The effects of thickness variation on the physical properties of Al-doped NdNiO₃ thin films

M.Sc. Thesis

By VISHAL



DEPARTMENT OF PHYSICS INDIAN INSTITUTE OF TECHNOLOGY INDORE MAY 2024

The effects of thickness variation on the physical properties of Al-doped NdNiO₃ thin films

A THESIS

Submitted in partial fulfilment of the requirements for the award of the degree of Master of Science

> by VISHAL



DEPARTMENT OF PHYSICS INDIAN INSTITUTE OF TECHNOLOGY INDORE MAY 2024



INDIAN INSTITUTE OF TECHNOLOGY INDORE

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **The effects of thickness variation on the physical properties of Al-doped NdNiO₃ thin films** in the partial fulfillment of the requirements for the award of the degree of **MASTER OF SCIENCE** 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 2022 to May 2024 under the supervision of Professor Krushna R. Mavani.

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.

105124

Signature of the student with date VISHAL

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

16.05.2024 Signature of the Supervisor of M.Sc. thesis (with date) **Professor Krushna R. Mavani**

Vishal has successfully given his M.Sc. Oral Examination held on 16th May 2024.

Signature of Supervisor of MSc thesis

Date: 16.05.2024

Convener, DPGC

Date:

Dedicated to my Parents, Mrs. Indra and Mr. Rajesh Kumar

ACKNOWLEDGEMENTS

I wholeheartedly acknowledge that the completion of my thesis work was a collective effort involving the support and guidance of numerous individuals, without whom this endeavor would not have been possible. It is with immense gratitude that I express my appreciation to each one of them. First and foremost, I extend my deepest gratitude to Prof. Krushna R. Mavani, Department of Physics at the Indian Institute of Technology Indore, for graciously welcoming me into her Thin Film Laboratory. Her unwavering support, invaluable suggestions, and guidance were the cornerstone of my project journey. Prof. Mavani's profound knowledge and logical approach were a constant source of inspiration, propelling me forward and keeping me focused on the path to completing my M.Sc. project thesis. I sincerely appreciate my dedicated lab partners, whose unwavering support for my efforts. I sincerely thank Mr. Ketan Shivaji Navale for his invaluable assistance in sample preparation, characterization, data analysis, and plotting. I am also indebted to Mr. Manish Kumar and Girijha Shankar Tripathy for their support and encouragement throughout this endeavor. Their presence and encouragement provided much-needed motivation during challenging times. Furthermore, I extend my gratitude to the entire faculty and staff of the Discipline of Physics, IIT Indore, for their constant support and assistance. Their collective efforts created a nurturing environment conducive to academic and personal growth. I thank my friends Naveen Sharma, Shivansh Raj Pandey, and Kashish Arora for their unwavering encouragement and support. Your friendship has been a source of strength and inspiration throughout this journey. Thank you for always being there for me.

TABLE OF CONTENTS

Chapter 1: Introduction

- 1.1 Introduction to Complex Oxides
- 1.2 Rare Earth Nickelates
- 1.3 Thin Film Deposition
- 1.4 Electrical Transport
- 1.5 Metal-to-Insulator Transition
- 1.6 Conduction Mechanism
- 1.7 Motivation

Chapter 2: Experimental Techniques

- 2.1. Sample Preparation
 - a) Bulk synthesis using a solid-state reaction method.
 - b) Thin Film synthesis using the PLD method.
- 2.2. Characterization Techniques
 - a) X-ray Diffraction (XRD) techniques
 - b) Raman Spectroscopy
 - c) Temperature-dependent resistivity measurement

Chapter 3: Result and Discussion

- 3.1. X-ray diffraction
- 3.2. Temperature-dependent resistivity measurement
- 3.3. Raman Spectroscopy
- 3.4. Conclusion

