas is maintained meanwhile using the gas flowmeter and gate valve. When the required temperature and pressure are achieved, deposition is carried out. To prevent the internal heating of the chamber, two small fans have been attached to the walls of the chamber.

2.2 Characterization Techniques

After deposition, the various physical properties of the thin films have been investigated using different characterization techniques. These include the determination of structural, vibrational, optical, magnetic, and electrical properties of the deposited films.

2.2.1 Structural and vibrational properties:

The structural properties of the system have been investigated by carrying out X-Ray Diffraction (XRD), Reciprocal Space Mapping (RSM), X-Ray Reflectivity (XRR), X-Ray Absorption Near Edge (XANES), X-Ray Photoelectron Spectroscopy (XPS), and Raman spectroscopy measurements.

2.2.1.1 X-Ray Diffraction (XRD):

X-Rays are electromagnetic waves which have wavelength in the range of few angstroms which is comparable to the interatomic spacing of a crystal. When a beam of X-rays interacts with the crystal, it gets diffracted by the atoms of the crystal. The constructive interference of these scattered waves gives rise to a pattern, known as X-Ray diffraction (XRD) pattern. XRD is one of the basic techniques which is reliably used to get a primary idea about the phase purity and crystal structure of the system. Being non-destructive in nature, XRD is used as a major technique to identify crystal structure, interplanar spacing, lattice parameters, crystallographic strain, crystallite size, *etc* [13, 14].

Bragg's condition

When X-Rays of sufficient energy, having wavelength λ , fall on a material with an incident angle θ , it gets diffracted through the set of parallel planes present in the crystal lattice as shown in fig. 2.3. A constructive between these diffracted rays occurs when the following condition is satisfied

$2dsin\theta = n\lambda$

where d is the interplanar spacing, θ is the incidence angle, n is an integer defining the order of diffraction, and λ is the wavelength of incident light. This is known as Bragg's condition and was proposed by W. L. Bragg in 1921. A pictorial representation of Bragg's condition is shown in the ray diagram in Fig. 2.3. When the above criterion is fulfilled, a peak in the diffraction pattern appears at a particular angle.



Fig. 2.3: Diffraction of X-Rays by atoms of a crystal

It is worth mentioning here that the XRD pattern of every material is unique and different, and therefore, can be used to confirm the phase purity and chemical stoichiometry of a material. In addition to this, XRD is a helpful technique to determine whether a material is crystalline, polycrystalline, or amorphous in nature. XRD is a versatile technique that can be used to diffract a variety of samples in form of powders, pellets, or thin films [15]. In the case of thin films, due to the difference in the lattice parameters of the substrate and thin film, lattice-mismatch-induced strain is experienced by the film.

XRD can be used to estimate out-of-plane epitaxial strain, both qualitatively (by sign) and quantitatively (by percentage). Strain can be of two types:

- **1. Tensile strain:** When the pseudocubic lattice parameter of thin film is smaller than that of the substrate, an expansion in in-plane and compression in out-of-plane lattice parameters occurs (Fig. 2.4). It causes a shift of XRD peaks towards higher 2θ side to satisfy Bragg's condition.
- **2. Compressive strain:** When the pseudocubic lattice parameter of thin film is larger than that of the substrate, the in-plane lattice parameters compress and an expansion in out-of-plane lattice parameters occurs in order to conserve unit cell volume (Fig. 2.4). It causes a shift of XRD peaks towards lower 2θ side.



Fig. 2.4: Representation of compressive and tensile strains for thin films deposited on a substrate.

The typical experimental setup of the X-Ray diffractometer is shown in Fig. 2.5. Here, θ is the angle between the incident X-Ray and the surface of the sample and is known as the angle of incidence, ϕ is the angle of rotation about a plane perpendicular to the sample surface, ψ is the angle of rotation parallel to the surface, and 2 θ is the angle between the incident and diffracted beam. The appearance of intense peaks in the XRD patterns gives a signature of atomic crystal planes. Since the epitaxial films are extremely thin as compared to the penetration depth of X-rays, an intense peak originating from the substrate appears in the θ -2 θ scan of thin films.


Fig. 2.5: Representation of X-Ray Diffractometer.

In the present thesis work, the phase purity, crystallinity, and epitaxial strain in thin films have been examined by carrying out X-Ray diffraction measurement using Cu K_{α} radiation ($\lambda = 1.54$ Å) using a Rigaku SmartLab X-Ray diffractometer.

2.2.1.2 Reciprocal Space Mapping (RSM):

A reciprocal space is a Fourier transform of a real periodic lattice. It is an imaginary space, consisting of a set of points, where each point describes a set of parallel planes. As it is difficult to analyze a large number of planes in a direct lattice; reciprocal space mapping (RSM) is used as an alternate technique to deal with this problem. RSM is an efficient technique to determine structural parameters such as in-plane lattice constants, strain relaxation, mosaicity, superlattice periods, *etc.* in the case of epitaxial thin films [16, 17]. A reciprocal space map consists of a collection of several θ -2 θ scans at different ω values around a Bragg's peak, where ω is the angle between the incident X-Ray and sample surface, and 2 θ is the angle between the incident and diffracted beam, as depicted by the ray diagram shown in Fig. 2.6. Based on the nature of Bragg's reflection, RSM scans can be of two types:

1. Symmetric Scan: In this scan, ω remains equal to θ and it provides information about the lattice planes parallel to the sample surface.

Asymmetric Scan: Here, ω≠θ, it scans the reciprocal maps around different ω values, and provides information of the planes which are not parallel to the sample surface, and in-plane crystal structure of the sample. This scan is very complex in nature.



Fig. 2.6: Schematic representation of reciprocal space coordinates

When an X-Ray beam scatters from a crystal lattice, the conservation of momentum is given by the scattering vector: $Q = k_f \cdot k_i$, where kf and ki are the wave vectors of scattered and incident beams, respectively. In case of coplanar scattering, the incident wave, the scattered wave and the normal to the surface lie in same plane. If the reciprocal space axis Q_x is taken parallel to the sample and Q_z is taken parallel to the normal, then the relations between instrumental coordinates 2θ , ω and components of scattering vector Q are represented as [10]:

$$Q_x = K[\cos\omega - \cos(2\theta - \omega)]$$
$$Q_z = K[\sin\omega + \sin(2\theta - \omega)]$$

Where, $K=2\pi/\lambda$ is the magnitude of the X-ray wave vector.

A typical reciprocal space map consists of fringes representing the film and substrate peak separately. It is represented in reciprocal space by scattering vectors Q_x and Q_y . In the case of a coherent growth of thin film, the substrate and film peak lie along the same pseudomorphic line. However, for a relaxed film, there is a slight shift between the film and substrate peak.

In the present thesis, the RSMs of the prepared thin films were recorded by a PanAlytical-made diffractometer using 5-axes cradle with Cu- K_{α} source. Epitaxy software was used to analyze the recorded RSM data.

2.2.1.3 X-Ray Reflectivity (XRR):

X-Ray Reflectivity (XRR) technique is used to determine the thickness, surface roughness, and electron density profile of single-layer and multilayer thin films [18]. This technique is based on the principle of total internal reflection. When the refractive index of the material surface for X-rays is less than 1, the beam may undergo reflection or refraction based on the incident angle. When the incident angle is less than the critical angle, 100% reflection is observed, known as 'total internal reflection'. When X-Ray incidents on an angle greater than the critical angle, the beam entering into the material gets reflected by the interface between film and substrate. The X-Rays reflected from the surface and the interface interfere with each other and give rise to an oscillatory fringe pattern in the XRR profile (Fig. 2.7).



Fig. 2.7: Geometry of X-Ray Reflectivity in specular coordinates

The incident angle for XRR measurements is generally kept from 0.1° to 3°. The obtained oscillatory fringes are known as Kiessing fingers, and the thickness of the layer can be obtained from the separation of two consecutive fringes. In XRR geometry, the incident angle is α_i , the scattering angle is α_f ,

and q_z is the component of the scattering vector. The scattering vector can be described as:

$$\Delta q = \left(\frac{4\pi}{\lambda}\right) \sin \alpha_i$$

An approximate idea about the thickness of thin film can be obtained as

$$t = \frac{2\pi}{\Delta q}$$

whereas, the sharpness of the decay in the reflectivity patterns gives an idea about surface roughness, and the amplitude of oscillation is indicative of electron density. The exact idea of these parameters can be obtained by fitting the X-Ray reflectivity data with Paratt's exact recursive method [19, 20]. The X-Ray reflectivity can be formulated as:

$$R(q_z) = R_F(q_z) \left[\frac{1}{\Delta q_z} \int \frac{d\rho(z)}{dz} \exp\left(-iz\sqrt{q_z(q_z^2 - q_c^2)^{\frac{1}{2}}}\right)^2 \right] dz$$

Where R_F is the 'Fresnel reflectivity' obtained from a single ideal interface, $\Delta \rho$ represents the overall change in density of electron across the interface, and *qc* denotes the momentum transfer at the critical angle for total external reflection. In the present thesis, the thickness and surface roughness of the thin films have been obtained by fitting the XRR data with the Paratt's recursive formalism described above.

2.2.1.4 X-Ray Absorption Spectroscopy (XAS):

X-Ray absorption spectroscopy (XAS) is an important technique which is used to analyse the local structure of materials by obtaining XAS data of selected atoms. It is a vital technique that can be applied on a variety of samples including bulk, thin films, and liquids *etc*. It is based on the principle of absorption of X-Rays by materials, and the absorption coefficient (μ) is measured with respect to incident beam energy (*E*). As per Beer-Lambert law, the intensity (*I*) of transmitted X-rays is given as follows [21]:

$$I = I_0 e^{-\mu t} \tag{3}$$

where I_0 is the intensity of the incident X-rays, and t is the sample thickness.

The XAS measurements can be carried out either in transmission or fluorescence mode based on the nature of sample as shown in Fig. 2.9. In transmission mode, the absorption coefficient is given as:

$$\mu(E)t = \log \frac{l_0}{l} \tag{3}$$

In case of fluorescence mode, it is given by:

$$\mu(E) \propto \log \frac{l_f}{l} \tag{3}$$

where I_f is the intensity of fluorescence line related to the absorption process. In fluorescence mode, the detectors are usually placed perpendicular to the incident X-Ray direction. Fluorescence mode is used to collect XAS data of thin film samples. The absorption coefficient is also dependent on the properties of sample as

$$\mu = \frac{\rho Z^4}{AE^4}$$

Where ρ is density ρ , Z is atomic number and A is atomic mass of the sample.



Fig.2.8 Schematic representation of the energy levels of an absorbing atom.

XAS measurements can be carried out both in lab source or synchrotron radiation source; however synchrotron source is preferred since it provides intense X-Ray beams with tunablity in energy range. The typical energy of X-Rays varies from ~500 eV to 500 keV, which is sufficient to eject electrons from different levels of an atom. When X-Ray absorption by an atom takes place, the electrons get promoted to the excited states and it leaves behind empty core-holes. The schematic depicting the absorption process of an atom consisting of different energy levels is shown in Fig. 2.8. This absorption gives rise to a sharp increase in the intensity. With increase in the incident energy, the atoms absorb the energy and release a photo-electron at the continuum level. There can be two mechanisms for the decay of excited electrons. One is X-Ray fluorescence of specific energy in which a core-level electron, containing high energy, fills a deeper-core hole. This represents the characteristic property of an atom. The other process is 'Argur effect' in which an electron decays from the higher energy level and a second electron is ejected out into the continuum.



Figure 2.9: *Schematic diagram of the XAS setup. Fluorescence detector is at a right angle with the incident X-ray beam.*

The XAS is generally characterized into two regions: X-Ray Absorption Near Edge Structure (XANES) and Extended X-Ray Absorption Fine Structure (EXAFS) as shown in the schematic. The XANES edge carries information about oxidation state, and octahedral or tetrahedral surrounding of an atom. However, EXAFS is used to get idea about bond distances between neighbouring atoms, and coordination number of an atom. In the present thesis, the XANES measurements on CFMO thin films have been carried out to determine the oxidation state of Fe and Mo ions. The measurements were performed on BL-9 at INDUS-2 synchrotron source, Raja Ramanna Centre for Advanced Electronics (RRCAT), Indore, India. The measurements were carried out in fluorescence mode using an energy dispersive detector. This beamline operates in the energy ranging from 4 to 25keV. In the present case, the XAFS data has been calibrated using Fe and Mo metal foils at respective energy ranges. The beamline consists of Rh/Pt coated meridional cylindrical mirror for collimation and a Si (111) double crystal monochromator (DCM) to select excitation energy of Fe (7112 eV) and Mo (20000 eV) K-edges. The second crystal of the DCM is a sagittal cylinder that provides a beam focused in a horizontal direction. The XANES spectra has been normalized using the ATHENA software.

2.2.1.5 X-Ray Photoelectron Spectroscopy (XPS):

X-ray photoelectron spectroscopy (XPS) is a surface technique which is used to provide quantitative information about the chemical state, elemental composition, and electronic state of materials [22]. It was discovered by Noble laureate Kai Siegbahn in the year 1960. It is based on the principle of photo-electric effect, and it involves the photo-ionization and determination of kinetic energy of the ejected photoelectrons. When X-Rays of sufficient energy fall on a sample surface, it causes excitation of electrons in the bound states giving rise to ionization and emission of the core electrons (Fig. 2.10). The ejected photoelectrons are collected with the help of a hemisphere shaped electron analyzer which is used to measure their kinetic energy. The electron analyzer gives an energy spectrum of the ejected photoelectrons vs binding energy as per the relation [23]:

$$E_B = h\nu - E_k - \Phi \tag{()}$$

Where E_B is the binding energy of photoelectrons, hv is the incident photon energy, E_k is the kinetic energy of the ejected photoelectrons, and Φ is the work function of the metal. X-Ray spectra is obtained by irradiating the sample surface with X-rays beam and continuously measuring the kinetic energy and the number of ejected photoelectrons from top surface to about 10nm. Here, soft X-Rays with energy ranging from 100-2500eV are used to study the core-levels of the sample surface [22]. This technique requires ultrahigh vacuum chamber, and it can be applied on bulk as well as thin films.



Fig.2.10: Schematic representation of energy levels of an atom in XPS.

In the present thesis, the XPS experiments were performed on Niedge for Cu-doped PrNiO₃ thin films, on Fe and Mo-edges for Sr_2FeMoO_6 and Ca_2FeMoO_6 thin films. The spectroscopy measurements were performed on beamline BL-14 of the Indus-2 synchrotron source at RRCAT, Indore, India. The measurements were carried out in an ultra-high vacuum chamber with the monochromatic X-ray beam of 4357 eV energy.

2.2.1.6 Raman Spectroscopy:

Raman effect was discovered by sir Chandrasekhara Venkata Raman and his student K. S. Krishnan in 1928 in India [24]. Raman spectroscopy is a characterization technique which is used to analyze vibrational and rotational motions of a material which happen at low energy. When an intense and monochromatic laser falls on a material surface, some part of it gets absorbed and some part is scattered into different directions [25]. The scattered light provides the information about vibrational properties of the material. The scattered light can be of two types, known as elastic and inelastic scatterings. When the scattered light is of same frequency (v_0) as that of the incident one, it is known as Rayleigh scattering (elastic scattering). This scattering contains most of the part of the scattered light. On the other hand, the inelastic scattering is very weak in nature and it is also known as Raman scattering. When the frequency of the scattered light is less than the incident one *i.e.*, v_0 - v_m , it is known as stokes line, where v_m is the frequency of the characteristic phonon [25]. In anti-stokes line, the frequency of the scattered light is more than the incident one *i.e.*, v_0 - v_m as shown in Fig. 2.11.



Fig. 2.11: Schematic representation of (a) interaction of laser light with a molecule and (b) Energy level diagram representing the various emissions.

In case of inelastic scattering, the light-matter interaction and transfer of energy and momentum gives rise to creation and annihilation of elementary phonons, creating stokes and anti-stokes lines. The main advantage of Raman spectroscopy is that the diameter of laser beam is very small *i.e.*, in mms, so it can be carried out on very small samples also. In addition to this, Raman spectroscopy can be carried out a variety of samples including powder, pellets, thin films, and aqueous solutions *etc*. We can record Raman spectra in broad region *i.e.*, from 50-5000 cm⁻¹ in a single scan. It is a very quick technique. The major drawback of Raman spectroscopy is that it can cause laser heating in the sample.

The Raman spectrometer typically consists of lasers, fitters, microscopes, charge-coupled device (CCD) detector, and software (Fig. 2.12). The low temperatures can be achieved by connecting liquid nitrogen supply to the sample stage. In the present thesis, Raman spectroscopy measurements has been carried out using a Horiba LabRAM-made HR-Evolution Raman microscope consisting of a Charge Coupled Device (CCD) detector. Micro-Raman signals were recorded in back-scattering mode. A *HeNe* laser with excitation light 632.8 *nm* and a laser power of 1 mW, to avoid overheating of sample was used. Temperature-dependent Raman measurements were carried out by placing the sample on a commercial Linkam stage and varying the temperature using temperature controllers and the LN₂ module. The basic components of Raman spectrometer are:

1. Plasma line filter:

This filter is used to remove the plasma lines generated by the gas laser due to plasma formation. Since the plasma lines are quite intense, it is required to remove them to accomplish good Raman spectra.

2. Edge Filter:

It is used to remove the Rayleigh lines, as the intensity of Rayleigh lines is 106 times higher than the Raman lines and can overshadow its effects. The edge filter has a very narrow width of transition which allows it to measure even the smallest Raman shifts.

3. Microscope:

There are three objective lenses provided with the spectrometer *i.e.*, 100X, 50X and 10X for the collection Raman scattered radiation. These lenses

possess different their working distance, numerical aperture and resolution. In the present work, a 100X objective lens is used to acquire the room temperature Raman spectra. However, the 50X objective lens is used for the low-temperature Raman measurements, as in this case, the long working distance is required because of the height of the stage used for taking the sample to low temperature.

4. Grating:

Grating is a dispersive element which separates the scattered photons on the basis of wavelength before they enter the detector. The Raman set up is equipped with the two gratings, 600 grooves/mm and 1800 grooves/mm. The spectral range covered by the spectrograph in one shot depends on the grating and wavelength used for the excitation.

5.CCD detector:

The output of the spectrograph is detected by the charge-coupled device (CCD). It collects the scattered photons and gives an electrical signal to the computer, where the software (Labspec6.0) processes the signal by subtracting the energy of the scattered photon from the incident photon and generates the pattern of intensity versus Raman shift (cm⁻¹) with reference to the zero set energy of the incident photon.



Figure 2.12: Schematic diagram of micro-Raman spectroscopy setup.

2.2.2 Surface Morphology:

The surface morphology of the synthesized thin films has been analyzed using Atomic Force Microscopy (AFM) technique which is described in detail here.

2.2.2.1 Atomic Force Microscopy (AFM):

AFM is a characterization technique which is used to scan the sample surface down to nanometer scale and creates a 3D profile. It gives information regarding surface morphology, surface roughness and sometimes thickness of thin film samples. AFM set-up consists of sharp cantilever tip which is used to scan the sample surface (Fig. 2.13). The tip scans the surface very gently and determines the force between the sample surface and cantilever tip. The force is defined by the spring constant of the cantilever and the distance between the tip and the surface. Any change in the force constant causes deflection in the cantilever tip which is monitored by a laser beam [26]. Thus, the measurement of cantilever deflection helps in mapping the surface topography. One of the advantages of AFM is that it doesn't require any sample preparation and it can be performed on electrically nonconductive sample also. AFM operates in three different modes which are described here:

1. Contact mode: This is the most basic operating mode of AFM. Here, the cantilever tip is in soft physical contact with the material surface. This mode operates two ways: *i*) Constant Height where the deflection in cantilever tip maps the surface topography, *ii*) Constant Force, where a feedback loop is provided to maintain a constant force by maintain a fixed distance between the cantilever and the sample. This mode provides fast scanning of the samples. But it could damage the sample due to dragging of the probe. To overcome such issues, tapping or non-contact mode is generally preferred.

2. Non-contact mode: This mode is operated when the distance between the sample is tip is more. Here, the oscillation of cantilever is larger than its resonance frequency with small amplitudes.



Fig.2.13 Schematic representation of Atomic Force Microscope

3. Tapping mode: This is the most preferred mode of operation of AFM for high quality images. Here, the cantilever tip oscillates up and down near its resonant frequency and intermittently contacts the sample [27]. The image is obtained by variation in the amplitude of oscillations when the cantilever tip taps the sample surface during scanning.

In the present thesis, tapping mode has been used for examining the surface morphology of PrNiO₃ thin films. An Atomic force microscope from Park Systems, NX10 was used to record the AFM images. The growth rate and thickness of thin films were confirmed by performing AFM across a step created on the thin film. Here, the cantilever travels across the step, giving an idea of the step height in nm units.

2.2.3 Electrical measurements:

This section includes the electrical, magnetic and optical characterizations of the prepared thin films. The electrical transport properties of all the thin films have been studied using temperature-dependent dc resistivity measurements using four-probe method. The optical conductivity of thin films has been studied using Terahertz time-domain spectroscopy. In addition to this, the magnetic properties of the thin films have been

investigated using temperature and field dependent magnetization measurements using SQUID magnetometer. The details of these characterization techniques are provided here.

2.2.3 Temperature-dependent Resistivity Measurements

Resistance means some kind of obstacle in the normal flow of current in a material. Resistivity is a material property which determines how much a material restricts the flow of charge carriers through it. In material science, the determination of temperature dependence of electrical resistivity is a crucial measurement for understanding the material property. Broadly, the materials can be categorized as metal, semiconductor or insulator based on their temperature dependence of *dc* resistivity. In case of metals, the electrical resistivity increases with increase in temperature, however for insulators the electrical resistivity varies inversely with temperature [28]. So, it becomes crucial to determine the temperature dependence of *dc* resistivity for the materials which exhibit metal-insulator phase transitions, or structural or magnetic transitions associated with the electronic one [29].

Generally, the resistance of a material *i.e.*, R is calculated using Ohm's law i.e., V=IR, where V and I are the voltage and applied current, respectively. Then, resistivity (ρ) of the sample can be calculated as,

$$\rho = R \frac{A}{l}$$

where A (= $w \times t$) is the cross-sectional area of the sample, and *l* is the distance between voltage probes (Fig. 2.14). There two methods to perform resistivity measurements *i.e.*, two-probe method and four probe method. Two probe method is used for samples which possess very high resistance. In two-probe method, the outer probes are used to supply current and same leads are used to measure the voltage. In contrast to this, the four-probe method is suitable for conducting samples which have low resistance. Here, two outer leads are used to supply current, and the middle two probes are used to measure the voltage drop across a length. The advantage of four-probe method over two





Fig.2.14: Schematic showing temperature-dependent resistivity measurement setup.

In the present thesis, the resistivity of nickelate and double perovskite thin films has been measured using four-probe method. The schematic diagram and actual experimental setup is shown in Fig. 2.14. The sample size is usually 2mm*5mm. Four collinear contacts are made on the surface of thin film using conductive silver paint (SPI supplies), and the samples were heated for 10-15 minutes before putting them into the measurement chamber. The chamber is evacuated for 1-2 hours before starting the experiment. A closedcycle refrigerator (CCR) cryostat system (Janis and Sumitomo) were used for the measurements. The temperature is monitored and controlled by a Lakeshore made temperature controller. The measurements were performed over a temperature range of 300-8K using Sumitomo made compressor. The current is supplied and measured through a Keithley made Source-Meter (2612 A, dual channel), and voltage is measured through the same system. The actual experimental setup of temperature-dependent resistivity measurement used for the present thesis is shown in Fig. 2.15.



Fig.2.15: Actual experimental setup of temperature-dependent resistivity measurement

2.2.4 Magnetization measurements

The magnetization of a sample at a given temperature is dependent on the applied magnetic field, magnetic exchange interactions and thermal excitons. It is generally measured using Superconducting Quantum Interference Device (SQUID). Fig. 2.16 shows the working mechanism of SQUID. Here, the sample is placed inside a detection coil which is inductively coupled to the applied magnetic field. A SQUID consists of two Josephson junctions formed in a semiconducting ring [30]. The voltage drop across the Josephson junctions can be altered by the magnetic flux. During the measurement, when the sample is moved up and down, an alternating magnetic flux is generated in the detection coil. As this magnetic flux is sent to the SQUID, a voltage difference generates across the Josephson junction which depends on the magnitude of magnetic flux. In this way, SQUID is a magnetic flux to voltage convertor where obtained voltage is magnified and processed by the magnetometer's electronics. SQUID is kept in a complete superconducting shield to prevent magnetic flux from the magnet or surrounding.



Fig.2.16 Schematic representation of magnetic measurement setup

In the present thesis, the magnetic properties of the system have been studied by carrying out magnetic characterizations using Quantum design made magnetometer. SQUID provides magnetic field up to ± 7 T and temperature range from 1.8 K to 300 K, and higher temperature can be achieved with oven attachment.

2.2.5 Terahertz spectroscopy

Terahertz spectroscopy is a potential tool to investigate low energy dynamics of materials which includes the investigations on various intriguing phenomena such as charge/spin density waves, orbital ordering, magnons, topological phases *etc.* in transition metal oxides, and can be used to analyze various such phases and excitations [31]. As THz radiation has very low energy, it can be used to investigate material systems without perturbing their current states. The non-ionizing nature, high penetration depth, high opacity to metals and transparency to insulators and strong sensitivity towards water *etc.*, make THz radiation highly applicable in different fields. The response of the materials towards THz radiation provides the idea of fabricating high speed computers working Terabit/sec, and electronic devices at picosecond time scale [32].

The electromagnetic spectrum contains a broad range of frequencies from radio waves, microwaves to x-rays and γ -rays (fig. 2.17). THz lies between microwaves and infrared radiation in the electromagnetic spectrum [32]. A THz band is roughly defined from 0.1-10 THz. 1 THz corresponds to \sim 4.1 meV energy and \sim 33 cm⁻¹ wavenumber (Fig. 2.17). Initially there was some difficulty in generating THz signals as compared to established technologies for electronic and optical devices. However, recent advancement in fabricating new semiconducting materials has led to high-speed devices in the THz gap. For example, laser diodes, high electron mobility transistors, quantum cascade laser, *etc*.



Figure 2.17: Electromagnetic spectrum showing THz radiations.

We have carried out our experiments in Terahertz time domain spectroscopy (THz-TDS) in transmission configuration. Here, the THz pulse is first collected without loading the sample and is considered as reference pulse. Then, the THz pulse is collected after transmitting from the sample. The transmitted waveform is collected in time-domain, where magnitude and phase vary with time (ps). Fourier transform of temporal waveform gives amplitude and phase of the THz pulse as a function of THz frequency. From amplitude and phase of both pulses, various optical constants such as transmission coefficient, refractive index, complex electrical conductivity and dielectric constants can be extracted.

The Terahertz spectrometer consists of a femtosecond fiber laser, THz emitter and detector, time-delay stage, lock-in amplifier and opto-electronics for data acquisition. Some additional optics is required to focus, direct and split the laser/THz beams. The schematic of THz-TDS used for experiments is shown in Fig. 2.18. A femtosecond laser pulse which is emitted from femtosecond fibre laser is incident on a beam splitter. It splits the incident beam into two beams of equal power (~10 mW). One beam is sent to THz emitter while the other to THz detector. The emitted THz pulse first passes through the sample and then reaches the detector. One of the beams is delayed by using time-delay stage and then the transmitted THz pulse gets detected at the detector. The detected signal is then sent to lock-in amplifier and finally to computer for data acquisition.



Figure 2.18: Schematic representation of THz time-domain spectroscopy setup.

A THz pulse can be emitted or detected using transient current from the photoconductive (PC) antenna. The PC antenna-based emitters and detectors are based on the emission of electromagnetic radiation. There are many ways to produce electromagnetic radiation such as by accelerating charge, oscillating electric or magnetic field, or by varying current with frequency. If the frequency of an accelerating charge is in THz band, it will emit THz radiation. This phenomenon is used to generate and detect THz radiation in PC based emitter and detector. The schematic of a typical PC antenna is presented in Fig. 2.19. It comprises of two parallel gold stripes arranged in an 'H' shape structure, which are separated by a few micrometers. These stripes are patterned on a thin film of low-temperature-grown GaAs (LT-GaAs).



Figure 2.19: *Schematic of PC emitter and detector antenna for generation and detection of THz pulse.*

When a femtosecond laser pulse with energy higher than the bandgap of GaAs film interacts with the film, it produces pairs of electrons and holes. In the emitter, the gold stripes are biased with direct current (DC), resulting in the accelerated movement of the generated electron-hole pairs towards their respective electrodes. As a result, a transient current J(t) is produced, since these processes occur within picoseconds. Over longer periods of time, carrier recombination takes place either within the semiconductor or at the metal electrodes, leading to the decay of the transient current and the reestablishment of a static DC bias. In the case of THz detection using PC antenna, no DC bias is given. Here, the femtosecond laser pulse generates the electron-hole pairs. These charge carriers get accelerated by the electric field of emitted THz pulse, that is collimated onto the detector. This creates a transient current, and by measuring the transient current at different times, a temporal profile of emitted THz pulse is obtained. The THz-TDS of a thin film is completed in three steps: i) The THz pulse is passed through the free space inside cryostat and the temporal waveform is recorded, ii) A blank substrate from the same batch of thickness (0.5 mm) is mounted on the aperture and the temporal waveform is again recorded, and iii) The thin film deposited on the very same substrate is mounted on the aperture for the recording of the temporal waveform of the passing THz pulse through the both substrate and film. In this way, the original contribution originating from the film can be studied.

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Chapter 3

Effect of Cu-doping and thickness variation on the structure and electrical properties of PrNiO₃ thin films

This chapter deals with the effects of Cu-doping and thickness variation on the structural and electrical transport properties of PrNiO₃ thin films. For this purpose, two series of PrNiO₃ thin films have been synthesized on LaAlO₃ (100) (LAO) single-crystal substrates using the Pulsed Laser Deposition (PLD) technique. The first series contains five epitaxial PrNi₁₋ $_xCu_xO_3$ (x=0-0.1) thin films of thickness 12nm deposited on LAO substrate. Here, the effect of carries injection via Cu-doping at Ni-site has been studied. In the second series, a study consisting of four $PrNi_{0.95}Cu_{0.05}O_3$ thin films with thickness varying from 5 to 25nm has been presented. This study demonstrates the tuning of epitaxial compressive strain on thin films by varying film thickness. Structural properties of both the series have been examined by performing XRD and RSM measurements. The vibrational modes and the variation in structural symmetry are investigated using Raman spectroscopy. Temperature-dependent resistivity measurements have been performed to understand the electrical transport behavior of the prepared thin films.

The present study indicates that both *i.e.*, Cu-doping and thickness variation significantly influence the physical properties of the PrNiO₃ system. The obtained results are published in peer-reviewed journals.

^{1.} Yadav et al, Vibrational Spectroscopy, 112 (2021), 103185.

^{2.} Yadav et al, Thin Solid Films, 735 (2021), 138877.

3.1 Introduction:

Among various functional materials, strongly correlated perovskites have gained significant interest of the scientific community due to the notable correlation of electronic, magnetic, structural, and optical properties [1, 2]. In addition to this, these oxides offer outstanding properties such as colossal magnetoresistance (CMR), high T_C superconductivity, metal-insulator phase transitions, multiferroicity, etc. due to a strong interplay between spin, charge, lattice, and orbital degrees of freedom [3-6]. Rare earth nickelates ($RNiO_3$), exhibiting first-order metal-to-insulator phase transition, are one of the wellknown strongly correlated materials that are potential candidates for several applications such as in fuel cells, gas sensing, photovoltaics, spintronics, and thermochromic materials, etc. [7, 8]. In addition to this, the emergence of novel features like quantum-phase transition, pseudo-gap phases, non-Fermi liquid (NFL) behavior, resistivity saturation above semi-classical limits, etc., have regenerated interest in RNiO3 thin films from the fundamental point of view, too [9, 10]. All these features exhibit distinct behavior in bulk, thin films, heterostructures, and superlattice structures due to dimensionality crossover [11, 12]. Nowadays, most of the research in nickelates is focused on thin films and heterostructures with a general objective of modifying their physical properties through monitoring strain, doping, pressure, and interface effects [7, 13].

RNiO₃ belongs to a class of negative charge-transfer insulators as described by Zaanen, Sawatzky, and Allen scheme, where electronic properties mainly depend on the degree of hybridization of Oxygen 2p and Nickel 3*d* orbitals [14, 15]. In this case, the ground state electronic wave function can be described as $\alpha | d^7 \rangle + \beta | d^8L \rangle$, where *L* is a ligand hole [16]. One of the major characteristics of nickelates, except for *R* = La with the largest ionic radii, is a sharp metal-to-insulator transition (MIT), which is mainly controlled by the Ni-O-Ni bond angle [16–18]. LaNiO₃ remains paramagnetic metal in the entire temperature range (300-10K) [18]. With a decrease in the size of *R* ion, the insulating ground state starts appearing and the electronic as well as magnetic transition coincide for *R*= Pr and Nd. At

this juncture, $PrNiO_3$ gives an opportunity to explore the simultaneous structural, electronic, and magnetic phase transitions. The incorporation of a relatively smaller *R*-site cation in the perovskite structure causes bandgap opening and leads to a distortion in the NiO₆ octahedra. As a result, for all the other members of RNiO₃, there is a significant difference between T_{MI} (metal-to-insulator transition temperature) and T_N (magnetic transition temperature) [16, 19].

There are various parameters affecting the physical properties of the $RNiO_3$ system, such as carrier injection via doping, oxygen nonstoichiometry, deposition temperature, epitaxial strain, thickness variation, *etc* [12, 13]. Doping alters the carrier concentration and controls the transport properties of strongly correlated materials [21, 22]. There are many reports on the effect of substrate-induced strain, hydrostatic pressure, thickness variation, *etc.* on PrNiO₃ but doping at Ni-site is a less studied factor [12]. In the present case, we have replaced Ni with a more electronegative ion Cu. Since both Ni³⁺ and Cu²⁺ are Jahn-teller active ions, the replacement may cause some change in the structure of the PrNiO₃ system. Also, Cu has extra electrons in the *d*-band, therefore, some changes in the electronic states can also be expected [21–23]. To understand the effect of Cu-doping on structural and electronic properties, we have prepared a series of PrNi_{1-x}Cu_xO₃ thin films with compressive strain and studied its effects.

The variation of epitaxial strain via thickness modification is an established way to influence the structural and transport properties of low dimensional mott materials. Also, modifying thin film properties by varying thickness, surface, and interface properties can be used for various desired applications [10, 35]. A dimensionality crossover from three-dimensional (3D) to two-dimensional (2D) changes the orbital polarization, which leads to a weakening in carrier hopping in the transverse direction. In this manner, a change in thickness results in the transition from metallic to Mott insulating state in ultrathin films [14, 23, 26]. Many reports are available on the effect of dimensionality crossover in RNiO₃ thin films, where thickness variation plays an important role [14, 36, 37, 38]. It has been studied earlier that change in

thickness also leads to a variation in the oxygen content of thin films, which in turn affects the transport properties [11]. Under the influence of epitaxial strain, films with lower thickness (higher strain) possess minimum oxygen vacancy formation energy [11]. In addition to strain, even the oxygen deficiency causes a variation in the bond-lengths and bond-angles of the perovskite system, and hence, the electronic state of the system gets affected. While a reasonable amount of work is reported on these variations, a few reports can be found on the evolution of vibrational characteristics of *R*NiO₃ thin films [29-31, 39].

Previously, a thorough study on the structural and transport properties of $PrNi_{1-x}Cu_xO_3$ (0<x<0.1) thin films was carried out [21, 39]. It was found that merely 1% Cu-doping was sufficient to suppress the metal-insulator transition, which was otherwise present in pristine PrNiO₃ film with tensile strain [21]. Even by this small doping at Ni-site, a variation in the octahedral tilt angles and hence in phonon modes of PrNiO₃ was observed by means of Raman spectroscopy [39]. The temperature-dependent resistivity plots for $PrNi_{1-x}Cu_xO_3$ (0<x<0.1) thin films showed an overall decrease in the resistivity with Cu doping [21]. The rate of change in resistivity per atomic percentage is highest for 5% Cu-doped PrNiO₃ thin film. Any further increase in doping beyond 5% leads to a decrease in resistivity. Furthermore, the temperature coefficient of electrical resistivity ($\alpha = \frac{1}{\rho_0} \frac{d\rho}{dT}$, where ρ_0 is residual resistivity) was also found to be maximum for 5% Cu-doped PrNiO₃ [39]. The above findings suggested that 5% is an efficient doping level that enhances the metallicity of PrNiO₃ thin films. Therefore, we planned to understand the effect of thickness variation and epitaxial strain at 5% Cudoping. We prepared a series of 5% Cu-doped PrNiO₃, *i.e.*, PrNi_{0.95}Cu_{0.05}O₃ (PNCO) thin films with varying thickness on LaAlO₃- LAO (001) single crystal substrate using pulsed laser deposition (PLD) method.

3.2 Experimental

A standard solid-state reaction route was used to prepare bulk polycrystalline pellets of $PrNi_{1-x}Cu_xO_3$ ($0 \le x \le 0.1$). These bulk pellets were used as target material to deposit thin films (12 nm) on LaAlO₃ -LAO (001) single-crystal substrate using the PLD technique. Prior to the deposition, single-crystal LAO substrates (from MTI corporation, USA) have been cleaned with acetone followed by propanol using an ultra-sonicator. After loading the target and the cleaned substrate in the chamber, the vacuum was brought to a base pressure of $\sim 5 \times 10^{-4}$ Pa using a turbo molecular pump. KrF Excimer pulsed laser ($\lambda = 248$ nm, Coherent Compex pro) with 10 ns pulse width at a repetition rate of 4 Hz and energy of 310 mJ was used. The target rotated with a motor at 10 rpm to avoid material depletion at one spot. The substrate temperature was maintained at 720°C, and the distance between the target and substrate was fixed at 45 mm. The oxygen partial pressure was 40 Pa. To maintain the oxygen stoichiometry, in-situ post-annealing of all the films was done for 3 minutes in the presence of oxygen at 1000 Pa after deposition inside the chamber. For PNCO thin films of different thicknesses, the total number of laser shots was varied systematically to create the desired thickness variation. According to our previous XRR measurements, the number of laser shots was optimized for a specific thickness growth rate. The total number of laser shots was 1750, 1400, 700, and 350 for the estimated thickness of the film to be 25 nm, 20 nm, 10 nm, and 5 nm, respectively. After deposition, the films were cooled down to room temperature at the rate of 10°C/minute.

The phase purity and in-plane strain coherency has been confirmed using X-ray diffraction (XRD), and reciprocal space mapping (RSM) measurements by PANalytical Empyrean made diffractometer. Cu- K_{α} radiation (λ =1.5406 Å) was used as a source in the two-circle diffractometer in Bragg-Brantano geometry (θ -2 θ mode). Atomic force microscope (AFM) (Park Systems, NX10) was used to get an idea about the surface morphology and surface roughness of thin films. The growth rate and thickness of thin films were confirmed by performing AFM across a step created on the thin film. Here, the cantilever travels across the step, giving an idea of the step height in nm units. The X-ray photoelectron spectroscopy (XPS) experiments were performed on beamline BL-14 of the Indus-2 synchrotron source at Raja Ramanna Centre for Advanced Electronics (RRCAT), Indore. The measurements were carried out in an ultra-high vacuum chamber with the monochromatic X-ray beam of 4357 eV energy. Raman spectra were recorded on a Horiba Jobin Yvon Lab RAM HR-Evolution Raman microscope using *HeNe* laser (633 nm). The micro-Raman signals were collected in back-scattering geometry with ×100 objectives. The Raman Spectrometer is equipped with liquid nitrogen-cooled Charge Coupled Device (CCD) detector. The films were placed on a commercial Linkam stage, and the temperature was varied from 340 to 90K. To investigate the electronic properties, temperature-dependent resistivity was measured using the four-point probe method in a closed-cycle cryostat.

3.3 Results and discussions:

Effect of Cu-doping on the physical properties of PrNiO₃ thin films

First, we discuss the structural, morphological, vibrational, and electrical properties of $PrNi_{1-x}Cu_xO_3$ ($0 \le x \le 0.1$) thin films.

3.3.1 X-Ray Diffraction:

XRD is a primary tool to get information about phase purity, strain, disorder, space group etc. In the present case, structural characterizations of the PrNi_{1-x}Cu_xO₃ (*x*=0-0.1) thin films have been performed by XRD measurements as shown in Fig. 3.1. It is evident from the XRD patterns that there are no undesirable peaks observed, which suggests that all the films are grown impurity-free and are in single phase. XRD patterns also show that all the PrNi_{1-x}Cu_xO₃ films are crystallographically oriented towards LAO (001) substrate. The pseudo-cubic lattice parameter of bulk PrNiO₃ (a_f) is 3.820Å, and that of LAO (a_s) is 3.789Å. The lattice-mismatch can be calculated as:

lattice mismatch (%) =
$$\frac{a_s - a_f}{a_s} \times 100$$
 (3.1)

The calculated value of lattice mismatch is -0.81% for PrNiO₃ thin film. The negative value of lattice-mismatch suggests that LAO induces compressive strain in the PrNiO₃ system.



Figure 3.1: X-ray diffraction patterns of $PrNi_{1-x}Cu_xO_3$ (x=0-0.10) thin films and LAO (001) substrate. Some peaks from the substrate having reflection other than (001) are represented by label "s".

This is also evident from figure 3.2 which shows the magnified view of the second-order Bragg's reflection of the XRD patterns of the PrNi₁₋ $_x$ Cu_xO₃ (*x*=0-0.1) thin films. The figure shows that the XRD peaks of films lie towards a lower 2 θ value as compared to that of LAO substrate, indicating compressive strain in the system. As discussed in the experimental section (Chaper-2), the in-plane compressive strain, which compresses the in-plane lattice parameters, causes an elongation in the out-of-plane lattice parameters to preserve the unit-cell volume. This increased value of out-ofplane lattice parameters causes a decrement in the diffraction angle in accordance with Bragg's relation which explains the lower 2 θ value in compressive strained films.



Figure 3.2: Magnified view of the XRD patterns of $PrNi_{1-x}Cu_xO_3$ (x=0-0.10) thin films and LAO substrate.

3.3.2 Reciprocal Space Mapping:

In order to check the in-plane strain coherency present in the prepared thin films, Reciprocal Space Maps (RSM) were recorded as shown in figure 3.3.



Figure 3.3: Reciprocal Space Maps of $PrNi_{1-x}Cu_xO_3$ thin films for (a) x = 0, and (b) x = 0.1.

The figure shows the RSM images of undoped and maximally doped *i.e.*, 10% Cu-doped PrNiO₃ thin films around asymmetric (103) Bragg's reflection. It is evident from the RSM images that for both the thin films, the peak of the substrate and thin film lies along the same pseudomorphic line, suggesting that the films are epitaxially strained. This clearly suggests that the in-plane lattice parameters of substrate and film are locked together, *i.e.*, are identical which creates an epitaxial (layer-by-layer) growth of PNO films over LAO substrate. It can be noted here that this epitaxy is maintained upto 10% Cu-doping in 12 *nm* thick PNO films.

3.3.3 Atomic Force Microscopy:

In order to check the influence of Cu-doping on the growth and surface morphology of PrNiO₃ thin films, atomic force microscopy (AFM) measurements have been carried out. Figure 3.4 (a, b) shows the AFM images of undoped and 10% Cu-doped PrNiO₃ thin films in $2\times 2 \ \mu m^2$ area. The surface roughness and density of grains is found to be different for both the PrNiO₃ thin films. The average surface roughness is ~3 and 5 Å for undoped and 10% Cu-doped PrNiO₃ thin films, respectively.



Figure 3.4: (*a*-*d*) 2D and 3D AFM images of $PrNi_{1-x}Cu_xO_3$ thin films for (*a*, *b*) x = 0, (*c*, *d*) x = 0.10.