LIST OF FIGURES

Figure 1.1. Crystal structure of perovskite material 1
Figure 1. 2. (a) Crystal field splitting and Jahn-Teller distortion for Mn3+ in an octahedral structure. (b) z-out and z-in distortion of BO ₆ octahedra
Figure 1.3. Phase Diagram of Rare Earth nickelates
Figure 1.4. Schematic of potential well for free electrons with infinite potential at surface and zero otherwise
Figure 1. 5. Schematic of allowed and forbidden energy band with a band gap ΔE [11]
Figure 1.6. Schematic of bands in metal, semiconductor, and insulator9
Figure 1.7. Schematic of energy vs density of states for a metal having a half- filled d band caused by weak electron-electron correlation and splitting of the d band into LHB and UHB for an insulator due to a strong correlation
Figure 2.1. Schematic diagram of the pulsed laser deposition (PLD) system [2].
Figure 2.3. Schematic diagram illustrating three fundamental growth model: (a)Frank-van der Merwe growth model (b) Frank-van der Merwe growth model (c)Stranski-Krastanov mode.27
Figure 2.4. X-ray diffraction through Bragg's reflection in the atomic plane 31
Figure 2.5. Schematic of X-Ray diffraction. 32
Figure 2.6. Thin film showing compressive strain on the substrate
Figure 2.7. Thin film showing tensile strain on the substrate

Figure 2.8. Schematic of energy level diagram showing various types emissions.	of . 36
Figure 2.9. Schematic of Four Probe method	. 38
Figure 2.10. The setup for temperature-dependent resistivity measurement in	the
thin film laboratory at IIT Indore	. 39

Figure 3.1. Full-scale XRD Patterns of 10,20, and 30 nm NdNi _{0.95} Al _{0.05} O ₃ thir
films on LAO (001) substrate 41
Figure 3.2. Resistivity vs Temperature behavior of 10,20 and 30 nm
NdNi _{0.95} Al _{0.05} O ₃ thin films on LaAlO3 (LAO) (001) substrate43
Figure 3.3. Fitting of Resistivity data of NdNi0.95Al0.05O3 (a) 10 nm, (b) 20nm
and (c) 30 nm thin films grown on LAO (001) Substrate 44

ABSTRACT

NdNiO₃ is the prototype of RNiO₃ (R=Rare earth ion) type strongly correlated systems which show metal-to-insulator transitions (MITs), mainly because of structural change. The RNiO₃ class of materials demonstrates a fascinating phase diagram where NdNiO₃ and PrNiO₃ show simultaneous magnetic and electronic transitions along with a structural transformation, unlike other RNiO₃ materials. At low temperatures below MIT, these materials show insulating behaviour due to a charge disproportion. The charge disproportion arises due to the conversion of Ni³⁺ to Ni²⁺ and Ni⁴⁺. An isovalent doping by Al³⁺ doping at the Ni³⁺ site should hinder this conversion and affect the electronic states. With this idea in mind, we previously studied Al-doped NdNiO₃ thin films and found that a small level of doping, like 5%, is enough to show a reasonable effect. Based on our earlier studies, we chose to synthesize 5% Al-doped NdNiO₃ thin films on LAO (001) single crystal substrate of varying thickness (10, 20, and 30 nm) using pulsed laser deposition (PLD) to understand the effects of thickness variation in the combination of Al-doping. We studied the films using X-ray diffraction (XRD) for phase formation, temperature-dependent Raman spectroscopy for structural modifications, and temperature-dependent resistivity for electronic behaviour. We present our results here in this thesis with detailed discussions.

Chapter 1 Introduction

1.1. Introduction to Perovskite oxides:

Perovskites exhibit phase-diagrams enriched with physics showcasing unique and promising functionalities in various transport and physical properties. The first perovskite oxide, known as CaTiO₃, was found in the Ural Mountains of Russia by Gustav Rose in 1839 [1]. It was named after a Russian mineralogist Lev Perovski, characterized by the chemical formula ABO₃, where A and B are cations and O is an oxygen anion. Cation A is occupied by larger ions, such as alkali, alkaline, or rare earth metals, while smaller ions, usually transition metals, fill cation B. Ideally, perovskite structures are cubic. (as shown in Fig. 1.1) [2]. B atoms occupy the corners of a simple cubic structure, bonding with six oxygen atoms and forming octahedra in the unit cell of an ideal perovskite structure. At the same time, A cations are in the cavity of BO₆ octahedra. In summary, BO₆ octahedra are situated at the corners of the simple cubic lattice, with the A atom at the center of the unit cell.