3.3.4 Raman spectroscopy:

Raman spectroscopy is a versatile technique that is used to study novel features associated with lattice vibrations such as structural phase transitions, electron-phonon coupling, doping-induced structural disorder, spin-phonon interactions *etc* [24-26]. It is worth mentioning here that probing these structural and vibrational features is relatively difficult in thin films where in-depth profiling is required, however, Raman spectroscopy emerges as a non-destructive alternate tool to give insightful information on the vibrational modes and structure of thin films.

Based on the crystal symmetry analysis, metallic $PrNiO_3$ at room temperature exhibits orthorhombically distorted perovskite structure with *Pbnm* space group [27, 28]. This orthorhombic distortion is acquired by an antiphase tilt of the adjacent NiO₆ octahedra (a-a-c+ in Glazer's notation). The primitive unit cell consisting of 20 atoms in the orthorhombic structure exhibits 60 normal vibrational modes at the zone center [27, 28]:

 $\Gamma = 7A_{1g} + 7B_{1g} + 5B_{2g} + 5B_{3g} + 8Au + 8B_{1u} + 10B_{2u} + 10B_{3u}$

Out of these 60 normal modes, only 24 vibrational modes are Raman active.

$$\Gamma_{Pbnm} = 7A_{1g} + 7B_{1g} + 5B_{2g} + 5B_{3g}$$

In insulating phase, $P2_{1/n}$ space group of PrNiO₃ also gives rise to 24 Raman-active modes as [26]:

$$\Gamma_{P2_{1/n}} = 12A_g + 12B_g$$

These Raman active modes are highly sensitive to any change in the structural symmetry of the perovskite system. It is discussed that LAO is the most suited substrate for Raman spectroscopic measurements of RNiO₃ thin films because it exhibits *R3c* space group with 5 ($A_{1g}+4E_g$) Raman-active modes [27] and these Raman-active modes for LAO (121 cm⁻¹, 150 cm⁻¹, and 487 cm⁻¹) don't coincide with that of PrNiO₃. There are many reports available on the Raman scattering study of RNiO₃ bulk as well as thin films but doping dependent studies are not much explored yet [28-31]. In the present study, we have performed Raman spectroscopy measurements on the

series of $PrNi_{1-x}Cu_xO_3$ (x = 0-0.1) films to study the vibrational characteristics of the system. We have focused on the correlation between the material's anharmonicity with the Raman peak position and linewidth and have studied the effect with chemical doping.



Fig. 3.5: Room-temperature Raman spectra of $PrNi_{1-x}Cu_xO_3$ (x=0-0.1) thin films

Fig. 3.5 represents the room-temperature Raman spectra of PrNi₁₋ _xCu_xO₃ (x= 0-0.1) thin films. Here, all the 24 Raman active modes arising from *Pbnm* space group are not detected probably due to low intensity or overlapping of some of the phonon modes. In the present Raman-spectra, 5 A_{1g} (94 cm⁻¹, 139 cm⁻¹, 233 cm⁻¹, 280 cm⁻¹ and 431 cm⁻¹), 1 B_{1g} (375 cm⁻¹) and 1 (A_{1g} + B_{1g}) (480 cm⁻¹) modes are observed for all the films. All these modes are associated with the vibrations arising due to stretching, bending, rotation as well as NiO₆ octahedral tilt angles accordingly. In order to get information about the doping-induced structural disorder, we have calculated Raman FWHM (full width at half maxima) of the most intense A_{1g} mode (~431 cm⁻¹) as shown in the inset of Fig. 3.5. It can be seen that FWHM of the mode increases with increment in Cu-doping. It is important to note here that the symmetric broadening of a Raman peak is an indication of disorder induced in terms of crystallographic strain, cation disorder, doping, *etc.* [29]. An increment in B-site cation disorder with the increase in Cu-doping in $PrNiO_3$ can affect this mode. Here, Raman spectroscopy gives an indication of induced structural disorder in the system.



Fig. 3.6: Magnified view of Raman spectra showing (a) low-frequency and (b) mid-frequency Raman modes of $PrNi_{1-x}Cu_xO_3(x=0-0.1)$ thin films

Recent Raman studies on various perovskite oxides illustrate that the behavior of low-frequency soft A_{1g} Raman modes essentially describes the octahedral tilting in these materials [24, 25]. Fig. 3.6 (a, b) represents the magnified view of a variation of soft A_{1g} mode (74 cm⁻¹, 94 cm⁻¹, 139 cm⁻¹, 233 cm⁻¹) for Cu-doped PrNiO₃ thin films which shows that A_{1g} modes shift towards higher wavenumber with increment in doping, which can be related to the increment in octahedral tilt angles. This shifting is prominent in the lower wavenumber side, and it decreases in higher wavenumbers. It is important to note here that a difference in the ionic radii of Ni and Cu ions imposes a change in the tolerance factor of the system. In doped AB_{1-x}C_xO₃ system, tolerance factor can be defined as [25]:

$$t = \frac{R_A + R_0}{\sqrt{2}(R_{eff} + R_0)} \tag{3.2}$$

Where $R_{eff} = (1 - x) * R_B + x * R_C$ and R_A , R_B , R_C and R_O are the ionic radii of A, B, C and O ions respectively. In the present case, the larger ionic radius of Cu as compared to Ni causes an overall increment in

 R_{eff} , which in turn, decreases the overall tolerance factor of the doped system. Also, it has been well established in the literature that a reduction in tolerance factor is governed by a decrement in the Ni-O-Ni bond angle, which essentially increases the octahedral tilt angles. So, in the present case, the blue-shift of soft A_{1g} Raman modes with Cu-doping suggests that Ni-O-Ni bond angles decrease, although the decrement is very less, which is consistent with the enhancement in tilt angles. As discussed earlier, parameters like octahedral tilting angles are chronically difficult to probe for thin films which require in-depth profiling. Hence, Raman spectroscopy emerges as an alternate tool to get an idea regarding octahedral tilting in perovskites.

As discussed earlier, Raman spectroscopy can also be used to probe the thermal evolution of vibrational properties of a system. So, to understand the effect of temperature on phonon modes in Cu-doped PrNiO₃ thin films, temperature-dependent Raman measurements were carried out for pure and 10% Cu-doped PrNiO₃ thin films. Fig. 3.6 and 3.7 show the Raman spectra of undoped and 10% Cu-doped PrNiO₃ thin films, respectively, from 300K to 90K. Neither appearance of new mode nor disappearance of existing Raman modes suggest that the thin films don't undergo any phase transition in the investigated temperature range.



Fig. 3.7 (a): Temperature-dependent Raman spectra of PrNiO₃ thin film


Fig. 3.7 (b): *Temperature-dependent Raman spectra of PrNi*_{0.90}*Cu*_{0.10}*O*₃ *thin film*

It is evident from the Raman spectra that the phonon modes show redshift *i.e.*, shift towards the lower wavenumber side, diminish in intensity, and broaden with increment in temperature. For a more quantitative analysis, these Raman peaks are fitted with the Lorentzian profile to find the exact value of peak position and Raman line-width, and the corresponding values are shown in Fig. 3.8. The temperature-dependent red-shift of Raman modes occurs due to the lattice expansion and an increase in the phonon population with rise in temperature. The temperature dependence of Raman shift position can be described by the Grüneisen model [32]:

$$\omega(T) = \omega_0 + \alpha T \tag{3.3}$$

where ω_0 represents the phonon frequency at zero kelvin and α is the firstorder temperature coefficient. The Raman-shift position was fitted with the Grüneisen model and the corresponding fitting is shown in the upper panel of Fig. 3.8. The fitted value of α for undoped and 10% Cu-doped film is -0.031 cm⁻¹/K⁻¹ and -0.039 cm⁻¹/K⁻¹ respectively for the A_{1g} mode at ~435 cm⁻¹. However, the Raman mode at ~280 cm⁻¹ shows the value of α as -0.058 cm⁻¹



 $^{1}/K^{-1}$ and -0.069 cm⁻¹/K⁻¹ for undoped and 10% Cu-doped PNO film, respectively.

Fig. 3.8: Upper panel shows the Raman shift position with temperature with Grüneisen model fit, and lower panel shows the FWHM vs temperature plot fitted with Balkanski model.

The anisotropy in the value of α suggest that phonon vibrations corresponding to lower frequency (~280 cm⁻¹ occurring due to rotational vibration of NiO₆ octahedra) are more sensitive towards temperature as compared to the mid frequency Raman modes (~435 cm⁻¹ occurring due to stretching vibrations of Ni-O bond). Moreover, the value of first-order temperature coefficient increases with the incorporation of Cu in the system. It should be noted that the present value of temperature coefficient is in agreement with earlier reports on various 2D materials [32].

The major reason behind temperature induced red-shift of phonon modes is the vibration of lattice parameters which changes the lattice vibrational frequencies. It is described in literature that the phonon depends on volume and temperature as [32]:

$$(\frac{\partial \ln \omega}{\partial T})_{P} = (\frac{\partial \ln V}{\partial T})_{P} \cdot (\frac{\partial \ln \omega}{\partial \ln V})_{T} + (\frac{\partial \ln \omega}{\partial T})_{V}$$

= $\frac{\gamma}{\kappa} (\frac{\partial \ln \omega}{\partial P})_{T} + (\frac{\partial \ln \omega}{\partial T})_{V} = -\gamma * \beta + (\frac{\partial \ln \omega}{\partial T})_{V}$ (3.4)

where $\gamma = (\frac{\partial \ln V}{\partial T})_P$ is volume thermal coefficient, $\kappa = (\frac{\partial \ln V}{\partial P})_T$ is isothermal volume compressibility and $\beta = -(\frac{\partial \ln \omega}{\partial \ln V})_T$ is Grüneisen parameter. The first term in equation (3.4) $(-\gamma * \beta)$ links to the contribution due to volume at constant temperature and the second term $(\frac{\partial \ln \omega}{\partial T})_V$ signifies the contribution due to temperature at constant volume. The equation (3.4) can be modified as [32]:

$$\left(\frac{\partial \ln \omega}{\partial T}\right)_{V} - \left(\frac{\partial \ln \omega}{\partial T}\right)_{P} = -\gamma * \beta$$
(3.5)

Comparing equation (3.3) and equation (3.5) leads that α is proportional to $-\gamma * \beta$. This suggests that the thermal expansion coefficient and Grüneisen parameter vary in similar fashion and larger value of thermal expansion coefficient will lead to high Grüneisen parameter in the material. This also leads to stronger anharmonic effect and stronger phonon-phonon coupling in these materials. This suggests that Cu-doped thin film undergoes more thermal expansion with temperature as compared to the undoped one.

Another noteworthy observation of the temperature-dependent Raman spectra is the systematic broadening of Raman modes with temperature. This systematic increase in the FWHM of phonon modes with temperature for both undoped and 10 % Cu-doped films is shown in figure 3.8. Higher order anharmonic terms and disorder imposed on the system due to temperature induces this increase in FWHM. In order to quantify the anharmonic terms contribution, the temperature dependence of Raman line-width has been fitted with Balkanski model which is given as [33]:

$$\Gamma(T) = \Gamma(0) + A[1 + \sum \frac{1}{exp(\frac{h\omega_i}{2\pi kT}) - 1}]$$
(3.6)

Where $\Gamma(0)$ signifies the temperature-independent contribution to Raman FWHM which exists due to compositional disorder, inhomogeneity *etc.* and A denotes the anharmonic coefficients for three phonon process. Fig. 3.8 shows the Balkanski fit to the Raman FWHM of A_{1g} mode for both undoped and 10% Cu-doped film. It is clear from the fitting parameters that the factor $\Gamma(0)$ increases with Cu-doping due to incorporation of compositional and structural disorder. Also, these materials possess very high contribution due to anharmonic terms which also upsurges with doping content. This increase in anharmonicity with doping is consistent with the finding of Grueinsen parameter. Also, Raman FWHM fits well with Balkanski model without any anomaly suggesting that there is not any structural or magnetic transition in the investigated range.

3.3.5 Temperature-dependent resistivity measurement:

In order to get an idea about the electronic transport behavior of prepared thin films, temperature-dependent dc resistivity measurements were carried out. Fig. 3.9 shows the temperature dependence of dc resistivity of $PrNi_{1-x}Cu_xO_3$ (x = 0-0.1) thin films from 300 to 10K. Here, an absence of MIT has been observed for PrNiO₃ film till low temperatures. All the other Cudoped PNO films also show metallic state in the complete range of temperature, however, with slightly lower values of electrical resistivity. It is noteworthy here that the electrical resistivity of the thin films decreases systematically with increased Cu-doping. This effect can be attributed to the supply of extra charge carriers in 3d band by Cu ions. The effect of temperature on electrical resistivity was examined by calculating the temperature coefficient of electrical resistivity (α) of all the thin films. Temperature coefficient of electrical resistivity (α) determines the rate of change of electrical resistivity with temperature and is given as $\alpha = \frac{1}{\rho_0} \frac{d\rho}{dT}$, where ρ_0 is the residual resistivity. The value of α remains positive for metals and negative for insulators. It has a unit of K^{-1} . Variation of α with changing

Cu-doping is shown in the inset of Fig. 3.9. It can be seen that the value of α first increases Cu-content and then decreases. 5% Cu-doped PNO film shows maximum α .



Fig. 3.9: *Temperature-dependent resistivity plot of* $PrNi_{1-x}Cu_xO_3$ (x=0-0.1) *thin films*

It is extensively described in the literature that in RNiO₃ system, the metallic state is essentially described by the power-law behaviour of temperature-dependent electrical resistivity as given below [9, 10]:

$$\rho(T) = \rho_0 + AT^n \tag{3.7}$$

here, ρ_0 is the residual resistivity arising because of impurities, lattice imperfection, dislocations, and defects present in the sample and serves as a temperature-independent contribution to electrical resistivity. Factor *A* governs electron-electron scattering strength. According to the conventional Fermi-Liquid theory, the value of exponent *n* is 2 for a Landau Fermi Liquid (LFL) state [9, 10]. However, in the case of strongly correlated systems like RNiO₃, a deviation from classical fermi-liquid state takes place, and the compound falls in the category of non-Fermi Liquid (NFL). In NFL state, two other values of *n*, *i.e.*, 1.6 and 1.3, are highly reported [9, 10, 19, 21]. This drives the system towards a semi-classical state where quantum fluctuations take place. Since this power law equation is valid to a limited temperature range only. So, in order to develop a complete understanding of metallic phase, resistivity saturation is accounted in strongly correlated systems. Resistivity saturation is extremely important in RNiO₃ where interband transitions take place, and the power-law equation modifies as [9, 10, 34]:

$$\rho^{-1}(T) = \rho_{NFL}^{-1}(T) + \rho_{SAT}^{-1}$$
(3.8)

here, ρ_{SAT} is a component to electrical resistivity which acts as a parallel channel to the classical Boltzmann conduction network. In case of certain correlated metallic systems, the usual theory of electrical conduction fails when the carrier mean free path *l* approaches the interatomic distance *a* [34]. At this point, the concept of particle scattering becomes unphysical and leads to minimum conductivity. Equation 3.8 is generally known as parallel-resistor formula (PRF).



Fig. 3.10: *Temperature-dependent resistivity plots of* $PrNi_{1-x}Cu_xO_3$ (x=0-0.1) *thin films, fitted with the parallel resistor formula.*

Fig. 3.10 shows the temperature-dependent electrical resistivity of all the PNCO films fitted with eq. 3.8 and the fitting parameters are listed in Table-3.1. It is clear from the fits that all the PrNi_{1-x}Cu_xO₃ (*x*=0-0.1) thin films have the NFL state. In Table-3.1, the fitting parameters with *x*=0 do not fall in the trend. In case of all the Cu-doped PNO films, the parameters ρ_0 and *A* decrease with increasing Cu-doping. The Cu doping affects distortion of NiO₆ octahedra as also corroborated by Raman spectroscopy. Thus, Cu doping causes a change in the structure and hence NFL state here.

-				
x	п	$A (\times 10^{-8}) (\Omega.cm(K^n)^{-1})$	$ ho_0(imes 10^{-5})$ ($\Omega.cm$)	ho sat
				$(m\Omega.cm)$
0	1.6	6.40±0.08	7.95±0.05	0.542±0.05
0.01	1.3	8.63±0.23	7.06±0.02	0.445 ± 0.01
0.02	1.3	6.21±0.34	5.62±0.03	0.805±0.03
0.05	1.3	6.01±0.24	1.88 ± 0.05	0.810±0.03
0.10	1.3	4.48±0.11	1.30±0.02	0.361±0.03

Table 3.1: Transport properties of $PrNi_{1-x}Cu_xO_3$ (x=0-0.10) thin films deposited on LAO.

Tuning epitaxial strain via thickness variation in PrNi_{0.95}Cu_{0.05}O₃ thin films

Here, we will discuss the effect of structural, morphological, vibrational, and electrical properties of PrNi_{0.95}Cu_{0.05}O₃ thin films with thickness varying from 5 to 25nm.

3.3.2.1 X-Ray diffraction:

The structure of the prepared films was investigated by XRD measurements (Fig. 3.11). The absence of any undesired peak in the XRD patterns confirms that all the films are single phase and impurity-free. It can be seen that the films are highly oriented towards the [001] axis of LAO.

LAO has a lattice constant of ~3.792 Å, whereas PNO has a pseudo-cubic lattice constant of ~3.83 Å. Because of the lattice-mismatch of (-0.81%), an in-plane epitaxial compressive strain is experienced by the PNCO films. This is evident from Fig. 2 (a) where films' peaks lie towards lower 2 θ side as compared to LAO. increases. The derived lattice spacing *d* decreases with increased thickness (Fig. 3.12) suggesting a partial relaxation of the epitaxial strain.



Fig. 3.11: Full scale XRD patterns of PNCO thin films with various thicknesses

The figure shows a very systematic shift of (002) peaks towards higher 2 θ along with a systematic broadening as the thickness. To quantify the value of lattice mismatch induced strain, the lattice mismatch % between PNCO film and LAO (001) substrate has been calculated using equation (3.1) described in previous section. The lattice mismatch for the films is displayed in Table-3.2. It can be seen from the table that lattice mismatch and epitaxial strain vary from -2.64% at 5 nm to -1.8% at 25 nm as a function of thickness. The increased thickness causes a decrease in the unit-cell volume as well as an enhancement of the surface-to-volume ratio. Thus, more oxygen vacancies form in the thinner films because of the smaller energy requirement for the formation at the surface and interface [11]. These oxygen vacancies convert Ni^{3+} (0.56 Å) into Ni^{2+} (0.69 Å) ions and thereby increase the unit cell volume. This is also supported by the XRD data.



Fig. 3.12: Magnified view of the second order Bragg's reflection of PNCO thin films with various thicknesses

Thickness	Lattice Parameter	Lattice
	(Å)	Mismatch (%)
5 nm	3.893	-2.64%
10 nm	3.89	-2.57%
20 nm	3.867	-1.99%
25 nm	3.860	-1.8%

Table 3.2 The calculated value of pseudo-cubic lattice parameter and latticemismatch with thickness variation of PNCO thin films.

3.3.2.2 Reciprocal Space Mapping:

The in-plane strain coherency of the prepared films has been confirmed by RSMs recorded around the (103) asymmetric Bragg's reflection as shown in Fig. 3.13 (a-d). It is notable that for films with lower thickness, *i.e.* 5 and 10 nm, the substrate peak and the film peak lies along the same pseudomorphic line, suggesting the epitaxial nature of the films.



Figure 3.13 (a) *RSMs of the PNCO thin films substrate with various thicknesses (b) Variation of the in-plane lattice parameters with thickness.*

However, there is a difference between the film and substrate peak in the reciprocal space maps which suggests that the in-plane strain is slightly relaxed for 20 nm and 25 nm films. Since there is a systematic shift in the Q_x values of film peak and substrate peak in RSMs, it has been used to calculate the in-plane lattice constants, as shown in Fig. 3.13(e). It can be seen that the in-plane lattice constants increase systematically with varying thickness. This is consistent with XRD results.

3.3.2.3 Atomic Force Microscopy:

The surface morphology of the prepared series of thin films has been investigated using Atomic Force Microscopy (AFM) measurements. Fig. 3.14 (a, b) shows the AFM images of PNCO films with 5nm and 25 nm thickness. The average surface roughness is ~0.25 and 0.71 nm for PNCO films with 5 nm and 25 nm thickness, respectively.



Figure 3.14 (a) *AFM images of PNCO thin films with thickness (a) 5nm, and (b) 25 nm.*

3.3.2.4 X-Ray Photoelectron Spectroscopy (XPS):

To investigate the oxidation state of Ni ions in PNCO system, we have carried out XPS measurements on 5 nm and 25 nm PNCO films at Niedge as shown in Fig. 3.15. For analysis, background is subtracted, and the peak is deconvoluted into constitutes. For the calibration of different elements, carbon C1s peak is assumed to have a binding energy of 284.6 eV. Fig. 3.15 shows the peak position of Ni $2p_{3/2}$ core level of (a) 5 nm and (b) 25 nm PNCO films. The reference binding energy for Ni²⁺ and Ni³⁺ is 853.9 and, 855.9 eV respectively [41]. The deconvolution of Ni $2p_{3/2}$ peak for PNCO-5nm film shows two peaks, one corresponding to Ni³⁺ and the other one corresponding to Ni²⁺. However, there is only single Ni $2p_{3/2}$ peaks in the present XPS data suggests that there is presence of mixed oxidation state in PNCO thin film with 5 nm thickness. It can be seen from the figure that the area under the curve for peak corresponding to Ni²⁺ in PNCO- 5nm film is very less as compared to the Ni³⁺ peak. This suggests that in 5 nm film, majority of Ni³⁺ ions are present with a small amount of Ni²⁺. However, only Ni³⁺ is present in 25 nm thin film.



Figure 3.15: *XPS spectra of PNCO thin films with* (*a*) 5 *nm and* (*b*) 25 *nm thickness.*

3.3.2.5 Raman Spectroscopy:

As discussed earlier, based on the crystal symmetry analysis, metallic PrNiO₃ at higher temperatures exhibits an orthorhombically distorted perovskite structure with the space group *Pbnm* [30, 39]. In order to get more insight into the change in local symmetry of the system, Raman spectroscopy measurements have been performed, and the spectra are shown in Fig. 3.16. It is visible from the figure that there are two narrow modes at 95 and 165 cm⁻¹ and two broad modes at 272 and 437 cm⁻¹, respectively. From the earlier reported lattice dynamics calculations on RNiO₃, it is contemplated that the mode at ~435 cm⁻¹ arises due to the bending and breathing vibrations of NiO₆ octahedra along the z-axis [26, 29-31]. All the Raman active modes undergo softening with the increase in thickness, as shown in Fig. 3.16 (a). This softening is caused by the extent of epitaxial strain imparted by the substrate, which has been again tuned by the thickness of the films in the present case.



Fig. 3.16 (a) Room-temperature Raman spectra of PNCO films. The inset figure shows the variation of FWHM of soft A_{1g} Raman modes with thickness. Variation of Raman shift position with thicknesses for Raman modes at (b) 165, (c) 270, and (d) 430 cm⁻¹.

This result also corroborates well with the XRD results where the outof-plane lattice constant along the c-axis changes with varied thickness [Fig. 3.12]. The inset of Fig. 3.16 (a) shows the variation of Raman Full width at half maxima (FWHM) of A_{1g} mode with thickness. The increase in FWHM with thickness can be attributed to the increase in scattering centers, which decrease the phonon lifetime. To obtain the information quantitatively, we have plotted the peak position of each Raman mode as a function of thickness as shown in Fig. 3.16 (b, c, d).

Following observations can be summarized from the Raman spectra: (*a*) Lower frequency mode (~270 cm⁻¹) shows a substantial shift of ~ 20 cm⁻¹ with an increase in thickness from 5 to 25 nm.

(b) However, this shift is ~ 10 cm⁻¹ in mid-frequency mode (~435 cm⁻¹).

(c) The red-shift of these Raman modes gives a signature of epitaxial strain release with the increase in thickness.

(*d*) Variation in epitaxial strain changes the Ni-O bond-length and force-constant.

To understand the thermal evolution of vibrational modes and the state of the strain in each film, the temperature-dependent Raman spectroscopy has been carried out and shown in Fig. 3.17 (a, b, c). Due to the dominating substrate contribution in 5 nm film, it was difficult to record temperature-dependent Raman spectra. It can be noted from the figure that the overall spectral signature is maintained without any drastic change, which suggests that PNCO films maintain *Pbnm* symmetry and undergo no phase transition in the studied temperature range. All the peaks indicating Raman modes become broader, diminish and shift towards the lower wavenumber side with an increase in temperature. This suggests the expansion of the material with an increase in thermal energy and causes interatomic bondlengthening.

It is described in the literature that any change in the Raman peak position with temperature occurs due to contributions from thermal expansion, volume contribution, and anharmonicity [42]. Hence, for a more quantified estimation, we have fitted the temperature-dependent Raman spectra by the Grüneisen model, which states that a change in temperature creates a change in the force constants and vibrational frequencies [42,43]. The first-order temperature coefficient of the material can be calculated by fitting the position of Raman shift at various temperatures to the Grüneisen model described by the following equation [42, 43]:

$$\omega = \omega_0 + \alpha T \tag{3.9}$$

where ω_0 is the Raman shift position at zero Kelvin, α is the firstorder temperature coefficient, and ω is the Raman frequency. The slope of the Raman modes position vs. temperature plot directly gives the value of the temperature coefficient, which is displayed in Fig. 3.18 (a, c, e) (Table 3.3). The temperature coefficient of the PNCO films increases linearly with increasing thickness due to the partial relaxation of the strain.

Table 3.3: Raman shift position of A_{1g} mode with temperature coefficient and anharmonicity coefficient of PNCO thin films with thickness variation.

Thickness	Raman shift position (cm ⁻¹)	Temperature Coefficient (cm ⁻¹ /K)	Anharmonicty Coefficient (cm ⁻¹)
25 nm	288	-4.8×10 ⁻²	
25 nm	428	-2.8×10 ⁻²	78.84
20 nm	433	-2.5×10 ⁻²	65.45
10 <i>nm</i>	435	-2.3×10 ⁻²	53.25

For 25 nm thin film, the derived values of temperature coefficient are found to be -0.048 cm⁻¹/K and -0.028 cm⁻¹/K for Raman active A_{1g} modes at 285 cm⁻¹ and 435 cm⁻¹, respectively. At this point, it should be noted that the Raman mode at 285 cm⁻¹ appears by the rotational vibration of NiO₆ octahedra while the other mode at 435 cm⁻¹ is associated with the stretching vibrations of the Ni-O bond [27]. The present results show that the NiO₆ octahedral vibrations are more sensitive to temperature than Ni-O stretching vibrations.

In order to quantify the anharmonic terms contribution, the temperature dependence of Raman line-width has been fitted with the Balkanski model, described in previous section. The fitted data is shown in

Fig. 3.18 (b, d, f), and the corresponding parameters are listed in table-3.3. It is clear from the fitting parameters that the anharmonicity increases with an increase in thickness due to an increase in the scattering surface area.



Fig. 3.17 *Temperature-dependent Raman spectra (90K-340 K) of PNCO thin films with (a) 25 nm, (b) 20 nm and (c) 10 nm thickness*



Fig. 3.18 Variation of Raman peak positions with temperature of 288 and 433 cm^{-1} modes of PNCO thin films with (a) 25 nm, (c) 20 nm and (e) 10 nm thickness. Variation of Raman FWHM with temperature fitted with Balkanski model for PNCO thin film with thickness (b) 25 nm, (d) 20 nm and (f) 10 nm.

It is discussed earlier that the Raman modes are very sensitive to temperature. However, the change in local temperature of the films by varying incident laser power can also cause a difference in the position of phonon modes and can be used to estimate the thermal conductivity of the material. For a plane laminar surface, the rate of the heat flow can be expressed as [44]:

$$\frac{\partial Q}{\partial t} = -\kappa \oint \nabla T. \, dA \tag{3.10}$$

where A is the surface area, T is the absolute temperature, and κ is the thermal conductivity. It was suggested by Balandin *et al.* that thermal conductivity can be estimated by considering a radiant heat flow as [44]:

$$\kappa = \frac{1}{2\pi t} \left(\frac{\Delta P}{\Delta T} \right) \tag{3.11}$$

where ΔP is the change in laser power, ΔT is the change in temperature, and t is the thickness of the film.

By differentiating equation (3.9) with respect to laser power, we get:

$$\frac{\partial \omega}{\partial \mathbf{P}} = \alpha \frac{\partial \mathbf{T}}{\partial \mathbf{P}}$$
(3.12)

Substituting equation (3.11) in equation (3.10), the thermal conductivity can be described as:

$$\kappa = \alpha \left(\frac{1}{2\pi t}\right) / \left(\frac{\delta \omega}{\delta p}\right)$$
(3.13)

Here $\frac{\delta \omega}{\delta p}$ represents the variation of phonon frequency with laser power. The 25 nm thin film was further investigated for thermal conductivity estimation. Fig. 3.19 shows the Raman spectra of PNCO film with varied laser power density from 0.412 mW to 5.06 mW. With increased power, a red-shift shift of Raman mode is observed at ~ 425 cm⁻¹. The slope, $\frac{\delta \omega}{\delta p}$ has been calculated as shown in the inset of Fig. 3.19. The value of $\frac{\delta \omega}{\delta p}$ comes out to be -2.3 cm⁻¹/mW. Using eqn. 8, the thermal conductivity is 5.4 W/mK for 25 nm thin film. This value of thermal conductivity agrees well with the reported value of the NdNiO₃ system [45].



Fig. 3.19 Laser Power density-dependent Raman spectra of PNCO film with 25 nm thickness.

3.3.2.6 Temperature-dependent resistivity measurement:

To investigate the electronic properties of the thin films, temperaturedependent resistivity measurements have been carried out in the temperature range 300-10K, as shown in Fig. 3.20. Under the impact of the compressive strain, all the films remain metallic below room temperature, which is consistent with the earlier observed results [12, 46]. There is an increment in the overall resistivity of thin films with an increase in the thickness (and reduction in strain) up to 20 nm, and then the resistivity decreases for 25 nm. This can be explained as follows. It is observed that in the case of charge transfer insulators, *i.e.*, PrNiO₃, the transfer integral is governed by the degree of overlap between Ni 3d and O 2p orbitals, which varies linearly with the magnitude of compressive strain [7, 16]. Hence, the thin film with a lower thickness (higher strain) possesses higher orbital overlap and lower resistivity. As shown in Fig. 3.12, the 25 nm thin film has XRD peaks with larger FWHM, indicating an incoherent state of strain and hence does not follow the trend of the resistivity.



Fig. 3.20 *Temperature-dependent resistivity plots for PNCO films with 5, 10, 20 and 25 nm thicknesses.*

To order to understand the electronic transport behaviour in detail, the temperature-dependent resistivity data has been fitted with parallel resistor formula (in red line) with equation 3.8 (Fig. 3.21), and all the fitted parameters are enlisted in Table 3.4.

Table 3.4 Fitting parameters of PNCO thin films of various thickness grown on LAO (001) substrate.

Thickness	п	A (×10 ⁻⁸) (Ω.cm(K ⁿ) ⁻¹)	ρ ₀ (×10 ⁻⁵) (Ω.cm)	ρ _{SAT} (mΩ.cm)
5 nm	1.3	4.13	4.59	1.49
10 nm	1.3	10.8	10.2	0.918
20 nm	1.3	11.4	12.99	4.21
25 nm	1.6	1.506	5.91	0.441

It is clear from the table that all the PNCO films remain in non-Fermi liquid state within the given thickness range, but the NFL constant, *i.e.*, *n*, changes from 1.3 to 1.6 with an increase in thickness. The factor residual resistivity, which accounts for lattice imperfections, defects, dislocations, etc., increases linearly with thickness up to 20 nm due to increased scattering surface area.



Fig. 3.21 The inverse of resistivity (ρ^{-1}) versus temperature (T) plots of all PNCO thin films. The red line shows the parallel resistor equation (eq. 3.8) fit to the resistivity.

Likewise, the factor governing electron-electron scattering strength, *i.e.*, *A*, also increases with thickness due to the increase in the scattering of charge carriers. In contrast, saturation resistivity remains thickness independent and doesn't show any systematic trend with thickness. A similar kind of ρ_{SAT} behavior with thickness is earlier reported by Mikheev *et al.* [10]. So, variation in epitaxial strain via modification of the thickness of thin films affects the transport properties in a systematic manner.

3.3.3 Summary

Firstly, a set of $PrNi_{1-x}Cu_xO_3$ (x=0-0.1) thin films have been synthesized using pulsed laser deposition method, and the phase purity, surface morphology, vibrational properties and electronic transport properties have been studied. XRD results show that all the films are grown phase pure with the same crystallographic orientation as underneath substrate. RSM measurements suggest that the prepared films are epitaxial. The surface roughness of the films has been examined using AFM, which shows a slight variation with doping. Raman spectroscopy is used as an alternate tool to get insightful information regarding the increment in octahedral tilt angles of the PrNiO₃ thin films with incorporation of Cu-doping. This is consistent with the decrease in the overall tolerance factor of the system due to replacement of large ion Cu in place of Ni. Also, Cu-doping imposes structural disorder in the system. Raman modes undergo red-shift and broadening with increase in temperature due to thermal expansion of the material. The values of first order temperature coefficient and Grüneisen parameter calculated from temperature-dependent Raman spectra are anisotropic and increase with incorporation of Cu in the system. Balkanski model fitted to the present results suggest that these samples exhibit high contribution due to anharmonic terms which increases with doping. Thus, Raman spectroscopy can be used as an alternative and non-destructive tool to get an idea about the lattice characters, tilt angles, anharmonicity and expansion coefficient of thin film materials. All the films remain metallic below room temperature. Theoretical fittings to the resistivity plots suggest that non-Fermi liquid transport exists in all the films.

Secondly, we have investigated the effect of epitaxial strain on the structural, vibrational, and electronic properties by varying thickness of PNCO thin films grown on LAO single crystal substrate. Our results suggest that all the PNCO films are highly oriented towards the substrate, and out-of-plane lattice parameters and unit cell volume decrease with thickness. Apart from strain, the variation in thickness also causes a change in the oxygen stoichiometry of the films as detected by XPS. Also, the epitaxial strain

shows a slight relaxation with thickness, as shown by RSM results. This is consistent with the substantial softening of Raman active modes with an increase in thickness. The value of the first-order temperature coefficient and Grüneisen parameter calculated from the red-shift of Raman modes with temperature shows an upsurge with thickness. The expected anharmonic behavior in the temperature-dependent Raman linewidth has been understood by invoking the Balkanski model for the three phonon process. The value of the anharmonicity coefficient seems to increase with thickness due to an increase in scattering surface area. A combination of power-dependent and temperature-dependent Raman spectra has been used to estimate the value of thermal conductivity for the 25 nm thin film. Theoretical fits on metallic resistivity-region highlight the persistence of non-Fermi liquid behavior.

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Chapter 4

Enhanced cation ordering, spinphonon coupling and Fano resonance in half-metallic Sr₂FeMoO₆ thin films

This chapter presents the effect of different deposition conditions of process gas on the phase purity, cation ordering, and physical properties of Sr_2FeMoO_6 (SFMO) thin films. For this purpose, two series of SFMO thin films were prepared on $SrTiO_3$ (001) and $LaAlO_3$ (001) single-crystal substrates in different conditions using Pulsed Laser Deposition (PLD) technique. These films were grown in vacuum, in nitrogen and oxygen gas pressure, and the results were compared to understand the effects of cation ordering and disordering. The phase purity and structural properties of the films were investigated by XRD measurements. Magnetic properties were studied by magnetic field and temperature-dependent magnetization measurements. Raman spectroscopy was used to investigate the vibrational modes and spin-phonon coupling in SFMO thin films. Temperature-dependent resistivity measurements were carried out to study the electrical transport behavior.

The present study shows a very systematic effect of cation ordering on the structural, vibrational, electrical, and magnetic properties of SFMO thin films, which are again dependent on deposition conditions. The obtained results are published in peer-reviewed journals.

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4.1 Introduction:

The room-temperature half-metallic double perovskites of A₂BB'O₆ type comes with the flexibility of using various elements at A, B, and B' sites to tune the physical properties [1, 2]. These materials have a wide range of applications such as in multiferroic solar cells, magneto-optic devices, spin valves, solid oxide fuel cells, and data storage. In addition to this, they are fundamentally important crystal structures and provide suitable pathways to explore and modify the characteristic properties. Among various double perovskites, Sr₂FeMoO₆ (SFMO) is one of the most promising conducting ferrimagnet double perovskites with high Curie temperature (T_C) ~415K [3]. The discovery of low field magnetoresistance (LFMR) at room temperature in sintered SFMO by Kobayashi et al in 1998 opened up new avenue for progressive research towards spintronics [5,6]. The ground state of SFMO is half-metallic with 100% spin polarization at Fermi level [7,8]. The low-field magnetoresistance, high T_C and fully spin-polarization make SFMO a very potential candidate for spintronic devices, which can work well above room temperature as compared to low T_C doped manganites [8].

SFMO exhibits an ordered double perovskite structure which crystallizes in *I4/mmm* space group [9]. It consists of a regular arrangement of corner sharing FeO₆ and MoO₆ octahedra which are three-dimensionally connected in an alternate pattern and Sr ion is present in the center. The theoretically predicted value of saturation magnetization (M_S) due to ferrimagnetic interactions between the alternately distributed Fe and Mo ions is 4 μ_B /f.u. [10,11]. However, the experimentally observed value of M_S is always smaller owing to the presence of intrinsic anti-site disorder [11]. These disorders arise as a result of the similar ionic radii of Fe and Mo ions, providing an ease to exchange their positions in the crystal. It results in a discontinuity in the long-range Fe-O-Mo superexchange interactions in SFMO which weakens the magnetic response of the system. Band structure calculations suggest that anti-site disorder suppresses the spin polarization and reduces the half-metallic character of SFMO [8]. Therefore, it becomes extremely important to fabricate a chemically homogenous and B-site ordered SFMO thin film for required spintronic applications [10, 12, 13].

During the course of last few years, a lot of efforts have been made to minimize the anti-site disorder in SFMO films. It can be noted here that the anti-site disorder in SFMO is greatly influenced by the conditions under which it is synthesized. Amongst various thin film deposition techniques, Pulsed Laser Deposition (PLD) method has been extensively used for synthesizing SFMO films at high deposition rates [11,16–18]. The requirement of stringent conditions like high deposition temperature and narrow window of deposition parameters have hampered the fabrication of high-quality ordered SFMO films [14]. Earlier reports suggest that vacuum, reducing (H₂+Ar) or inert (N₂) background gas is more suitable for the growth of SFMO films as compared to oxygen (O₂) [10,11,17]. In addition, lattice-mismatch induced strain imparted by underlying substrate also acts as a controlling parameter in deciding the growth and cation ordering of SFMO films [16]. However, achieving B-site ordering in SFMO films at ambient conditions is still a challenging task.

In the present study, we have synthesized two series of SFMO thin films in different background conditions on $SrTiO_3$ - STO (001) and $LaAlO_3$ -LAO (001) single crystal substrates by Pulsed laser Deposition (PLD) method. The depositions are carried out in vacuum and in nitrogen and oxygen background gases to improve Fe-Mo ordering in SFMO films. A substantial effect of different background conditions on cation-ordering, Fano resonance and transport properties of SFMO thin films has been shown here. In addition to this, temperature-dependent Raman spectroscopy has been used to probe T_C and spin-phonon coupling in these thin films.

4.2 Experimental

Two series of SFMO thin films were prepared on STO (001) and LAO (001) single-crystal substrates using pulsed laser deposition (PLD) technique. Bulk polycrystalline pellet of SFMO was synthesized using standard solid-state reaction method. Stoichiometric amounts of high-purity (~99.99%) powders of SrCO₃, Fe₂O₃ and MoO₃ were ground and calcined at 900 °C for 12h. The resulting mixture was reground and pressed into pellets using hydraulic press and then sintered at 1150 °C for 12h in Ar +5% H₂ atmosphere. This pellet was used as target for thin film deposition in PLD. KrF excimer laser ($\lambda = 248 \text{ nm}$, Coherent Compex Pro) with laser energy of 350 mJ and pulse repetition rate of 5 Hz was used for the depositions. The substrate temperature was 770 °C, and the target to substrate distance was 4 cm. The substrates were sequentially cleaned in acetone and propanol prior to the deposition. The depositions were carried out in vacuum, under nitrogen (0.1 Pa, 0.5 Pa) and under oxygen (0.05 Pa) process gases. Just after deposition, the samples were cooled down to room temperature at 10°C/minute.

To determine the phase purity and growth orientation, X-ray diffraction (XRD) measurements were performed using Bruker D8 Diffractometer in Bragg-Brantano geometry with Cu k_{α} radiation. The Magnetization measurements were performed using SQUID-VSM (Quantum Design) magnetometer in the temperature range of 300 to 500K and in magnetic field ranging from -5T to 5T. The electrical properties were investigated by temperature-dependent resistivity measurements using Janis Research made closed-cycle cryostat with a four-point probe method. Keithley (2612A) made source and measurements meters were used for the same. The vibrational properties were explored using Raman spectroscopy carried out using a Horiba LabRAM made Raman microscope equipped with Charge Coupled Device (CCD) detector. *HeNe* laser with excitation light 633 *nm* was used with a laser power of 1 mW. All the micro-Raman scattered signals were collected in the back-scattering mode.

4.3 Results and discussion:

4.3.1 Structural Characterization:

X-Ray diffraction

Fig. 4.1 shows the XRD patterns of the SFMO films grown on STO. It is clear from the figure that the films grown in vacuum, 0.1 Pa N₂, 0.5 Pa N₂ and 0.05 Pa O₂ are phase pure and *c*-axis oriented.



Fig. 4.1: XRD patterns of SFMO films grown on STO (001) substrate in vacuum, 0.1Pa N_2 , 0.5Pa N_2 , and 0.05 Pa O_2 partial pressure and. The XRD peaks from the substrate having reflections other than (001) are denoted by symbol "s".

Since SFMO has tetragonal crystal structure while STO is cubic, we considered pseudocubic lattice parameter of SFMO for comparison. The pseudocubic lattice parameter of SFMO is 7.879 Å, corresponding to twice the lattice parameter equal to 7.81 Å for cubic STO. The lattice parameter of STO substrate is less than that of the film-material, therefore the film experiences in-plane compressive strain, which can be quantified as:

$$strain(\%) = \frac{a_s - a_f}{a_s} \times 100 \tag{1}$$

where a_s and a_f are the lattice parameters of substrate and film, respectively. Here, the lattice-mismatch-induced strain is -1.14%. While the material experiences an in-plane compression due to substrate-induced strain, an expansion of film-material occurs towards the out-of-plane direction in order to accommodate the unit-cell-volume on the substrate. As a result, the film's XRD peak lies towards lower 20 value which is evident from the enlarged view of (004) Bragg's reflection of SFMO films shown in Fig. 4.2.



Fig. 4.2: Magnified view of the (400) Bragg's reflection of the SFMO films deposited on STO (001).



Fig. 4.3: XRD patterns of SFMO films on LAO (001) substrate in vacuum, 0.1Pa N_2 , 0.5Pa N_2 , and 0.05 Pa O_2 partial pressures. The XRD peaks from the substrate having reflections other than (001) are denoted by symbol "s".

It can be seen that the lattice parameter of the SFMO films grown doesn't vary much with the process gas and remains 8.09 ± 0.01 Å. On the Y-axis of the XRD plots, we show intensity on log-scale with arbitrary unit. If we compare the ratio of material's (004) peak intensity to the substrate's (002) peak intensity, for all the films, the ratio is very similar (0.26\pm0.002). It can be observed from the plots that the FWHM of the vacuum-grown film is minimum. This suggests high crystallinity of the vacuum-grown film. With the increase in the background gas pressure, the FWHM of XRD peaks increases systematically, indicating decreased crystallinity. This could be

attributed to the increased amount of anti-site disorder in SFMO films after incorporation of process gas as suggested by previous reports [19].