Figure 1.1. Crystal structure of perovskite material

The stability of the structure of perovskite oxide is given by the Goldschmidt tolerance factor *t*, which is defined as [3] :

$$t = \frac{R_A + R_0}{\sqrt{2}(R_B + R_0)}$$
(1.1)

Where R_A , R_B , and R_O are the radii of A, B, and oxygen ions, respectively. The tolerance factor value is unity for the simple cubic structure, i.e., the ideal structure of the perovskite oxides. In this situation, there is no structural distortion.

Mathematically, this condition can be expressed as:

$$a = \sqrt{2}(R_A + R_0) = 2(R_B + R_0) \tag{1.2}$$

where a is the lattice parameter and R_A, R_B, and R_O denote the radii of the A, B, and O ions, respectively. Generally, the tolerance factor (t) value is between 0.75 < t < 1 for a stable perovskite oxide structure. For the values of the tolerance factor from 0.7 to 0.9, the rhombohedral and orthorhombic structure of the perovskite oxides are stable. As the distortion increases, the angle between the B-O-B bonds decreases, leading to a more significant tilt [4]. In transition metal oxides, besides orthorhombic distortion, there can be another structural distortion known as the Jahn-Teller Effect [5]. This effect depends on the metal ion's electronic configuration. When an electron has the availability of more than one degenerate energy state (states with the same energy), the energy of the structure becomes higher. The structure undergoes a distortion to reduce its energy, making it less symmetrical and leading to a lower energy state. For instance, in the octahedral structure, there are five degenerate energy states in d orbitals which split into three t_{2g} (lower energy) and two e_g (higher energy) states because of crystal field splitting (Figure 1.2a) [6]. Transition metal ions with d¹, d², d⁴, d⁶, d^7 (high spin), and d^9 electronic configurations have more than one energy state available for the last electron. This can increase the energy of the structure. To ensure the lower energy of the structure BO₆ octahedra go under compression or elongation so that the energy of a few orbital states becomes lower than other states. This elongation or compression along the Z-axis (Figure 1.2b) [6] is known as z-out and z-in distortion, respectively. The B-O-B bond lengths and angles govern the electronic and magnetic properties of ABO₃ perovskite oxides.

Thus, the Jahn-Teller distortion plays a vital role in studying the properties of these oxides. Rare Earth manganates (RMnO₃) compounds with Mn³⁺ $(t_{2g}^3 e_g^1)$ are notable examples of Jahn-Teller distortion [5]. This unique structural versatility enables their use in various advanced applications, such as photovoltaics for solar energy conversion, light-emitting diodes (LEDs), laser materials, fuel cells, and catalysts for chemical reactions. Additionally, they are pivotal in developing high-performance sensors, capacitors, and memory devices, underscoring their significance in both the renewable energy and electronics industries [7].



Figure 1. 2. (a) Crystal field splitting and Jahn-Teller distortion for Mn3+ in an octahedral structure. (b) z-out and z-in distortion of BO₆ octahedra.

1.2. Rare earth nickelates:

The general formula for rare earth nickelates is RNiO₃. Nickelates go under a very sharp first-order Metal to Insulator transition (MIT) which makes them functional materials for making electronic switches, electronic switches, thermal and chemical sensors, etc. The physical and structural properties of these compounds are illustrated in the phase diagram [7] (Figure 1.3):



Figure 1.3. Phase Diagram of Rare Earth nickelates.