For SFMO films grown on LAO, phase purity and highly oriented nature has been observed for vacuum, 0.1 Pa N₂, 0.5 Pa N₂ and 0.05 Pa O₂ background pressures (Fig. 4.3). The pseudocubic lattice parameter of LAO (2c=7.64 Å) causes a lattice mismatch -3.27% in the SFMO films which is roughly three times higher than the previous series (Fig. 4.4). The *c* parameter of SFMO films grown on LAO is 8.03 ± 0.01 Å, which is slightly lower than the films grown on STO. The XRD data shows that the SFMO films grown in vacuum are more crystalline as compared to the other films in both the series. This could be attributed to the increased amount of anti-site disorder in the films after incorporation of background gas as suggested by previous reports [20]. Moreover, the FWHM of LAO grown films ($2.74\pm0.01^{\circ}$) is higher as compared to that grown on STO ($2.56\pm0.01^{\circ}$), due to strain induced disorder.



Fig. 4.4: Magnified view of the (004) Bragg's reflection of the SFMO films deposited on LAO (001).

Fig. 4.5 (a, b) shows the XRD patterns of SFMO films grown in 1 Pa N_2 and 0.1 Pa O_2 . It is that a slight increase in the background gas partial

pressure gives rise to impurity phases of SrMoO₄ and SrFeO₃ in the system along with the desired SFMO phase as corroborated with earlier reports [10]. This suggests there is a very narrow window of deposition pressure available where phase pure SFMO films can be synthesized. Since the synthesis of single-phase SFMO thin films is still a challenging task, it can be inferred that these films can be grown either in vacuum or in ≤ 0.5 Pa N₂ or in ≤ 0.05 Pa O₂ regardless of the underlying substrate. After the successful optimization, we will now discuss the properties of only phase pure SFMO films.



Fig.4.5: (a) XRD patterns of SFMO films grown in 1Pa N_2 and $0.1O_2$ partial pressure on (a) STO (001) and (b) LAO (001) substrate.

X-Ray Reflectivity

The thickness and surface roughness of SFMO films has been estimated by X-Ray Reflectivity (XRR) measurements. Fig. 4.6 shows the typical reflectivity scan of the SFMO film grown in vacuum, with incident angle varying from 0° to 3°. Considering $q = k_s - k_i$ as the momentum transfer vector and k_i and k_s as the incident and scattered X-Ray wave vectors, respectively, this geometry makes the components in the sample plane, $q_x = q_y = 0$. The component normal to sample surface can be written as:

$$q_Z = \left(\frac{4\pi}{\lambda}\right) sin\theta_{in} \tag{2}$$

where θ_{in} is the incident angle and λ is the wavelength of incident X-Ray. The component normal to the sample surface varies from 0 to 0.21 Å⁻¹. The reflectivity data has been analyzed using Parratt recursive formalism [19]. The calculated value of film thickness is ~65 nm with a surface roughness of ~0.6 nm.



Fig.4.6: X-Ray Reflectivity (XRR) profile of the SFMO film grown in vacuum. The red line shows the XRR data fitted with the Paratt Recursive Formalism.
4.3.2 Magnetic Properties:

The effect of background conditions on the magnetic properties of SFMO thin films has been investigated by magnetic field and temperaturedependent magnetization measurements. Fig. 4.7 shows the magnetic hysteresis (M versus H) loops collected at 300K for the SFMO films grown on STO in vacuum, 0.1 Pa N₂ and 0.05 Pa O₂ pressures. The diamagnetic contribution from the STO substrate has been eliminated from the data to present the actual magnetization of SFMO films. The M versus H curves indicate the presence of macroscopic ferromagnetism in SFMO thin films at room temperature. The SFMO film grown in vacuum shows the highest saturation magnetization (M_s) *i.e.*, 2.5 μ_B /f.u. while the SFMO film grown under oxygen pressure shows the lowest M_s value *i.e.*, 1.25 μ_B /f.u. The M_s for nitrogen grown SFMO film is 1.79 μ_B /f.u.



Figure 4.7: Magnetization versus magnetic field (MH) plots of SFMO films grown in vacuum, 0.1Pa N_2 , and 0.05 Pa O_2 partial pressures on STO (001) recorded at 300K. Inset shows the enlarged M versus H plots.

Fig. 4.8 shows the M versus H plots at room-temperature for the SFMO films grown on LAO. The M_S of SFMO films grown in vacuum, 0.1 Pa N₂ and 0.05 Pa O₂ pressures is 3.17 μ_B /f.u., 2.35 μ_B /f.u. and 1.62 μ_B /f.u.,

respectively. It is imperative from the data that the M_S of SFMO films is quite lower than the theoretical predicted value *i.e.*, 4 μ_B /f.u. This could be attributed to several factors such as oxygen vacancies, anti-site disorder, and non-stoichiometry in the Fe:Mo ratio which affects the magnetization [20]. Here, the SFMO film grown in oxygen has lowest magnetization, the possibility of reduction of magnetization due to oxygen vacancies can be ruled out. So, the decrement in saturation magnetization of SFMO thin films could be attributed to the finite amount of anti-site disorder. Anti-site disorder reduces the net magnetization of the sample by destroying the specific spin arrangement of Fe and Mo sub-lattices without creating any significant effect on the individual magnetic moments at these sites.



Figure 4.8. Magnetization versus magnetic field (MH) plots of SFMO films grown in vacuum, $0.1Pa N_2$, and $0.05 Pa O_2$ partial pressure on LAO (001) recorded at 300K.

The strength of anti-site disorder present in these A₂FeMoO₆ compounds can be quantified as [20]:

$$M_S = (4 - 8\chi)\mu_B \tag{2}$$

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where χ is the concentration of anti-site disorder and M_S is the saturation magnetization. The calculated value of anti-site disorder is 18.75%, and 27.6% and 34.3% for the SFMO films grown on STO in vacuum, under 0.1 Pa N₂ and 0.05 Pa O₂ pressures, respectively. The present results suggest that vacuum grown SFMO films exhibit highest cation ordering, and the ordering decreases for nitrogen and oxygen grown films. The oxygen grown SFMO film is highly disordered. Inset of Fig. 4.7 shows the enlarged MH hysteresis loops to display the coercive field. The coercive field for all the SFMO thin films is around 50-60 Oe. As the data density is low near Zero-field to see exact coercivity, we can say these are close by values.

Fig. 4.9 shows the MH curves for the vacuum-grown SFMO film collected at 300K, 350K and 400K. The film retains ferromagnetism upto 400K with a decrease in the M_s with increase in temperature, which could be attributed to reduced magnetic interactions in SFMO at higher temperatures.



Fig. 4.9: *M versus H plots of the SFMO film grown in vacuum at 300K, 350K and 400K.*

The temperature-dependent magnetization (M versus T) measurements were carried out for the SFMO films grown on STO from 300K to 550K as shown in Fig. 4.10. The measurements were performed after field cooling the sample from 500 K down to 300 K with a magnetic field H=100 Oe parallel to the film surface. It is clear from the figure that all the SFMO films display ferromagnetic to paramagnetic *i.e.*, Curie transition, although the magnitude of the transition differs. The inset figures display the *dM/dT* plots, which show that the T_C of vacuum-, nitrogen-, and oxygen-grown SFMO films is about 420K, 400K, and 375K, respectively. This decreased T_C value is also associated with increased anti-site disorder and antiferromagnetic regions that the oxygen-grown SFMO film is highly disordered, and therefore it shows a very weak Curie transition ~375 K.



Figure 4.10. Magnetization versus temperature (MT) plots of SFMO thin films grown in vacuum, 0.1Pa N_2 , and 0.05 Pa O_2 partial pressure on STO (001).

Fig. 4.11 shows the temperature-dependent magnetization measurements performed for the SFMO films grown on LAO. The χ vs 1/T plots in the figure show that all the films exhibit a Curie transition. The Curie temperature (T_C) of the SFMO films grown in vacuum, 0.1 Pa N₂, and 0.05 Pa O₂ pressures is around 425K, 400K, and 380K, respectively. The decreased T_C value is again indicative of better cation ordering in vacuum-grown film and higher anti-site disorder in SFMO films grown in background gases.



Fig.4.11: Magnetization versus temperature plots of SFMO thin films grown on LAO (100) in vacuum, 0.1Pa N_2 , and 0.05 Pa O_2 partial pressures.

4.3.3 Surface Morphology

The surface morphology of the SFMO thin films has been investigated by Atomic Force Microscopy (AFM) measurements. Fig. 4.12 (a-c) shows the 3D AFM images of SFMO films grown in vacuum, 0.1 Pa N₂ and 0.05 Pa O₂ pressures, respectively. It can be seen that all the films show similar surface morphology. The surface roughness of vacuum, nitrogen and oxygen-grown SFMO films is about 2 nm and the particle size is about 70 nm.



Fig.4.12 (a-c): AFM images of SFMO films grown in vacuum, 0.1 Pa N_2 and 0.05 Pa O_2 pressures.

4.3.4 Electrical Properties

It is reported that SFMO may exhibit metallic, semiconducting or insulating state depending on the synthesis methods, annealing temperature and time *etc.* [10, 21]. To investigate the electrical properties, temperature-dependent resistivity measurements have been carried out for all the SFMO films from 300-10K. Fig. 4.13 and Fig. 4.14 show the resistivity versus temperature plots for the SFMO films grown on STO and LAO substrates, respectively. All the SFMO films show semiconducting behavior ($d\rho/dT < 0$) with the room-temperature resistivity values in the order of several milliohm centimeters. Moreover, the SFMO film synthesized in vacuum exhibits lowest resistivity, and the overall resistivity of the films increases systematically with increase in background gas pressure. The highest resistivity of oxygen grown film is consistent with earlier observed results and is attributed to the increased anti-site defects [22].



Figure 4.13: Temperature dependent resistivity plots of SFMO films deposited in vacuum, 0.1Pa N_2 , 0.5Pa N_2 , and 0.05 Pa O_2 partial pressure on STO.



Figure 4.14: Temperature dependent resistivity plots of SFMO films deposited in vacuum, $0.1Pa N_2$, $0.5Pa N_2$, and $0.05 Pa O_2$ partial pressure on LAO.

In order to get a deeper insight in the semiconducting behavior, temperature-dependent resistivity data has been fitted with Variable Range Hopping (VRH) model, in the temperature range 10K-80K, as described below [23]:

$$\rho(T) = \rho_0 \exp\left(\frac{T_0}{T}\right)^{\frac{1}{4}}$$
(7)

where ρ_0 is the pre-exponential factor and T_0 stands for characteristic Mott temperature. This model applies at lower temperature where conduction takes place only by hopping of charge carriers.

 T_0 is the critical temperature below which a material undergoes a phase-transition to Mott insulating state in case of strong electron-electron correlations. T_0 can be calculated by doing a linear fit on $\ln(\rho)$ vs $1/(T)^{1/4}$ plot. Also, characteristic Mott temperature can be defined as

$$T_0 = \frac{18}{k_B N(E_F)(\alpha)^3}$$
 (8)

where $N(E_F)$ represents the density of states near the Fermi level and α is the localization length for hopping of charge carriers. The temperaturedependent resistivity plots fitted with VRH model are shown in Fig. 4.15 and Fig. 4.16 for SFMO films grown on STO and LAO, respectively. Table-1 shows that T₀ increases with increase the background pressure for both series of films. It is described in literature that T₀ can be considered as an effective energy barrier between the localized states and the extent of disorder in the disordered region [31]. This implies that a larger value of T₀ indicates stronger localization, and more disorder in the system. In the present case, VRH fits also suggest the maximum cation ordering in the vacuum-grown film and a systematic reduction in the cation ordering of SFMO films with increase in the gas pressure. These findings from resistivity corroborate well with the results of the magnetization and Raman spectroscopy.

Deposition Pressure (Pa)	STO T ₀ (10 ⁴ K)	LAO T ₀ (10 ⁴ K)
Vacuum	1.68	2.20
0.1 Pa N ₂	2.34	2.75
0.5 Pa N ₂	2.71	3.45
0.05 Pa O ₂	3.32	3.77

Table-4.1: Characteristic Mott temperature (T_0) calculated from VRH fits to the resistivity plots of SFMO films.



Figure 4.15 (a-d): Variable Range Hopping (VRH) model fitting to the resistivity plots of SFMO films grown on STO.



Figure 4.16 (a-d): Variable Range Hopping (VRH) model fitting to the resistivity plots of SFMO films grown on LAO.

4.3.5 Vibrational Properties

Micro-Raman spectroscopy gives insightful details about local structure, phase purity, and electron-phonon interactions in a material [25, 26]. It can be noted that Raman spectroscopy of SFMO is less explored regardless of the extensive research carried out on this system. For the very first time, Son *et al* carried out Raman spectroscopy on bulk SFMO in 2001 to show the phase decomposition of this double perovskite system [27]. In 2004, the Raman spectra of highly aligned SFMO thin films grown on LaAlO₃ single crystal substrate were shown by Zhang *et al* [28]. Raman spectroscopy on bulk SFMO was also carried out by Marrocchelli *et al* in 2007 [29]. Both Zhang *et al* and Marrocchelli *et al* observed a phonon mode with asymmetric lineshape, termed as Fano feature, in the Raman spectra of SFMO. The Fano feature occurs due to a resonance between discrete phononic states with electronic continuum, suggesting electron-phonon coupling in the system [28].



Fig. 4.17 Raman spectra of SFMO films deposited on STO in vacuum, 0.1Pa N_2 , 0.5Pa N_2 , and 0.05 Pa O_2 partial pressure. The Raman modes from the substrate are denoted by symbol "s".

Fig. 4.17 shows the Raman spectra of SFMO thin films grown on STO, with varyied anti-site disorder. It is worth mentioning here that STO substrate provides huge background contribution; therefore, it is difficult to record Raman spectra of perovskite films grown on STO. As a result, only one B_g Raman mode around 455 cm⁻¹ is observed in the Raman spectra of SFMO films as shown in Fig. 4.17. This B_g Raman mode results from the vibrations of Sr-O bonds of SFMO [28]. The asymmetric lineshape of B_g Raman mode (Fano feature) indicates a strong coupling between the phononic and electronic states in SFMO films. From Fig. 4.15, it is clear that the Fano peak is highly asymmetric, well-defined and sharp in the Raman spectrum of vacuum grown SFMO film, implying stronger electron-phonon coupling in the film. With an increase in the anti-site disorder, the asymmetry of the Fano peak decreases systematically for the SFMO films grown in different process gases which indicates that electron-phonon interaction decreases. The Fano feature is very weak in the oxygen-grown SFMO film which has a high antisite disorder and less electron-phonon coupling.



Fig. 4.18 Raman spectra of SFMO films deposited on LAO in different background conditions.

Fig. 4.18 shows the room temperature Raman spectra of SFMO films grown on LAO. The Raman spectra are indicative of tetragonal space group of SFMO. There are 3 A_g modes (at 99, 210 and 240 cm⁻¹) and 2 B_g modes (at 402 and 453 cm⁻¹) observed for all the SFMO films. The Raman spectra give a signature of *c*-axis oriented SFMO films when compared with literature [24]. Here, A_g modes result from the vibrations of only oxygen atoms and B_g modes are associated with the vibrations of Sr-O bonds. The B_g Fano mode centered around 453 cm⁻¹ is in asymmetric lineshape, giving indication of strong electron-phonon interactions in a material. To quantify the electronphonon interaction, the B_g peak is fitted with Fano equation [24]:

$$I(\omega) = I_0 \frac{[\Gamma + q(\omega - \omega_0)]^2}{\Gamma^2 + (\omega - \omega_0)^2}$$
(3)

where Γ is the half of Raman FWHM, ω_0 is the peak position, q is the asymmetry factor of the Fano peak. The parameter q is inversely proportional to the electron-phonon scattering strength and at q=0, the peak acquires a symmetric Lorentzian lineshape.



Fig. 4.19: B_g Raman mode fitted with Fano equation for the SFMO films.

Fig. 4.19 shows the B_g mode fitted with Fano equation and the fitting parameters are presented in Table 4.2. It can be seen from the table that qvalue is minimum for the SFMO film grown in vacuum, and upsurges with increase in background gas pressure. This suggests maximum electronphonon coupling in the vacuum-grown SFMO film which gets decreased higher anti-site disorder. The anti-site disorder enhances the tendency of electron localization in SFMO system and hence decreases the electron-lattice interaction. This gradual change with anti-site disorder is also indirectly observed by magnetization measurements, as mentioned earlier also.

Table 4.2: Electron-phonon coupling (q) parameter derived from the Fano fit on Raman spectra of SFMO thin films.

Deposition pressure	Peak position (cm ⁻¹)	<i>q</i> parameter	1/q
Vacuum	463.11	0.672	1.48
0.1 Pa N ₂	466.50	0.695	1.43
0.5 Pa N ₂	465.10	0.712	1.40
0.05 Pa O ₂	463.86	0.746	1.34

The thermal evolution of Raman modes of SFMO thin films has been studied by carrying out temperature-dependent Raman spectroscopy measurements on the prepared films. Fig. 4.20 (a) shows the temperature-dependent Raman spectra of the vacuum-grown SFMO film from 90-480K. Neither the appearance of new mode nor the disappearance of existing modes discards the possibility of any structural phase transition in SFMO in the investigated range. Fig. 4.20 (b) shows that there is a red-shift in the Raman peak position and a blue shift in Raman FWHM with increase in temperature, due to thermal lattice expansion and increase in the phonon population.



Fig. 4.20 (a): Temperature-dependent Raman spectra of vacuum-grown SFMO film



Fig. 4.20 (b): Variation of Raman shift position and FWHM with temperature for SFMO film grown in vacuum.

For a magnetic material, the red-shift of Raman modes can be attributed to various factors such as [35]:

$$\omega(T) = \omega_0 + \Delta \omega_{ph-ph} + \Delta \omega_{sp-ph} + \Delta \omega_{anharmonic} \qquad (9)$$

where, ω_0 is the Raman shift corresponding to 0 K, $\Delta\omega_{ph-ph}$ is the lattice volume contribution, $\Delta\omega_{sp-ph}$ is spin-phonon coupling contribution and $\Delta\omega_{anharmonic}$ signifies the contribution of anharmonic terms in the system. Here, $\Delta\omega_{sp-ph}$ arises because of a modulation of spin exchange integral by a change in the lattice vibrational frequencies, and hence signifies contribution from spin-phonon interactions. The term $\Delta\omega_{lattice}$ represents the isotropic variation in volume and found negligible here. Thus, the observed red-shifts of the Raman modes are mainly contributed by higher-order anharmonicity, ($\Delta\omega_{anharmonic}$), and spin-phonon coupling, ($\Delta\omega_{sp-ph}$), in the system. To quantify the anharmonic term contribution, the Raman-shift versus temperature plots have been fitted with Balkanski model (Fig. 4.21) described as:

$$\boldsymbol{\omega}(T) = \boldsymbol{\omega}_0 - A \left[1 + \sum \frac{1}{exp\left(\frac{\hbar \boldsymbol{\omega}_i}{k_{\boldsymbol{\beta}}T}\right) - 1} \right]$$
(4)

where ω_0 is the Raman shift at 0 K and A is the anharmonicity coefficient.



Fig. 4.21: Variation in Raman shift with temperature for SFMO films grown in vacuum. The red line shows the data fitted with Balkanski model. The yellow highlighted portion shows the T_C region.

The Balkanski fittings show an anomaly in the normal anharmonic behaviour around 420K *i.e.*, T_C of SFMO. Moreover, the SFMO films grown in nitrogen and oxygen gases also show similar anomaly in the temperaturedependent Raman spectra as shown in Fig. 4.22 (a, b). As discussed earlier, the deviation of Raman-shift versus temperature data from normal anharmonic behavior gives an indication of spin-phonon coupling in the system. As a result of spin-phonon coupling, the magnetic ordering induced phonon renormalization takes place near magnetic transition temperature has been observed recently in perovskites like Ca₂FeReO₆, HoFeO₃, YCrO₃ *etc.* [28]. Considering the mean field approximation, the phonon renormalization function has a dependency on magnetization as follows [28]:

$$\Delta \omega = \omega(T) - \omega_{anharmonic} = \Upsilon \frac{M^2(T)}{M_{Sat}^2(T)}$$
(6)

where M(T), $M_{sat}(T)$, and γ denotes the temperature-dependent magnetization, saturation magnetization and spin-phonon coupling strength, respectively. This equation indicates that the spin-phonon coupling strength is directly proportional to $\Delta \omega$.



Fig. 4.22 (a): Variation in Raman shift with temperature for SFMO films grown in 0.1 Pa N_2 . The red line shows the data fitted with Balkanski model. The yellow highlighted portion shows the T_C region.



Fig. 4.22 (b): Variation in Raman shift with temperature for SFMO films grown in 0.05 Pa O_2 . The red line shows the data fitted with Balkanski model. The yellow highlighted portion shows the T_C region.

The Raman shift position versus temperature plot has been fitted with Balkanski model in both the regions above and below magnetic transition, and the calculated value of $\Delta \omega$ is 30.12cm⁻¹ for the SFMO film grown in vacuum (Fig. 4.21). Similarly, the calculated value of $\Delta \omega$ is 27.69 cm⁻¹ and 22.77 cm⁻¹ for SFMO films grown in nitrogen and oxygen atmosphere, respectively (Fig. 4.22 (a, b)). This suggests a stronger spin-phonon coupling in the vacuum-grown SFMO film which decreases with increase in the cation disorder. No such feature indicating spin-phonon coupling is reported in the temperature-dependent Raman spectra of bulk SFMO system [25]. It can be noted here that the emergence of spin-phonon coupling indicates the high crystalline quality of SFMO films which enhances the technological applicability of these materials. In addition to this, the T_C of these SFMO films has also been probed as the temperature at which the deviation from normal anharmonic behavior takes place. The T_C of SFMO films grown in vacuum, nitrogen and oxygen gases is around 420K, 400K, and 380K, respectively, as corroborated with the magnetization results.

4.4 Conclusion:

In summary, two series of SFMO thin films have been deposited in different deposition conditions (vacuum, nitrogen and oxygen pressures) on STO and LAO single-crystal substrates to improve the Fe-Mo ordering. It is seen that background conditions significantly influence the crystalline quality of SFMO films, and the vacuum-grown film is more crystalline in both the series. Magnetization measurements show that the SFMO film grown in vacuum has the highest saturation magnetization and Curie temperature amongst the series, indicating higher cation ordering. The M_S and T_C values get reduced for the nitrogen- and oxygen-grown SFMO films due to increased anti-site disorder. A systematic reduction of M_S and T_C values with increment in anti-site disorder has been observed. Raman spectra show a Fano feature, indicating electron-phonon coupling in the SFMO films. The electron-phonon coupling is maximum for vacuum-grown film and gets systematically decreased with increasing anti-site disorder. Temperature-dependent Raman spectra show an anomaly in the normal anharmonic behavior of phonon modes near T_C due to phonon renormalization. This feature indicates spinphonon coupling in SFMO films, which was absent in the bulk counterpart. The spin-phonon coupling strengthens with increase in the Fe-Mo ordering in SFMO films. There is a systematic increase in the overall resistivity of the films with an increase in the anti-site disorder. The VRH fits to the resistivity plots also indicates increased disorder in SFMO films grown in background gases. The present presents a key role of anti-site disorder in tuning all the physical properties of SFMO films. The SFMO film grown in vacuum exhibits the highest level of B-site ordering.

4.6 References:

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Chapter 5

Growth-orientation dependent cation order, phase transitions and spin-phonon coupling in half-metallic Ca₂FeMoO₆ Thin Films

The disorder due to anti-site cation distribution is intrinsic to the double perovskites wherein the crystal orientations of the substrate template are predicted to offer different degrees of cation order in thin film form. To demonstrate this effect, epitaxial thin films of half-metallic double perovskite Ca₂FeMoO₆ (CFMO) were prepared on (100) and (111) oriented LaAlO₃ substrates in vacuum and nitrogen atmospheres. The findings using X-ray absorption near-edge structure, Terahertz (THz) and Raman spectroscopies, in combination with magnetization show that (111) epitaxial template effectively restricts the Fe-Mo anti-site cation disorder. A resultantly enhanced cation order in (111) films induces dramatic transformations in its properties as follows: i) significantly enhanced ferromagnetic exchange interactions and saturation magnetization in (100) films, *ii*) a large increase in the Curie temperatures, iii) a metallic behaviour down to a temperature of ~75 K compared to that down to 200 K for (100) film, iv) an enhanced spin-phonon coupling. The complex THz optical conductivity spectra evaluated in the framework of Drude and Drude-Smith phenomenological models and the temperature-dependent Raman data fitted to the Balkanski model corroborate well to indicate an enhanced cation order in (111) films.

While this study establishes a dominant role of crystallographic orientation in much desired control of cation order in double perovskites, a demonstration of the same in room temperature half-metallic CFMO system could reinforce its technological utility both as active and passive components in emergent spintronic functionalities. The obtained results are published in an international journal*.

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5.1 Introduction:

 A_2 FeMoO₆ (A= Ca, Sr, and Ba) double perovskites exhibit promising attributes like high Curie temperature (T_C), 100% spin polarization at room temperature (RT), and half-metallicity which make potential spintronic candidates [1-6]. Ca₂FeMoO₆ (CFMO) crystallizes in a monoclinic structure with P21/n space group [7]. The lower symmetric structure of CFMO as compared to orthorhombic SFMO and cubic BFMO systems can be understood in terms of higher orthorhombic distortion due to smaller ionic radius of the Ca²⁺ ion (1.06 Å) as compared to Sr²⁺ (1.21 Å) and Ba²⁺ (1.38 Å) ions. In an ideal structure, FeO₆ and MoO₆ octahedra are arranged alternatively in a three-dimensional checkerboard arrangement. Here the magnetic ground state is described by an ordered arrangement where ferrimagnetic superexchange interactions across Fe-O-Mo happen between $Fe^{2+/3+}$ and $Mo^{6+/5+}$ ions, respectively, giving rise to a theoretically calculated saturation magnetization (M_S) of 4 $\mu_B/f.u.$ in either case [4, 5]. Here, the contribution of Fe ions to net magnetization is predominant with a spin-up state. The majority of Fe ions acquire trivalent state in these double perovskites. If Fe³⁺ ions have Mo⁵⁺ as the next nearest neighbor, Mo sublattice in ordered arrangement contributes negatively with spin-down state [5].

However, the experimentally observed value of M_S is always found to be lower than the theoretically predicted value [8] due to the presence of the anti-site disorder. The anti-site disorder occurs due to the similarity in ionic radii and ionic valence of B and B' cations, which provides an ease to readily exchange their positions and thereby modifying the physical properties of the system [8, 9]. In AFMO double perovskite system with an anti-site disorder, when the alternate arrangement is disturbed, the Fe-O-Fe interactions as well as the Mo-O-Mo interactions increase in number, causing antiferromagnetic and paramagnetic contributions, respectively. These contributions finally reduce the net magnetization of the overall ferromagnetic system [9, 10]. Thus, the Fe-O-Mo alternate arrangement is more often possible if the antisite disorder is reduced, and this arrangement contributes to higher net magnetization. With a high degree of anti-site disorder, the half-metallicity of these materials is also lost [5]. Therefore, controlling anti-site disorder in these double perovskites is a much-needed attribute to realize the functionality.

Many efforts have been made, both theoretical and experimental, in the last years to improve cation ordering in AFMO double perovskites. Improving B-site ordering is relatively easier in thin films due to the availability of a range of controlling parameters such as substrate-induced strain, oxygen stoichiometry, substrate temperature, and thickness variation, etc. [10-12]. It is seen that cation ordering can be enhanced by synthesizing thin films using Pulsed Laser Deposition (PLD) method at high substrate temperature (>1000 $^{\circ}$ C), or by deposition in a gas atmosphere of Ar and 5% H₂, or low oxygen pressure (10^{-4} mbar) [10-12]. Till now, there are no reports on improving B-site ordering by any other means. However, achieving such absurd growth parameters is difficult and not possible in every growth chamber. These parameters are not so suitable for all the double perovskites including CFMO. In 2017, Josée E Kleibeuker et. al proposed and explained a new hypothesis to achieve B-site ordering in La_2MnCoO_6 thin films [13]. In their model, they suggested that (100) oriented substrate, providing compressive strain, creates four reduced in-plane B-O bonds (d_{B-O}) and two elongated out-of-plane B-O bonds. However, all the six B-O bonds elongate themselves to preserve the unit cell volume in the case of (111) oriented substrate [13]. With octahedral rotations, strain causes a uniform effect on all the octahedra in the (100) oriented system. However, as shown in the schematic (Fig. 5.1), one set of BO_6 octahedra tilts towards the substrate plane, and the other set tilts along the out-of-plane direction, in the presence of octahedral rotations. In this way, an ordered arrangement of two different B-site cages can be formed in double perovskites using (111) oriented substrate with compressive strain [13].



Fig. 5.1: Schematic showing the FeO₆ and MoO₆ octahedra containing antiphase rotations in double perovskite CFMO films for; (a) (100) orientation and (b) (111) orientation. The zig-zag pattern of Fe-O-Mo chains is shown by black dashed line.

In order to validate the above-mentioned hypothesis, we chose Ca_2FeMoO_6 as a model system considering that the FeO₆ and MoO₆ octahedra are noticeably tilted due to the relatively smaller size of the Ca²⁺ cation. Also, anti-site disorder can be affected by a variation in the background gas pressure in the PLD chamber. Keeping these points in mind, we prepared two series of CFMO thin films on LaAlO₃ (LAO) single crystal substrate with varied anti-site disorder. One set of films was grown on LAO (100) while the other on LAO (111) substrate to verify the effect of substrate orientation on B-site ordering. Moreover, for each set of two films, one film was grown in vacuum and the other in nitrogen atmosphere. The orientation-dependent changes in the structural, electrical, magnetic, vibrational, and optical properties of these thin films are reported here.

5.2 Experimental

We synthesized two sets of Ca_2FeMoO_6 thin films (~ 65nm) on LaAlO₃ (LAO) single crystal substrate with two different orientations *i.e.*

(100) and (111), using Pulsed Laser Deposition (PLD) technique. For each set of films, one film was grown in vacuum and the other in nitrogen atmosphere. For the sake of clarity, the films are abbreviated as CFMO-Vac (100), CFMO-N₂ (100) for the CFMO films grown on LAO (100), and CFMO-Vac (111), CFMO-N₂ (111) for the other set grown on LAO (111). The bulk pellet of CFMO, used as the target material in the PLD chamber, was synthesized via conventional solid-state reaction method. For that purpose, high-purity (>99.99%) powders of CaCO₃, Fe₂O₃, and MoO₃ (Sigma Aldrich) in proper stoichiometric amounts were ground and calcined at 900 °C for 12h. The resulting mixture was reground and pressed into pellets (15mm) using a hydraulic press and then sintering was carried out at 1150 °C for 12h in Ar+5% H₂ atmosphere. A KrF excimer laser ($\lambda = 248 \text{ nm}$, Coherent Compex Pro) with laser energy 350 mJ operating at a frequency of 5 Hz was used to ablate the target material in a vacuum chamber (Excel Instruments). The substrate temperature was maintained at 770 °C, and the target to substrate distance was 4 cm. For one set, vacuum ($\sim 10^{-4}$ Pa) was maintained during deposition, while 0.5 Pa Nitrogen partial pressure was maintained for the other set. Just after deposition, the samples were cooled down to room temperature in the same atmosphere at 10°C/min.

The phase-purity and growth orientation of the synthesized thin films has been investigated by X-ray diffraction (XRD) measurements in Bruker D8 Diffractometer in Bragg-Brantano geometry using Cu k_a radiations. The Fe K-edge XANES spectra were recorded at BL-9, Scanning EXAFS Beamline of Indus-2 at RRCAT, Indore. The measurements were carried out in fluorescence mode using an energy-dispersive detector. The beamline consists of Rh/Pt coated meridional cylindrical mirror for collimation and a Si (111) double crystal monochromator (DCM) to select excitation energy of Fe (7112 eV) K-edge. The second crystal of the DCM is a sagittal cylinder that provides a beam focused in the horizontal direction. The electrical properties of the thin films have been studied by performing *dc* electrical resistivity measurements in a temperature range of 300-10K using the four-point probe method. For this purpose, Keithley (2612 A) made source and measurement meters were used. To understand the variation of optical properties with antisite disorder, Terahertz time-domain spectroscopy (THz-TDS) has been performed in a temperature range from 300 to 5K and frequency range from 0.2 to 1.2 THz. For this purpose, LT-GaAs photoconductive antenna-based THz spectrometer has been used. Vibrational characteristics of the thin films have been understood by Raman spectroscopy measurements using a Horiba LabRAM-made HR-Evolution Raman microscope consisting of a Charge Coupled Device (CCD) detector. Micro-Raman signals were recorded in back-scattering mode using a *HeNe* laser with excitation light 632.8 *nm* and a laser power of 1 mW. Temperature-dependent Raman measurements were carried out by placing the sample on a commercial Linkam stage and varying the temperature using temperature controllers and the LN_2 module. The Magnetization measurements for all the samples were performed using SQUID-VSM (Quantum Design) magnetometer in the temperature range of 1.8 to 300 K and in a magnetic field ranging from -5T to 5T.

5.3 Results and discussion:

5.3.1 Structural Characterization:

X-ray diffraction

In order to check the phase purity, structural orientation, and lattice strain of CFMO films, X-ray diffraction (XRD) measurements have been carried out. Fig. 5.2(*a*) shows the full-scale XRD patterns of the CFMO thin films grown on LAO (100) substrate. It can be seen that films are grown single-phase, impurity-free, and highly oriented toward the crystallographic orientation of the substrates. The pseudo-cubic lattice parameter of bulk CFMO is 3.86 Å, while that of LAO (100) substrate is 3.79 Å. This difference in lattice parameters gives rise to a lattice mismatch of -3.6% in CFMO (100) films. This suggests the presence of compressive strain in CFMO (100) films as shown in the magnified view of XRD patterns (Fig. 5.2 (b)). The *c*-axis





Fig. 5.2: (a) XRD patterns of CFMO films deposited on LAO (100) substrates in vacuum and nitrogen atmospheres. The XRD peaks from substrate having reflections other than (100) are presented by symbol "s".



Fig. 5.2: (b) Magnified view of the (400) Bragg's reflection of these films.

Fig. 5.3 (a, b) shows the XRD patterns of CFMO films grown on LAO (111) substrate. The films are grown phase-pure and highly oriented. The c-axis lattice parameter of CFMO (111) films is ~3.81 Å. The CFMO films oriented along the (111) axis have narrower peaks indicating more crystalline structure as compared to (100) films. LAO (111) [3.82 Å] impart a lattice mismatch of -0.49 % to CFMO [3.86 Å] films. Further, this lattice mismatch and the FWHM of the XRD peaks increase for nitrogen-grown films.



Fig. 5.3: (a) XRD patterns of CFMO films deposited on LAO (111) substrates in vacuum and nitrogen atmospheres. (b) Magnified view of the 2^{nd} order Bragg's reflection of these films.

X-Ray Absorption Near Edge Structure (XANES):

Depending upon the preparation conditions, the Fe and Mo ions in the A_2 FeMoO₆ compounds can arrange in a random or ordered fashion at their respective sites [4-7]. Previous X-ray absorption spectroscopy (XAS) data of polycrystalline SFMO at the Fe L-edge conclude that Fe is either in +3 oxidation state or in an intermediate valence Fe²⁺/Fe³⁺ [14]. Furthermore, Mössbauer data were also interpreted for either Fe³⁺ or Fe²⁺/Fe³⁺ valence

states in these compounds [15]. Many efforts are made for resolving the oxidation state of Fe ions in these compounds, but so far this is not understood clearly.

Therefore, to investigate the valence state and cation ordering in the present films, we carried out X-ray Absorption Near Edge Structure (XANES) spectroscopy on the set of CFMO films grown in vacuum. Fig. 5.4 (a) shows the Fe K-edge XANES spectra of both the CFMO films along with standard references of Fe^{2+} and Fe^{3+} . To quantify the amount of Fe^{2+} and Fe^{3+} . Fe XANES data were calculated using linear combination fitting (LCF) with Athena software [16] within an energy range of -20 eV below to +20eV above the edge (Fig. 5.4). The LCF method is used to quantify the relative percentage of mixed oxidation state present in a material. LCF of CFMO-Vac (100) (Fig. 5.4 b) and CFMO-Vac (111) (Fig. 5.4 c) were done using a combination of Fe²⁺ and Fe³⁺ standard spectra and goodness of fit parameters (reduced χ^2) along with the percent that contributes to each fit. The accuracy of this method depends on how well the spectra of the chosen reference compounds represent the components in the samples [16]. The relative percentage of Fe^{2+}/Fe^{3+} extracted from LCF fitting is presented in Table 1. The obtained reduced χ^2 for best fit are $\chi^2=0.011$ for all the samples. It is clear from the table that for both the CFMO films, Fe ions are present in divalent and trivalent states with the majority being in the trivalent state. However, it should be noted that the concentration of Fe^{2+} ions is higher in (111) oriented films than that in (100) oriented films.

Table 5.1: Relative percentage of the mixed oxidation state of Fe ions

 obtained from the Linear Combination Fitting (LCF) done on CFMO films.

Thin Films	Fe ²⁺ (%)	Fe ³⁺ (%)
CFMO-Vac (100)	28	72
CFMO-Vac (111)	36	64



Fig. 5.4: (a) X-Ray Absorption Near Edge Spectra (XANES) of CFMO-Vac (100) and CFMO-Vac (111) films at Fe-K edge. (*b*, *c*) Linear Combination Fitting (LCF) done on the XANES spectra.

5.3.2 Magnetic properties:

The magnetization of a sample at a given temperature is dependent on the interplay of applied magnetic field, exchange interactions and thermally excited spin waves. The effect of substrate orientation and background gas atmosphere on the magnetic properties of CFMO thin films has been investigated by magnetic field and temperature-dependent magnetization measurements. The diamagnetic contribution from LAO substrate has been eliminated from the data to present the actual sample contribution. The temperature-dependent magnetizations of the vacuum grown CFMO thin films of different orientations are shown in Fig.5.5 (*a*, *b*). Both films exhibit qualitatively similar magnetization curves, and the Curie temperature (T_C) is assigned as the onset temperature of rapid increase in magnetization. The T_C for (100) and (111) oriented films CFMO films is found to be 320K and 340K, respectively.



Fig. 5.5: Magnetization (ZFC and FC) versus temperature plots for (*a*) CFMO-Vac (100) and (*b*) CFMO-Vac (111) films.

The magnetic hystereses have been recorded at 300K, 150 K, 10K, and 2K for all the CFMO films. For a comparison, Fig. 5.6 (*a*) shows the magnetic hysteresis loops for all the films at 150 K. It can be noted here that CFMO-Vac (111) film possesses the highest saturation magnetization of 3.2 μ_B /f.u., while the CFMO-N₂ (100) film shows the least saturation magnetization of 2.4 μ_B /f.u. For the brevity of the presentation, the hysteresis plots recorded at different constant temperatures for only CFMO-Vac (111) film are shown in Fig. 5.6 (*b*). It can be seen from the figure that the maximum saturation magnetization of 3.5 μ_B /f.u. is achieved at 2 K, which is quite close to the theoretically predicted value of 4 μ_B /f.u. for a perfectly ordered system. The saturation magnetization goes on decreasing with an increase in temperature as expected.

It is imperative from the data that the saturation magnetization of CFMO films is quite lower than the theoretically predicted value of 4 μ_B /f.u., which could be attributed to the finite amount of anti-site disorder in CFMO thin films. As described earlier in a perfectly ordered CFMO system, the alternate arrangement of Fe and Mo gives rise to ferrimagnetic interactions

with a predominant contribution from Fe ions with spin-up state. In the present case, a higher degree of anti-site disorder in (001) oriented CFMO films affects the Fe-O-Mo alternate arrangement and causes paramagnetic and antiferromagnetic contributions, which finally decreases the magnetization and Curie temperature compared to those of (111) oriented films.



Fig.5.6: (a) Magnetization versus Magnetic field curves for all CFMO films recorded at 150K.

The strength of anti-site disorder present in these A_2FeMoO_6 type samples can be quantified as [17]:

$$M_S = (4 - 8\chi)\mu_B \tag{1}$$

where χ is the concentration of anti-site disorder and M_S is the saturation magnetization. The anti-site disorder is found to be 17.2% and 22.8% for the CFMO films grown on LAO (111) and LAO (100) substrates, respectively, confirming higher cation ordering in CFMO (111) films.



Fig. 5.6 (b) Magnetization versus Magnetic field curves of CFMO-Vac (111) thin film recorded at 300K, 150K, 10K, and 2K.

5.3.3 Electrical properties:

The electrical properties of the Fe-Mo based double perovskites, whether in bulk or thin film forms, are highly dependent on the synthesis conditions [5, 12]. In AFMO films, a variation in deposition temperature or background gas atmosphere brings only a moderate change in the electronic transport [2, 18]. CFMO may show metallic, semiconducting, or insulating behavior based on the degree of anti-site disorder [12]. However, the B-site ordered bulk CFMO exhibits metallicity below the Curie temperature of 350 K.

Fig. 5.7 shows the *dc* resistivity of all the CFMO films. The (100) oriented CFMO films grown in vacuum and nitrogen atmospheres display semiconducting behavior below 200K and 250K, respectively. In contrast to

this, both the CFMO (111) films grown in vacuum and nitrogen exhibit a metallic state with a transition to semiconducting state below 45K and 65K, respectively. The appearance of the metallic state of (111) oriented CFMO films is attributed to a large enhancement in the B-site cation ordering of the system by changing the underneath substrate orientation to (111) direction. This proves to be an alternate method to improve the cation ordering in CFMO films by the PLD method at optimum deposition temperature and pressure, without the requirement of absurd growth parameters as described earlier.



Fig. 5.7 Temperature-dependent resistivity plots of CFMO films grown on (111) and (100) oriented films.

In the present half-metallic CFMO system, two spin channels act parallel to each other [19, 20]. Here, the spin-up channel with a band-gap at the Fermi level is semiconducting, while the spin-down channel without any gap has metallic nature. The half-metallicity is preserved in the ordered CFMO; however, the introduction of anti-site disorder reduces the halfmetallic character, and a large amount of anti-site disorder gives rise to a semiconducting state. The band structure calculations show that the majority spin band mainly separates the Fe eg states from Mo t_{2g} states finally creating a gap, while the minority band consists of strongly hybridized Fe t_{2g} and Mo t_{2g} states [3, 21-23] giving rise to metallicity, in an overall half-metallic system. In general, the Fe³⁺-O-Mo⁵⁺ arrangement is predominantly present in CFMO facilitating the spin-up charge conduction with a semiconducting nature as well as the spin-down charge conduction with a metallic nature as schematically presented in Fig. 5.8. However, the conduction channel through Fe²⁺-O-Mo⁶⁺ arrangement can support only spin-down metallic type conduction.



Fig. 5.8: Schematic showing the superexchange interactions in Fe^{3+} -O- Mo^{5+} (type-I) and Fe^{2+} -O- Mo^{6+} (type-II) configurations in CFMO.