The phase diagram above indicates that except for LaNiO₃, all other rare earth nickelates show a sharp first-order metal-to-insulator phase transition with decreasing temperature. The transition temperature (T_{MI}) decreases with increasing as the size of the R ion increases. Similarly, MIT can be correlated to Goldschmidt tolerance factor *t*; as the size of the R ion decreases, the tolerance factor tends to decrease, causing the minimization of the overlap between the Ni-3d and O-2p orbitals. Due to this, the Ni-O-Ni bond angle is also taken as the control parameter. At high temperatures, RNiO₃ compounds are metallic and paramagnetic in orthorhombic structure with the Pbmn space group except for LaNiO₃, which has a rhombohedral structure with the R3c space group. PrNiO₃ and NdNiO₃ have gathered a lot of attention because they have metal-to-insulator, and magnetic transition (Antiferromagnetic to Paramagnetic) is first order, and for all other nickelates, it is second order transition. The synthesis of RNiO₃ compounds is complicated. Synthesis becomes more difficult with a decrease in

R ion size as it requires high pressure to stabilize the Ni^{3+} ion. The study of RNiO₃ at lower pressure is only possible by using thin film deposition.

1.3. Thin Film Formation:

A thin film is a layer of material ranging from a few nanometres to hundreds of nanometres. The material onto which thin films are deposited is known as substrate.

The substrate plays an important role in defining the physical properties of thin films. Thin films are widely used in industries to fabricate optoelectronic devices, memory storage devices, solar cells, electrodes, and so on. Deposition of thin film techniques can be broadly characterized into two categories – Physical vapor deposition and chemical vapor deposition [8]. These deposition techniques majorly depend on the nucleation followed by different development stages. Nucleation is the initial stage of thin film formation it involves the formation of clusters of atoms or molecules on the substrate surface. The development stages of development of thin films can be characterized by:

- 1. Island growth (Volmer-Weber)
- 2. Layer-by-layer growth (Frank-van der Merwe)
- 3. Mixed growth (Stranski-Krastanov)

There are various deposition techniques available for creating thin film. Some of these techniques are :

- 1. Thermal Evaporation
- 2. Magnetron Sputtering
- 3. Electron Beam Evaporation
- 4. Pulsed Laser Deposition
- 5. Molecular beam epitaxy

Among these techniques, we have opted Pulsed Laser technique for thin film synthesis.

1.4. Electrical Transport:

The electrical transport of a material refers to the amount of current that flows through it when a given voltage is applied. Based on electrical transport, materials can be divided into two types, conductors, and insulators. Typically, the electrical conductivity (σ) of conductors lies in the range 10⁷ to 10⁹ Ω^{-1} cm⁻¹, and for insulators, it lies in the range of 10⁻¹⁰ to 10⁻¹⁴ Ω^{-1} cm⁻¹. RNiO₃ exhibits both an insulating and conducting nature depending on the temperature range. We use the rate of change of resistivity concerning temperature (dp/dT) to find the transition from metal to insulator. In the conducting state (dp/dT) > 0 whereas in the insulating state (dp/dT) < 0. To explain why few materials act as conductors and others as insulators. Various theories were introduced to explain the conductivity of RNiO₃ which are given below [9]:

A. Free electron model

Paul Drude proposed the "Free electron model" in 1927. The free electron model was the first attempt to understand the behavior of electrons in a material, especially metals. In this model, conduction electrons inside the solid were treated like gas particles that do not interact with each other. The only potential (Figure 1.4) experienced by electrons is on the surface of the metal. The basic assumptions of the models are [10]:

- i. Conduction electrons have no mutual interaction.
- ii. The conduction electron moves in a constant potential field.
- iii. All positive ions are immobile due to their large mass.
- iv. There is no effect of the positive potential of ions on the lattice.

The electrical conductivity of a metal in the presence of an electric field is given by:

$$\sigma = \frac{ne^2\tau}{m} \tag{1.3}$$

Where *n* is the free electron density, τ is relaxation time, the average time between two consecutive collisions, e is the charge of the electron, and m is the mass of the electron.



Figure 1.4. Schematic of potential well for free electrons with infinite potential at surface and zero otherwise.

The Drude model successfully explained phenomena like electrical and thermal conductivity, ohm's law, magnetoresistance, and the Hall effect. However, it failed to explain the positive value of the hall coefficient for some metals and low conductivity in certain metals with a high number of carriers. This model can not explain the heat capacity and temperature-dependent resistivity, and the model was unable to distinguish the difference between metal, insulator, and semiconductor.