In the metallic state, the resistivity as a function of temperature can be described as [24, 25]:

$$\rho_m(T) = \rho_0 + \rho_n T^n \tag{2}$$

where ρ_0 is residual resistivity which is temperature-independent term, existing due to lattice imperfections, impurities, grain boundary contributions *etc.*, ρ_n governs the strength of electron-electron interactions, and *n* is an
adjustable parameter. According to the classical Fermi Liquid model, the value of exponent n remains 2, which explains the quadratic dependence of resistivity over temperature [21]. However, in case of strong electronic correlation, two other values of n are often reported *i.e.*, 1.6 and 1.3 which define the non-Fermi Liquid (NFL) state. This model describes the electrical conduction mechanism in spin-down metallic state only. On the other hand, the resistivity of spin-up semiconducting band can be described as [19]:

$$\rho_{SC}(T) = \rho_0 + \rho_d^{SC} e^{\frac{E_g}{KT}}$$
(3)

where ρ_0 is temperature-independent term, ρ_d^{SC} is a constant governing electrical charge density and E_g is the band-gap of the material in spin-up channel. In this context, the total resistivity for CFMO films, which takes into account the resistivity from spin-up semiconducting band (ρ_{SC}), spin-down metallic band (ρ_m) and the temperature-independent term (ρ_0), can be described by parallel spin channel given as [19, 26]:

$$\frac{1}{\rho} = \frac{1}{\rho_m} + \frac{1}{\rho_{SC}} \tag{4}$$

For the present data analysis, this parallel spin-channel model is applied to CFMO thin films where the anti-site disorder, oxygen vacancies and strain play a dominating role in deciding the transport properties and temperature dependent band-gap. The equation (4) was fitted to the resistivity data of all the CFMO films as shown in Fig. 5.9 in red line. The one-to-one correspondence of the experimental data with the model fitting shows that the resistivity is absolutely defined by the parallel spin channel model. A small upturn in the resistivity at low temperatures indicates that the semiconducting channel is rather more actively contributing for charge transport. The contributions of spin-down and spin-up channels towards the total resistivity of the samples have been separately estimated from the extracted parameters as presented in Table 5.2. It is worth mentioning here that the residual resistivity in spin-down channel (ρ_0) is quite low for all the CFMO films as compared to the that in spin-up channel (ρ_d^{SC}) due to the ease of conduction in the metallic channel. The values of residual resistivities in both channels increase with rise in anti-site disorder, showing the minimum value for CFMO-Vac (111) film and the maximum value for CFMO-N₂ (100) film. From Table-2, it can be seen that the spin-down channel is rather more active in (111) oriented films. As shown earlier by XANES results too, a higher concentration of Fe^{2+} -O-Mo⁶⁺ channels are available for spin-down conduction. Hence, the resistivity and XANES data analyses, in a combined way, show that Fe^{2+} -O-Mo⁶⁺ channels in (111) oriented films facilitate a dominant metallic conductivity.



Fig. 5.9: Temperature-dependent resistivity data of CFMO films fitted with the parallel spin channel model.

The NFL exponent as described in equation 2 is n=1.3 for (111) oriented films and n=1.6 for (100) oriented CFMO films, suggesting a non-Fermi liquid behavior for metallic state in all the films. The parameter governing electron-electron scattering strength (ρ_n), increases abruptly with change in the substrate orientation, which indicates an increase in the defect concentration or the anti-site disorder. The CFMO (111) films have a smaller

band-gap as compared to the CFMO (100) films. In this context, CFMO-Vac (111) film exhibits the lowest band gap of 0.13 meV and CFMO-N₂ (111) film has the highest band gap of 4.3 meV.

Thin Films	Spin-down channel Residual resistivity (mΩ.cm)	n	Electron- electron scattering strength (×10 ⁻⁷ Ω.cm)	Spin-up channel Residual resistivity (mΩ.cm)	Band gap (meV)
CFMO-Vac (111)	0.38	1.3	0.008	7.5	0.13
$CFMO-N_2 (111)$	0.53	1.3	0.03	8.9	0.19
CFMO-Vac (100)	1.7	1.6	2.3	58	3.7
CFMO-N ₂ (100)	4.5	1.6	3.5	98	4.3

Table 5.2: Parameters extracted from the parallel spin model fitted tothe temperature-dependent resistivity plots of all the CFMO films.

5.3.4 Terahertz Spectroscopy:

Terahertz (THz) spectroscopy is a potential tool to investigate various intriguing phenomena such as charge or spin density waves, orbital ordering, topological phases, phase transitions *etc.* [27, 28]. For the present investigations, the set of CFMO films grown in vacuum show highest cation ordering and hence the effects have been also studied by temperature-dependent THz spectroscopy. Fig. 5.10 and 5.11 (*a*, *b*) show the real (σ_1) and imaginary (σ_2) parts of the complex optical conductivity (σ^*) in the investigated frequency (0.2-1.2 THz) and temperature (5-300 K) range for both the vacuum grown CFMO films. It is worth noting here that for (111) oriented CFMO film, both (σ_1 and σ_2) exhibit positive values. Further, σ_2 increases with increasing THz frequency, while σ_1 decreases. These are characteristic features of Drude type of optical conductivity which describes the free carrier dynamics of nearly disorder-free systems. According to the Drude model, the complex conductivity as a function of frequency (ω) can be written as follows [27]:

$$\sigma^*(\omega) = \frac{\varepsilon_0 \omega_p^2}{\Gamma - i\omega} - i\varepsilon_0 \omega(\varepsilon_\infty - 1)$$
(5)

where ε_0 is the permittivity of vacuum, ω_p is the plasma frequency, ε_{∞} is the permittivity of the medium at higher frequencies, and Γ is the scattering rate of charge carriers. The optical conductivity of CFMO-Vac (111) film has been fitted to this Drude model (eqn. 5). Here, the real and imaginary parts are fitted simultaneously at all temperatures. The fittings for maximum (300 K) and minimum (10 K) temperatures of the measured range are presented in Fig. 5.10 (c, d).



Fig.5.10: The complex conductivity i.e., (*a*) real and (*b*) imaginary THz conductivity spectra of CFMO-Vac (111) film.



Fig. 5.10 (c, d): Drude model fitted to the complex conductivity data at 300K, and 10K.

The optical conductivity of CFMO-Vac (100) film (Fig. 5.11) shows that the values of imaginary conductivity remain negative in the investigated ranges of frequency and temperature. These features defy the Drude type of carrier dynamics. Rather, such features are often observed in disordered systems and can be described well using the Drude-Smith model. This model has been successfully applied to explain non-Drude like conductivity of many nanostructured metals, semiconductors, oxides, disordered materials so far [29]. It is an extension of Drude model which also accounts for the backscattered charge carries. As discussed in magnetization results, (100) orientated films have larger anti-site disorder in the system. Therefore, it creates irregularity at B and B' sites causing a larger scattering of the charge carriers. In other words, the anti-site disorder disrupts the charge transport network connected through B and B' site ions and increases back-scattering of carriers. The Drude-Smith model is expressed as [29]:

$$\sigma^*(\omega) = \frac{\varepsilon_0 \omega_p^2}{\Gamma - i\omega} \left(1 + \frac{cT}{\Gamma - i\omega} \right) - i\varepsilon_0 \omega(\varepsilon_\infty - 1)$$
(6)

where, c is the velocity parameter. In general, the more negative value of c suggests increased backscattering of charge carriers which in turn highlights more amount of disorder present in CFMO-Vac (100) film.



Fig.5.11: The complex conductivity i.e., (*a*) real and (*b*) imaginary THz conductivity spectra of CFMO-Vac (100) film.

As shown in Fig. 5.11, the THz conductivity data of (100) oriented CFMO film fits well with the Drude-Smith model. Again, the data is fitted simultaneously to both σ_1 and σ_2 of the film. Here, the value of disorder parameter *c* is almost independent of temperature, *i.e.*, it varies from -0.99 to -0.95±0.05 from room temperature to 10 K, respectively. This feature indicates a static disorder in the film. Any static disorder is inherent to the film and depends on the sample fabrication process. Unlike this, the disorder

in RNiO₃ systems is dynamic in nature which brings strong dependency of parameter c on the temperature [28].



Fig. 5.11 (c, d): Drude-Smith model fitted to the complex conductivity data at 300K, and 10K.



Fig. 5.12: (a, b) Temperature-dependent optical parameters derived from the Drude-Smith model fitted to THz conductivity of CFMO-Vac (100) film, (c, d) Temperature-dependent optical parameters derived from the Drude model fitted to THz conductivity of CFMO-Vac (111) film.

The derived values of ω_p and Γ for both the CFMO-Vac films are presented in Fig. 5.12. For CFMO-Vac (111) film, the ω_p increases with rising temperature suggesting strong electron-electron correlation in the metallic state. Also, Γ increases with increasing temperature. Both ω_p and Γ show variations presenting metallic conductivity in CFMO-Vac (111) film throughout the temperature range. These results of CFMO-Vac (111) agree well with the resistivity data. In contrast to this, for CFMO-Vac (100) film, ω_p first decreases up to T_{MI} and then it increases up to room temperature. Similarly, Γ also varies inversely with the temperature up to T_{MI} and after that, it follows normal metallic behaviour.

5.3.5 Vibrational properties

Earlier Raman spectroscopy has been used to study the impact of cation ordering and spin-phonon coupling in La_2CoMnO_6 thin films [30, 31]. In the present case, Raman spectroscopy measurements have been performed on the CFMO films [Fig. 12] to explore the B-site ordering and spin-phonon interactions in thin films.

Fig. 5.13 displays the room-temperature Raman spectra of all the CFMO thin films. The Raman modes are observed at 258, 294, 315, 422 and 450 cm⁻¹. The curves are de-convoluted, and the corresponding peak position and FWHM of the Raman modes are presented in Table 5.3. The Raman spectra shows that (111) oriented CFMO films show sharp and well-defined Raman modes. These intense and well-defined Raman modes indicate B-site ordering due to Brillouin zone folding [31]. In a disordered double perovskite, the B and B' ions are randomly distributed in the lattice. However, the B and B' are alternatively arranged in a long-range cation ordered double perovskite system, which gives rise to doubling of pseudocubic unit cell lattice parameter with respect to the primitive cell. It eventually causes Brillouin-zone folding and changing of symmetry. The present results suggest that CFMO-Vac (111) film has the highest degree of *B*-site ordering, while CFMO-N₂ (100) film exhibits lowest B-site ordering. Here, we emphasize on the point that although all the CFMO films are phase-pure as observed by

XRD, a significant difference in the cation ordering has been probed by Raman spectroscopy.

Table 5.3: Raman peak position and FWHM extracted afterdeconvolution of the room-temperature Raman spectra of CFMO thinfilms.

Thin Films	Peak position (cm ⁻¹)	FWHM (cm ⁻¹)	Peak position (cm ⁻¹)	FWHM (cm ⁻¹)	Peak position (cm ⁻¹)	FWHM (cm ⁻¹)
Vac (100)	259.47	112.21	299.54	24.56	312.20	61.71
N ₂ (100)	258.11	165.21	298.38	27.84	314.89	114.29
Vac (111)	257.45	57.64	297.24	16.25	319.17	38.81
N ₂ (111)	255.82	117.81	295.77	19.59	318.77	50.67



Fig. 5.13: *Room-temperature Raman spectra of* (*a*) *CFMO-Vac* (100), (*b*) *CFMO-Vac* (111), (*c*) *CFMO-N*₂ (100), and (*d*) *CFMO-N*₂ (111) thin films.

It is imperative to mention that any thermal perturbation in the lattice, spin or orbital degrees of freedom of a system can be sensed by temperaturedependent Raman spectroscopy. Bulk CFMO exhibits Curie transition at ~350 K [12]. However, in thin films, variation in lattice strain and anti-site order significantly modifies the transition temperature of the system. The thermal evolution of vibrational properties of CFMO system has been understood by temperature-dependent Raman spectroscopy from 90K to 400K. Fig.5.14 (a, b) shows the temperature-dependent Raman spectra of CFMO-Vac (100) and CFMO-Vac (111) films, respectively. The temperature induced thermal expansion of the lattice produces red-shift of the Raman modes as expected. For a magnetic material, the red-shift of Raman modes can be attributed to various factors such as [32]:

$$\omega(T) = \omega_0 + \Delta \omega_{ph-ph} + \Delta \omega_{sp-ph} + \Delta \omega_{anharmonic}$$
(7)

where, ω_0 is the Raman shift corresponding to 0 K, $\Delta \omega_{ph-ph}$ is the cell volume contribution, $\Delta \omega_{sp-ph}$ is spin-phonon coupling contribution and $\Delta \omega_{anharmonic}$ signifies the contribution of anharmonic terms in the system. Here, $\Delta \omega_{sp-ph}$ arises because of a modulation of spin exchange integral by a change in the lattice vibrational frequencies, and hence signifies contribution from spinphonon interactions. In the present case, the term $\Delta \omega_{ph-ph}$ represents the isotropic variation in volume and found negligible here. Thus, the observed red-shifts of the Raman modes are mainly contributed by higher-order anharmonicity and spin-phonon coupling in the system.

Balkanski model [33] is valid in absence of any structural phase change and it can quantify the $\Delta \omega_{anharmonic}$ contribution for the phonon behavior with temperature variation. To estimate the contribution due to anharmonic terms in Raman shift, the temperature dependent variations in Raman shift and FWHM are fitted by Balkanski model (eqns. 8 and 9) as shown in Fig.14 (*a*, *b*):

$$\omega(T) = \omega_0 - A \left[1 + \sum \frac{1}{exp\left(\frac{\hbar\omega_l}{k_{\beta}T}\right) - 1} \right]$$
(8)

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$$\Upsilon(T) = \Upsilon(0) + A \left[1 + \sum \frac{1}{exp\left(\frac{\hbar\omega_i}{k_{\beta}T}\right) - 1} \right]$$
(9)

where, ω_0 is the Raman shift at 0 K, $\Upsilon(0)$ is the FWHM at 0 K, parameter *A* is the anharmonic constant which describes the contribution from higher order terms for three phonon processes, and

 $\left[e^{\frac{\hbar\omega}{2k_{\beta}T}}\right]^{-1}$ corresponds to the thermal population factor of Raman modes.



Fig. 5.14 (a): Raman spectra of CFMO-Vac (111) thin film at different temperatures from 90K to 400K.



Fig. 5.14 (b): Raman spectra of CFMO-Vac (100) thin film at different temperatures from 90K to 400K.

The Balkanski model fits in both the temperature regions *i.e.*, above and below Curie temperature as shown in Fig. 5.15. The solid lines represent the Balkanski fit for Raman shift plot (Eqn. 8) and the dashed lines show the fits to FWHM (Eqn. 9) plots. As this model purely defines the contributions from anharmonic phonon vibrations, the deviation of data from the fits at Curie temperature strongly suggests the presence of spin-phonon coupling. At the vicinity of magnetic phase transition, the phonon renormalization takes place which influences the spin-lattice coupling and gives rise to an anomaly in the anharmonicity.



Fig. 5.15: (a, b) Raman shift and FWHM plots as a function of temperature for CFMO-Vac (111) and CFMO-Vac (100) thin films. Red and pink lines show the Balkanski fit to the Raman shift and FWHM plots.

Literature reports suggest that the difference in anharmonic coefficients ($\Delta \omega_0$) calculated by fitting Balkanski model both above and below magnetic transition remains proportional to the spin-phonon coupling strength [34]. The calculated value of $\Delta \omega_0$ comes out to be 79cm⁻¹ and 44 cm⁻¹ ¹ for (100) and (111) oriented CFMO films, respectively as shown in Table-4. This further suggests that CFMO (111) film exhibits stronger spin-phonon coupling. Earlier CFMO system was studied using Raman spectroscopy by D. D. Sarma et al., where they did not observe any spin-phonon interaction in the polycrystalline bulk materials [35]. Hence, it can be contemplated that the observation of spin-phonon coupling in the present case of CFMO films is a substrate induced strain-mediated phenomena. In addition, the temperature at which the deviation from normal anharmonic behaviour starts is different for both the thin films. It appears at 325K and 350K for the CFMO-Vac (100) and CFMO-Vac (111) thin films respectively, corresponding to T_C of the respective films. The estimated value of T_C here matches well with that observed from temperature-dependent magnetization measurements shown earlier. Eventually, the coupled spin and lattice degrees of freedom in these double perovskite CFMO thin films manifests itself in Raman results through above-mentioned deviations.

Table 5.4: Parameters derived from the Balkanski model fitted to

 temperature-dependent Raman spectra of CFMO thin films.

Thin Films	ω before T c	ω after T _C	Δω
	(cm ⁻¹)	(cm ⁻¹)	(cm ⁻¹)
CFMO-Vac (100)	282.42	326.54	44.12
CFMO-Vac (111)	269.59	348.87	79.28

5.4 Conclusions

In summary, a state of significantly improved cation order has been achieved in half-metallic Ca₂FeMoO₆ (CFMO) thin films by precisely choosing the substrate-orientation and deposition condition. XANES spectroscopy suggests that the CFMO films contain both the divalent and the trivalent Fe ions with a dominating presence of Fe^{3+} . In spite of overall dominant present of Fe³⁺ ions in all films, CFMO (111) films show slightly higher concentration of Fe^{2+} ions as compared to that in CFMO (100) films. As anti-site disorder disturbs the alternate Fe-O-Mo arrangement, it results into weakened ferrimagnetic interactions in (100) films. Thus, a reduced saturation magnetization and lower T_C observed for CFMO (100) films indirectly show a higher anti-site disorder in these films. This indirect observation of higher anti-site disorder in CFMO(100) films have also been supported by other measurements, namely, i) a drastic change from insulating to metallic state takes place by changing the growth orientation from (100) to (111), respectively; *ii*) terahertz spectroscopy suggests that (111) oriented CFMO film follows Drude conductivity, however, Drude-Smith model is followed by CFMO-Vac (100) film due to higher degree of cation disorder; iii) well-defined and intense Raman modes are observed for CFMO films grown on LAO (111). The spin-up and spin-down channel contributions to the resistivity have been distinguished by data analysis which is further supported by XANES data too. The Curie temperatures and the parameter indicating spin-phonon coupling strength have been derived for CFMO films using temperature-dependent Raman spectroscopy. The T_C derived using Raman data agrees very well with the magnetization. The spin-phonon coupling occurs in CFMO films in spite of its absence in the bulk counterpart. Spin-phonon coupling is stronger in CFMO (111) films than in CFMO (100) films. As shown in the present study, the substrate orientation plays a key role in modifying the structural, electronic, magnetic, vibrational, and optical properties of this half-metallic double perovskite system.

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Chapter 6

Effects of strain and thickness variation on structure and electronic transport of Ca₂FeMoO₆ Thin Films

Two sets of Ca₂FeMoO₆ (CFMO) double perovskite thin films were deposited on LaAlO₃ (100) and MgO (100) single-crystal substrates using the PLD technique. LAO provides compressive strain to CFMO system, and MgO provides tensile strain. Henceforth, the films deposited on LaAlO3 and MgO will be indicated as CFMO-L and CFMO-M, respectively. For each series, three thin films with varied thicknesses from 10 to 50nm were deposited to study the effects of thickness variation. The CFMO films of 10 and 30 nm thickness show insulating behavior irrespective of the type of strain. For higher thickness (50nm), the CFMO-L film shows a metal-to-insulator phase transition at \sim 220K, but the CFMO-M film remains insulating. Variable Range Hopping (VRH) model has been fitted on the resistivity data of CFMO thin films in the semiconducting region. Two CFMO films with 50 nm thickness, one from each series, were studied for temperature-dependent terahertz (THz) optical conductivity. The THz conductivity of these films fit to Drude-Smith (DS) model, which suggest a presence of disorder in both the films. The plasma frequency and relaxation time extracted from the DS model fittings show an unusual trend in the vicinity of the metal-insulator transition. Raman spectroscopy gives an indication of enhanced cation ordering with increased thickness of CFMO films. The spin-phonon coupling and Curie temperature has also been estimated using temperature-dependent Raman spectroscopy.

The manuscript has been prepared for submission.

6.1 Introduction:

As discussed in earlier chapters, amongst these double perovskites, Sr_2FeMoO_6 exhibits the highest T_C around 450 K [1–3]. Due to the better spintronic capability, most of the research has been carried out on SFMO thin films, and CFMO and BFMO films remain the less explored candidates [4-6]. CFMO exhibits a monoclinic structure with $P_{21/n}$ space group [7]. Here, the FeO₆ and MoO₆ octahedra are arranged in a three-dimensional alternate arrangement. Due to a similarity in the ionic radii of Fe and Mo ions here, there is an ease for these ions to readily exchange their positions which gives rise to anti-site disorder. This is one of the most commonly occurring disorders in double perovskites, and in higher concentrations can deteriorate the half-metallicity and magnetic properties of these double perovskites [6]. The observed value of saturation magnetization of these AFMO materials is always found to be less than the theoretically predicted value, *i.e.*, $4 \mu_B/f.u.$ due to the occurrence of anti-site disorders. These disorders are also known to affect the electronic transport of AFMO thin films, where ordered films exhibit metallic character and highly disordered films are semiconducting in nature [8-10].

Improving B-site ordering in double perovskites has been a longstanding interest of the scientific community. Various research groups have varied deposition temperature, background gas pressure, underneath substrate, the thickness of thin films, *etc.* to improve the cation ordering in these AFMO thin films [11-15]. Previously, an increment in the Curie temperature and saturation magnetization of Sr_2FeMoO_{6+x} thin films has been reported due to increasing film thickness and hence are related to the degree of B-site ordering [16]. Earlier investigations also show that half-metallicity and electronic transport of AFMO films is dependent on the strain relaxation [17]. There are few reports available showing the effect of film thickness on the structure, electrical and magnetic properties of SFMO thin films and there is no consistency and underlying mechanism explained in the published results [16-17].

Keeping the above points into consideration, we have prepared two series of CFMO thin films, one on LaAlO₃ (LAO) single crystal substrate which offers compressive strain, and the other on MgO single crystal substrate which provides tensile strain to the CFMO thin films. Each series consists of 3 thin films having thickness 10nm, 30nm and 50nm. The effects of film thickness on the structural, electrical, vibrational and optical properties of these thin films are discussed here.

6.2 Experimental

The bulk Ca₂FeMoO₆ target was prepared using the standard solidstate synthesis method. Ca_2FeMoO_6 thin films with thicknesses 10, 30, 50 nm were deposited by PLD technique on LAO (100) and MgO (100) single crystal substrates. KrF excimer laser (248 nm wavelength) was employed to ablate the target material with laser pulse repetition rate of 5 Hz and laser energy of 350 mJ. The target to substrate distance was kept 4 cm. All the depositions were carried out in vacuum and the substrate temperature was maintained at 770°C during the deposition. Just after deposition, all films were cooled to room temperature at 10°C/min. XRD measurements were performed using a Bruker D2-Phaser X-ray diffractometer to check the phase purity and structural orientation of the films. To analyze the vibrational modes of the films, Raman spectroscopy measurements were conducted using Horiba LabRam HR Evolution spectrometer with He-Ne LASER of wavelength 632.8 nm. Moreover, to elucidate the thermal behavior of the vibrational modes, temperature dependent Raman measurements were performed, enabling acquisition of Raman spectra across a range of temperatures spanning from 93K to 300K. The electrical transport behavior of the prepared thin films has been studied by carrying out temperaturedependent resistivity measurements using CCR cryostat with four-point probe method in the temperature range of 12K-300K. The Tera K-8 based on photoconductive (LT-GaAs) antenna was used to conduct terahertz time

domain spectroscopy (THz-TDS) measurements in the energy range of 0.8-6 meV and at the temperature ranging from 5-300K.

6.3 Results and discussion:

6.3.1 X-Ray diffraction:

The phase purity and growth orientation of the prepared thin films have been examined using XRD measurements. Fig. 6.1 shows the XRD patterns of CFMO thin films grown on LAO substrate. It is clear from the figure that all the CFMO-L films are phase-pure, crystalline in nature and are highly oriented towards the underlying substrate. No impurity is observed in the whole thickness range of the films from 10-50 nm. The pseudocubic lattice parameter of bulk CFMO is 3.86 Å, and that of LAO is 3.79 Å, which causes a compressive strain of -1.84% on the CFMO films. This is evident from the XRD patterns where CFMO film peaks lie towards lower 20 side as compared to that of LAO XRD peaks.



Fig. 6.1 Full scale XRD patterns of CFMO films grown of different thicknesses grown on LAO (100) substrate.

Fig. 6.2 shows the XRD patterns of CFMO films grown on MgO substrate. All the CFMO-M films are grown phase-pure and are highly oriented. MgO is a cubic substrate having lattice parameter 4.2 Å, providing a tensile strain of +8.09% to CFMO thin films as confirmed by XRD patterns.



Fig. 6.2 Full scale XRD patterns of CFMO films grown of different thicknesses grown on MgO (100) substrate.

Table 6.1 shows the out-of-plane lattice parameters and FWHM of all the CFMO thin films under investigation. There is a systematic shift in the XRD peaks of compressive strained CFMO thin films with thickness variation. The out-of-plane lattice parameters decrease with increase in thickness which suggests that 10nm CFMO film is maximally strained, and strain relaxation occurs with increase in thickness. In contrast to this, tensile strained CFMO films don't show significant variation in lattice parameter with thickness. Similar results had also been observed for thickness dependent SFMO films grown on MgO [18]. This suggests that epitaxial strain is not relaxed upto 50nm in case of MgO substrate. These distinct effects of film thickness on strain relaxation could be attributed to the different growth mechanisms.

Thickness	Compressive strained films		Tensile strained films	
	Out-of-plane FWHM(°)		Out-of-plane	FWHM(°)
	parameter (Å)		parameter (Å)	I.
10nm	3.96	0.38	4.08	0.58
30nm	3.94	0.36	4.09	0.46
50nm	3.92	0.32	4.08	0.37

Table-6.1: *Out-of-plane lattice parameters and FWHM of CFMO thin films of different thickness.*

6.3.2 Morphological properties:

The surface morphology of the CFMO thin films has been investigated by Atomic Force Microscopy (AFM) measurements. Fig. 6.3 (ad) shows the 3D AFM images of CFMO-L and CFMO-M films with 10 and 50nm thickness. It can be seen that similar growth morphology is observed for all the CFMO films. The particle size of films varies from 60-85 nm.



Fig. 6.3 AFM images of CFMO-L and CFMO-M films of thickness 10 and 50nm.

6.3.3 Electrical properties:

Fig. 6.4 shows the resistivity versus temperature plots for CFMO thin films grown on LAO substrate. CFMO-L films (10 nm and 30 nm) show insulating behavior, where 30 nm films show a decrease in the resistivity by one order of magnitude. On increasing the thickness to 50 nm, the CFMO-L film shows majority of insulating state with a metallicity arising above 200K. In addition to this, the overall resistivity of CFMO-L films decreases with increase in thickness.



Fig. 6.4: Resistivity versus temperature plots of CFMO-L filmsof different thickness.

On the other hand, Fig. 6.5 shows the temperature-dependent resistivity plots of CFMO films grown on MgO. All the CFMO-M films exhibit semiconducting behavior below room temperature. It can be noted that the overall resistivity of the decreases with increase in thickness which is very similar to the compressive strained films.



Fig. 6.5: Resistivity vs temperature plots of CFMO-M films of different thickness.

As reported earlier, an increase in thickness reduces the amount of anti-site disorder till the value of initial 200nm of thickness of AFMO films [16]. They observed an increment in saturation magnetization with increase in thickness of SFMO films [16]. This was explained by a combined effect of strain and inhomogeneity which abrupt the Fe-Mo arrangement in the thinner films. In the present case, the decrease in the overall resistivity of films with increasing thickness could be attributed to improved Fe-Mo ordering in thicker *i.e.*, 50 nm CFMO films, irrespective of the type of strain. Thus, Fe-Mo order gets affected by strain in films at lower thickness range.

Earlier theoretical studies demonstrate that CFMO is a half-metallic system which contains band-gap in the minority spin-band and density of states in the majority band [16]. However, this half-metallicty is lost with the higher amount of anti-site disorder, giving rise to semiconducting state [19]. In the case of CFMO-L films, the increment of Fe-Mo order with increase in thickness is such that it gives rise to metallic state above 200K by activating the spin-down metallic channel. The CFMO-L film with 50nm thickness approaches bulk-like metallic conductivity behaviour. However, for CFMO-M films, the semiconducting behaviour is preserved upto 50nm thickness. This suggest that the nature of epitaxial strain influences the electrical conduction of CFMO thin films in a very dramatic way, and the effect of tensile strain is more dominant as compared to that of the compressive strain.

To get more insight into the semiconducting behavior of CFMO films, temperature-dependent resistivity data has been fitted with Variable-range hopping (VRH) model in the temperature range 10K-100K as described below [20]:

$$\rho(T) = \rho_0 \exp\left(\frac{T_0}{T}\right)^{\frac{1}{4}}$$
(7)

where ρ_0 is the pre-exponential factor and T_0 stands for characteristic Mott temperature.



Fig. 6.6: VRH model fitted to the temperature-dependent resistivity data of CFMO-L films.

This model applies at lower temperature where conduction takes place only by hopping of charge carriers and the activation energy of charge carriers is not enough to cross the band-gap. The value of characteristic Mott temperature T_0 can be calculated by doing a linear fit on $ln(\rho)$ versus $1/(T)^{1/4}$ plot as shown in Fig. 6.6 and Fig. 6.7.



Fig. 6.7: VRH model fitted to the temperature-dependent resistivity data for all the CFMO thin films grown on MgO.

Table-6.2: Parameters obtained from VRH model fitted on the resistivityplots of CFMO thin films of different thickness.

Thickness	Compressive strained films		Tensile strained films		
	Slope T ₀ (10 ⁴ K)		Slope	$T_0 (10^4 K)$	
10nm	12.1	2.14	13.5	3.32	
30nm	11.25	1.60	12.4	2.36	
50nm	10.7	1.31	11.7	1.87	

The calculated value of T_0 has been presented in Table 6.2 and it matches well with the earlier reported literature [6]. For both the series, the value of T_0 decreases with rise in thickness, indicating reduced anti-site disorder. Also, the characteristic Mott temperature of tensile strained films is higher than that of compressively strained films. This could be attributed to the higher anti-site disorder in CFMO-M films.

6.3.4 Terahertz spectroscopy:

Terahertz optical conductivity measurements have been performed to understand the effect of epitaxial strain on the frequency dependent optical properties of CFMO thin films. Fig. 6.8 & 6.9 (*a*, *b*) shows the real (σ_1) and imaginary conductivities (σ_2) of CFMO-L and CFMO-M films with 50 nm thickness. It can be seen from the figures that for both the CFMO films, the real (σ_1) conductivity values are positive; the imaginary (σ_2) part exhibits negative values throughout the temperature and frequency regimes. These features are defined by Drude-Smith model of complex optical conductivity which takes into account a finite amount of disorders causing back-scattering of charge carriers [21]. In the present study, the anti-site disorder causes inhomogeneity in Fe and Mo sites in CFMO system and hence Drude-Smith model is followed. The Drude-Smith model for complex conductivity can be expressed as [21]:

$$\sigma^*(\omega) = \frac{\varepsilon_0 \omega_p^2}{\Gamma - i\omega} \left(1 + \frac{cT}{\Gamma - i\omega} \right) - i\varepsilon_0 \omega(\varepsilon_\infty - 1)$$
(8)

where ε_0 , ε_{∞} , ω_p , and Γ are the permittivity of vacuum, permittivity at higher frequencies, plasma frequency, and the scattering rate of charge carriers, respectively. Also, *c* is the fraction of carrier's initial velocity retained after collisions [21]. Generally, *c* ranges from -1 to 0, and more negative value of *c* suggests more backscattering of charge carriers indicating more disorder.



Fig. 6.8: (*a*) *Real and* (*b*) *Imaginary part of complex conductivity spectra of CFMO-L 50nm thin film.*



Fig. 6.9: (a) Real and (b) Imaginary part of complex conductivity spectra of CFMO-M 50nm thin film

The THz conductivity data of both the CFMO films are fitted simultaneously with the Drude-Smith model as shown in Fig. 6.10. The values of ω_p and Γ are extracted from the Drude-Smith model fitting and are presented in Fig. 6.11.



Fig. 6.10: THz conductivity data of (a)CFMO-L and (b) CFMO-M films fitted with Drude-Smith model.



Fig. 6.11: Temperature-dependent optical parameters derived from the Drude-Smith model fitted to the Terahertz conductivity of CFMO thin films.

It can be seen from the figure that for the CFMO-M film, both the plasma frequency and scattering rate decrease with temperature. These variations are due to the significant backscattering of charge carriers which dominatingly takes place in insulating state. The persistence of insulating state throughout the temperature range in this CFMO film is also corroborated with the *dc* resistivity results. In addition to this, the value of disorder parameter *c* remains -0.65 ± 0.05 in the entire temperature range which represents static anti-site disorder in the system. However, for CFMO-L film, the plasma frequency initially decreases, shows a dip at 180 K and then increases upto room temperature. This rise of plasma frequency with temperature gives a signature of strong correlation in the metallic phase. The relaxation time scales with temperature in the insulating phase, and then varies inversely providing a signature of metal-to-insulator phase transition at ~180K. This transition is also consistent with the *dc* resistivity results.

6.3.5 Vibrational properties:

In the present case, Raman spectroscopy has been used to study the effect of tensile and compressive strain on the vibrational properties of CFMO films.



Fig.6.12: Raman spectra of CFMO-L films grown with different thickness.

Fig. 6.12 shows the Raman spectra of CFMO-L films of thickness 10, 30 and 50nm. As discussed earlier, CFMO exists in monoclinic structure which shows 24 ($12A_g$ + $12B_g$) Raman active modes [5]. In the present case, only 4 Raman modes at ~ 262.14, 306.66, 418.53, and 457.85 cm⁻¹ are observed may be due to *c*-axis orientation of films or mixing of some of the modes. These modes are de-convoluted with multiple peak fitting model, and the peak position and FWHM is presented in Table 6.3.

Table 6.3: Raman peak position and FWHM extracted from the double-peakfit to the Raman spectra of CFMO-L films.

Thickness	Peak position (cm ⁻¹)	FWHM (cm ⁻¹)	Peak position (cm ⁻¹)	FWHM (cm ⁻¹)
10nm	262.14	42.50	306.66	89.45
30nm	260.81	33.71	304.26	78.54
50nm	258.22	35.23	302.51	56.58



Fig.6.13: Raman spectra of CFMO films grown on MgO substrate with different thickness.

Fig. 6.13 shows the Raman spectra of CFMO films grown on MgO. Since MgO shows a broad Raman spectrum with huge background contribution, proper baseline subtraction has been carried out for all the CFMO films. The corresponding peak-position and FWHM are presented in Table-6.4.

Thickness	Peak position (cm ⁻¹)	FWHM (cm ⁻¹)	Peak position (cm ⁻¹)	FWHM (cm ⁻¹)	Intensity ratio
10nm	260.21	29.11	316.94	53.65	1.66
30nm	260.62	25.94	316.52	49.69	2.29
50nm	260.42	23.68	316.16	44.52	2.53

Table 6.4: Raman peak position and FWHM extracted from the double-peakfit to the Raman spectra of CFMO-M films.

Table-6.3 shows that for CFMO-L films, a red-shift in the Raman modes is observed with increase in thickness which could be attributed to the epitaxial strain release in the system. In addition to this, sharper Raman modes with decreased FWHM are observed with increased in thickness of CFMO films for the series. The appearance of sharp and intense Raman modes indicates cation ordering in double perovskites [22]. The present data suggests that Fe-Mo ordering improves with increase in film thickness, irrespective of the type of strain. These Raman results regarding improved cation ordering are consistent with resistivity results. Table-6.4 also shows that Raman peak position of CFMO-M films doesn't change much with variation in thickness.

The thermal evolution of Raman modes has been studied by carrying out temperature-dependent Raman spectroscopy. Fig. 6.14 and 6.15 shows the temperature-dependent Raman spectra of 50 nm CFMO-L and CFMO-M films, respectively. A red-shift in Raman modes and blue-shift in Raman FWHM is observed with increase in temperature. This could be attributed to
the interatomic bond lengthening and increase in phonon population with rise in temperature.



Fig.6.14: Temperature-dependent Raman spectra of CFMO-L film.

In the case of a magnetic material, the red-shift of Raman modes can be attributed to various factors, including [23]:

$$\omega(T) = \omega_0 + \Delta \omega_{\text{ph-ph}} + \Delta \omega_{\text{sp-ph}} + \Delta \omega_{\text{anharmonic}}$$

Here, ω_0 represents the Raman shift at 0 K, $\Delta \omega_{ph-ph}$ denotes the contribution from changes in cell volume, $\Delta \omega_{sp-ph}$ accounts for the influence of spinphonon coupling, and $\Delta \omega_{anharmonic}$ represents the contribution from anharmonic terms in the system. The term $\Delta \omega_{sp-ph}$ arises due to the modulation of the spin exchange integral caused by variations in lattice vibrational frequencies, indicating the contribution of spin-phonon interactions. Here, $\Delta \omega_{ph-ph}$ represents the isotropic volume variation, which is considered





Fig.6.15: Temperature-dependent Raman spectra of CFMO-M film.

In order to quantify the anharmonic term contribution to the system, the Raman shift versus temperature plot has been fitted with Balkanski model explained as [24]:

$$\omega(T) = \omega_0 - A \left[1 + \sum \frac{1}{exp\left(\frac{\hbar\omega_i}{k_{\beta}T}\right) - 1} \right]$$

where, ω_0 is the Raman shift at 0 K, $\Upsilon(0)$ is the FWHM at 0 K, parameter *A* is the anharmonic constant which describes the contribution from higher order terms for three phonon processes, and $\left[e^{\frac{\hbar\omega}{2^{2}\beta^{T}}}\right]^{-1}$ corresponds to the thermal population factor of Raman modes.



Fig.6.16: Balkanski fit to the Raman shift versus temperature plot for CFMO-L fit.



Fig.6.17: Balkanski fit to the Raman shift versus temperature plot for CFMO-M film.

Fig. 6.16 and 6.17 shows the Balkanski model fits to the Raman shift versus temperature plots of CFMO-L and CFMO-M films, respectively. As this model purely defines the contributions from anharmonic phonon vibrations, the deviation of data from the fits at Curie temperature strongly suggests the presence of spin-phonon coupling. At the vicinity of magnetic phase transition, the phonon renormalization takes place which influences the spin-lattice coupling and gives rise to an anomaly in the anharmonicity. The T_C of the films has been estimated as the temperature at which the anomaly in

the normal anharmonic behavior starts to appear. The present data suggests that the T_C of CFMO-L film is ~340K, while T_C is ~300K for CFMO-M film.

6.4 Conclusion:

In summary, two series of CFMO thin films of different thicknesses (10, 30 and 50 nm) have been prepared on LAO and MgO single crystal substrates to investigate the effects of compressive and tensile strain, respectively. Regardless of the type of strain, the overall resistivity of CFMO films decreases with increase in thickness due to improved cation ordering. The CFMO films with lower thickness show insulating behavior. At higher thickness (50nm), the CFMO-L film shows metal-to-insulator phase transition around 220K. However, the CFMO-M film continues to show insulating behavior even at 50 nm of higher thickness, although overall resistivity decreases throughout the temperature range of the study. THz results show that Drude-Smith model of complex conductivity is followed for both the series of CFMO films, depicting the presence of anti-site disorder. The dc transition in CFMO films are also detected by THz ac conductivity measurements. Raman results give an indication of improved cation ordering in thicker CFMO films. The spin-phonon coupling and Curie temperature of CFMO films has been detected and estimated using temperature-dependent Raman spectroscopy.

6.5 References

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Chapter 7

Conclusions and future outlook

The thesis is summarized as follows:

Chapter 1 provides a general introduction to the perovskite-type oxides and their applications. Here, rare earth nickelates $RNiO_3$ (R= La-Lu) and A₂FeMoO₆ (A= Sr and Ca) double perovskites are investigated for structure-property correlations and doping and strain-induced modifications in the properties. The basic theories behind the charge transfer nature in $RNiO_3$ and half-metallic transport in A₂FeMoO₆ materials are also discussed in detail.

Chapter 2 encompasses the basic overview of the synthesis methods and characterization techniques used for the present thesis. The synthesis methods involve bulk target preparation using the solid-state reaction method, followed by thin film synthesis using the Pulsed Laser Deposition (PLD) technique. The thin films are characterized using X-Ray Diffraction (XRD) and Reciprocal Space Mapping (RSM) for phase purity and strain coherency, thickness estimation using X-Ray Reflectivity (XRR), surface morphology using Atomic Force Microscopy (AFM), oxidation states of elements using X-Ray Absorption Near Edge Spectroscopy (XANES) and X-Ray Photoelectron Spectroscopy (XPS), and vibrational properties using Raman spectroscopy. The transport properties have been investigated by temperaturedependent resistivity. The magnetization measurements are performed using SQUID magnetometer. The optical conductivity measurements are performed at terahertz frequency using Terahertz time-domain spectroscopy (THz-TDS).

Chapter 3 describes the effects of Cu-doping and thickness variation on the structural and electrical transport properties of PrNiO₃ thin films. For this purpose, two series of PrNiO₃ thin films have been synthesized on LaAlO₃ (100) (LAO) single-crystal substrates using the PLD technique. The first series contains five epitaxial $PrNi_{1-x}Cu_xO_3$ (*x*=0-0.1) thin films of thickness 12nm deposited on LAO substrate. Here, the effect of carrier injection via Cu-doping at Ni-site has been studied. In the second series, a study consisting of four $PrNi_{0.95}Cu_{0.05}O_3$ thin films with thickness varying from 5 to 25nm has been presented. This study demonstrates the tuning of epitaxial compressive strain on thin films by varying film thickness. The present study indicates that both *i.e.*, Cu-doping and thickness variation significantly influence the physical properties of the PrNiO₃ system.

Chapter 4 presents the effects of different background conditions on the phase purity, cation ordering, and physical properties of Sr₂FeMoO₆ (SFMO) thin films. The films were deposited in different deposition conditions (vacuum, nitrogen and oxygen pressures). Magnetization measurements show that the SFMO film grown in vacuum has the highest saturation magnetization and Curie temperature amongst the series, indicating higher cation ordering. A systematic reduction of M_S and T_C values with an increment in anti-site disorder has been observed. Raman spectra show a Fano feature, indicating electron-phonon coupling in the SFMO films. The electron-phonon coupling is maximum for vacuum-grown film and gets systematically decreased with increasing anti-site disorder. Temperaturedependent Raman spectra show an anomaly in the normal anharmonic behavior of phonon modes near T_C due to phonon renormalization. This feature indicates spin-phonon coupling in SFMO films, which was absent in the bulk counterpart. The spin-phonon coupling strengthens with increase in the Fe-Mo ordering in SFMO films. There is a systematic increase in the overall resistivity of the films with an increase in the anti-site disorder. The present presents a key role of anti-site disorder in tuning all the physical properties of SFMO films. The SFMO film grown in vacuum exhibits the highest level of B-site ordering.

Chapter 5 describes the effect of substrate orientation on the anti-site disorder of half-metallic double perovskite Ca_2FeMoO_6 (CFMO) thin films.

For this purpose, epitaxial thin films were prepared on (100) and (111) oriented LaAlO₃ substrates in vacuum and nitrogen atmospheres. A resultantly enhanced cation-order in (111) films induces dramatic transformations in its properties as follows: *i*) a metallic behaviour down to a temperature of ~75 K compared to that down to 200 K for (100) film, *ii*) a large increase in the Curie temperatures *iii*) an enhanced spin-phonon coupling, and iv) a significantly enhanced ferromagnetic exchange interactions and saturation magnetization. The complex THz optical conductivity spectra evaluated in the framework of Drude and Drude-Smith phenomenological models and the temperature-dependent Raman data fitted to the Balkanski model too corroborate well to indicate an enhanced cation-order in (111) films. This study establishes a dominant role of crystallographic orientation in much desired control of cation-order.

Chapter 6 shows the effect of strain and thickness variation on the properties of CFMO thin films. Two series of different thicknesses (10, 30 and 50 nm) have been prepared on LAO and MgO single-crystal substrates to investigate the effects of compressive and tensile strain, respectively. Regardless of the type of strain, the overall resistivity of CFMO films decreases with increase in thickness due to improved cation ordering. The CFMO films with lower thickness show insulating behavior. As the thickness increases, the overall resistivity decreases irrespective of the type of strain. At higher thickness (50nm), the CFMO-L film shows metal-to-insulator phase transition around 220K. However, the CFMO-M film continues to show insulating behavior even at 50 nm of higher thickness, although overall resistivity decreases throughout the temperature range of the study. THz results show that Drude-Smith model of complex conductivity is followed for both the series of CFMO films, depicting the presence of anti-site disorder. Raman results give an indication of improved cation ordering in thicker CFMO films. The spin-phonon coupling and Curie temperature of CFMO films has been detected and estimated using temperature-dependent Raman spectroscopy.

Future outlook:

The future outlook of the present work can be given as:

- 1. To explore the orientation-dependent half-metallicity in AFMO double perovskite thin films.
- 2. To further explore the effect of epitaxial strain on the properties of AFMO double perovskites at higher thickness range.
- 3. To further reduce the anti-site disorder in AFMO double perovskites by using different substrates.