To overcome these limitations, Arnold Sommerfeld made important changes to the Drude model in 1927, leading to the development of the Drude-Sommerfeld model. In this, Sommerfeld combined the classical Drude model with quantum mechanical Fermi-Dirac statics. In the enhanced model, electrons were treated as quantum particles. So, Schrödinger's equation can be easily applied.

This model was successful in describing electrical and thermal conductivity, temperature-dependent resistivity, electron heat capacity, the shape of the

electronic density of states, and paramagnetic susceptibility. However, it failed to distinguish between metal, semiconductor, and insulator.

B. Band Theory for Solids:

The major reason why free electron theory failed was completely ignoring the interaction between electrons and positive ions. These limitations of the free electron model were addressed by band theory by taking into consideration the potential of positive ions. By using quantum mechanics, Band theory was able to distinguish between metals, semiconductors, and insulators.

In Band theory, the potential field is assumed with a period equal to the lattice constant. The potential is given as [11]

$$V(a + x) = V(x)$$

$$(1.4)$$

where a is lattice constant. The true potential is parabolic by using the Kronig-Penney model we can consider potential as a rectangular pulse. The one dimensional Schrödinger equation for an electron in such potential is:

$$\left[\frac{-h^2}{8m\pi^2}\frac{d^2}{dx^2} + V(x)\right]\psi(x) = E\psi(x)$$
(1.5)

The possible solution of this equation according to Bloch theorem will be:

$$\psi(x) = e^{ikx} u_k(x) \tag{1.6}$$

Where $u_k(x)$ is a periodic function, and k is the wave vector of the electron. On solving the equation, we get this relation between wave vector k and energy E :

$$\cos(ka) = \cos(\alpha a) + P \frac{\sin(\alpha a)}{\alpha a}$$
(1.7)

where, $\alpha^2 = \frac{8\pi^2 mE}{h^2}$ and $P = \frac{4\pi^2 mVba}{h^2}$, h^2 is constant with b as barrier width and a period of the lattice. As the solution has the dependence of $\cos(ka)$ which have a value from -1 to 1. This imposes a constraint on energy states i.e. the wave function can not be solved for energy state where this condition is not satisfied (Fig. 1.5). These forbidden energy regions are called band gaps.



Figure 1. 5. Schematic of allowed and forbidden energy band with a band gap ΔE [11].

The width of the bandgap plays a vital role in characterizing a material into metal, semiconductor, and insulators. Metals do not have a bandgap, semiconductors have a low bandgap in the range of 0.5 - 5 eV, while insulators have a bandgap range of several eV. (Fig. 1.6)



Figure 1.6. Schematic of bands in metal, semiconductor, and insulator.

C. Mott-Hubbard model:

As Band Theory did not consider electron-electron interaction, it fails to explain the insulating state in some materials, especially oxides. According to the band theory, a partially filled conduction band should lead to a metallic state. However, this does not hold for many transition metal oxides such as Fe₃O₄, V₂O₃, NiO [12] *etc.* To explain this N.F. Mott proposed the idea of electron localization due to large coloumbic interactions. Later, Hubbard provided the theoretical interpretation of this possibility. The Hubbard Hamilton is given as:

$$H = -t\Sigma_{\langle i,j \rangle,\sigma} (C_{i,\sigma}^{+}C_{j,\sigma} + hc) + U \sum_{i=1}^{N} n_{i\downarrow} \eta_{j\uparrow}$$
(1.8)

The Hubbard Hamilton consists of two terms:

- a) The first term is the kinetic energy term in which t is the hopping integral, $C_{i,\sigma}^+$ and $C_{i,\sigma}$ are annihilation and creation operators.
- b) The second term is coulomb repulsion term in which U is on-site coulomb repulsion and is defined as [13]:

$$U = E(d^{n+1}) + E(d^{n-1}) - E(d^{2n})$$
(1.9)

It is the energy required for keeping two electrons at one site, maintaining the Pauli Exclusion Principle. This energy is quite high in correlated oxides, which results in the d orbital splitting into two bands. The lower band is completely filled and referred to as the Lower Hubbard band (LHB), while the upper band is empty and known as the Upper Hubbard Band (UHB). One of the main parameters to determine the strength of electron correlation is given by U/t. It helps in determining the conducting state of the material U/t<<1 indicating that the onsite coulomb repulsion is negligible but for insulators, U/t >>1 i.e. the coulomb repulsion is strong (fig. 1.7). Such insulators are called Mott-Hubbard insulators.

This model explained the behavior of many transition metal oxides. Still, it failed to explain the insulating state in some Transition metal oxides (TMO) consisting Ni, CO, Mn, etc. [13] and the metallic state of some sulfides.



Density of states



D. Zaanen-Sawatzky-Allen model

The Mott-Hubbard model explained the charge fluctuation of the type: $d_i^n d_j^n \rightarrow d_i^{n-1} d_j^{n+1}$, where *i* and *j* are neighboring sites, and the bandgap is the energy difference between d-d bands. But it fails to explain $d_i^n \rightarrow d_i^{n+1}$ L

Type of charge fluctuations, where L is legend hole. In the presence of these kinds of charge fluctuations, the band gap depends on the electronegativity of the anion. Zaanen, Sawatzky, and Allen formulated a framework (ZSA framework) (fig. 1.8) for transition metal compounds including oxides, sulfides, and halides to explain these charge fluctuations. ZSA framework consists of three parameters [14]:

- (i) Coulomb repulsion energy (U), the energy difference between unoccupied UHB and occupied LHB
- (ii) Bandwidth (W)

(iii) charge-transfer gap (Δ), the energy difference between the anion 2p band and unoccupied 3d band.

In this model, the band gap can either be U or Δ , depending on which one is smaller in magnitude on the energy scale. Light transition metal compounds have band gap U whereas heavy transition metal compounds have Δ . Hence, there can be two types of metals and two types of insulators:



Figure 1.8. Schematic for ZSA framework showing two types of insulators, a) Mott insulator, b) charge transfer insulator, and two types of metals c) low U metal and d) low Δ metal.

i. Mott-Hubbard insulators (W< U < Δ):

When the energy difference between unoccupied and occupied *d* bands (U) is lower than that between the unoccupied d band and filled oxygen 2p band (Δ). (fig. 1.8 a), such as NiO, La₂CuO₄, and V₂O₃.

i. Charge transfer insulators ($W < \Delta < U$):

When the energy difference (Δ) is lower than U, Figure 1.8 (b). Examples are RNiO₃ compounds, CuO, etc.

i. Low Δ metals:

Compounds having $\Delta < W$ and the oxygen 2p and metals unoccupied 3d bands overlap.

ii. Low U metals:

Here, U < W and the unoccupied and occupied d bands overlap in this case.

1.5. Metal to insulator Transition

Metal to insulator (MIT) is one of the most intriguing and mostly studied phenomena. MIT has become more interested in correlated Transition Metal oxides [5] [15] like NdNiO₃ and PrNiO₃. The transition from metallic to insulating state or vice-versa can be done by doping, pressure, external fields, temperature, and with the help of change in dimensionality. These external factors can alter the band filling, orbital overlap, and bandgap, leading to changes in the material's state. Based on the cause of transition MIT can be classified into different types:

(a) MIT due to band manipulation:

In insulators, the localization of charge carriers occurs due to a large energy gap between valance and conduction bands. By manipulating the bands, the transition to a metallic state can be done in two ways:

- i. By changing the carrier concentration i.e. band filling. This involves partially filling the conduction or valance band by introducing holes or electrons into the system. The same can be done by varying oxygen stoichiometry in the oxide compounds. A partially filled band leads to a metallic state. The MIT controlled by band-filling is an effective method to change the metallic or insulating state. Colossal magnetoresistance (CMR) manganites and high-temperature cuprates are the best examples of doping-induced MIT.
- ii. Without changing the carrier concentration, the MIT can be achieved by either closing or opening the band gap, by adjusting the relative positions of the conduction and valence bands. This adjustment can be accomplished by modifying the overlap of orbitals or by changing the magnetic structure [15].

(b) MIT due to electron correlation:

The metal-to-insulator transition in strongly correlated compounds happens due to the strong coloumbic interactions between electrons. From the Mott- Hubbard model we understand that metal-to-insulator transition depends on the correlation strength (U/t). The Mott metal-to-insulator transition occurs due to changes in pressure or temperature [12] [15] When strongly correlated compounds undergo metal-to-insulator transition brings some orbital ordering shift, magnetic ordering, and crystal structure transformation.

(c) MIT due to disorder:

In 1958, P. W. Anderson demonstrated that a system with a large number of defects or disorders tends to cause the localization of electrons [16]. In these materials, the motion of an electron can be viewed in a random potential instead of a periodic one. According to Anderson the energy spectrum of these materials can be continuous without any forbidden gap [15].

(d) MIT due to charge ordering:

One of the major reasons behind MIT in RNiO₃ is charge ordering. In charge ordering, the charge at various lattice sites is different and arranged in a specific order. This phenomenon is shown by Transition metal oxides because they tend to possess multiple valence states [11]. In the case of RNiO₃ compounds, Ni is in a 3⁺ state above the metal-to-insulator transition temperature (T_{MI}) but below T_{MI} there exists a charge ordering: Ni³⁺ \rightarrow Ni²⁺ + Ni⁴⁺. Generally, charge ordering is associated with magnetic or orbital ordering and structural change. In RNiO₃ compounds, the structure becomes monoclinic from orthorhombic. For R = Nd and Pr, MIT coincides with antiferromagnetic ordering [17].

1.6. Conduction Mechanism:

Temperature plays an important role in the electronic transport of solids. The conduction of metals, semiconductors, and insulators varies differently with temperature.

For metals, according to the classical picture resistivity at a constant temperature depends upon two factors:

- (i) Resistance due to defects such as impurity or disorder.
- (ii) Resistance due to scattering of phonons.

$$\rho_{\text{total}} = \rho_{\text{phonon}} + \rho_{\text{defect}} \tag{1.10}$$

The resistivity due to defects does not depend on the temperature but the resistivity offered by phonons depends linearly upon the temperature at high temperatures as:

$$\rho_{\rm phonon} \propto \frac{\hbar^2 \pi}{\rm kM} \frac{\rm T}{\theta^2}$$
(1.11)

However, the above theory deviates at low temperatures shown by experimental data. This theory fails at low temperatures because it considers electrons non-interacting. Lev Landau proposed the Fermi liquid theory, which considers electrons as weakly interacting fermions at sufficiently low temperatures. The temperature resistivity for such a system is given as:

$$\rho_{NFL} = \rho_0 + AT^2 \tag{1.12}$$

Where ρ_0 is the residual resistivity at absolute zero temperature that occurs due to the lattice - imperfections, dislocations, defects, and the constant A signifies electron-electron interaction. This model is valid in the low-temperature metallic state.

Various models and theories have been proposed to explain the conductivity in semiconducting or insulating states, describing temperature dependence of conductivity in terms of activation energy, hopping energy, etc. The following models describe conduction in oxides in an insulating state.

Arrhenius Model:

In semiconducting solids, the most common conduction mechanism at high temperatures is a thermally activated band. At high temperature, thermal energy is sufficient to move the charge carriers from the valance band to the conduction band. The temperature dependence of resistivity is given by the Arrhenius model:

$$\rho = \rho_0 \exp\left(\frac{\Delta}{k_B T}\right) \tag{1.13}$$

Where Δ is the activation energy, and K_B is Boltzmann's constant. The plot of $\ln \rho$ versus 1/T must be a straight line. At lower temperature, thermal energy is less than activation energy, conduction occurs due to the hopping of charge carriers. Since carrier hopping is confined to the nearest neighbor it is referred to as nearest neighbor hopping [19].

Variable range hopping:

Mott variable range hopping is another type of hopping method for conduction between localized states (VRH). This conduction mechanism was first observed in amorphous semiconductors but later it was discovered in many insulators having disorder. At low temperature, Thermal energy is not sufficient to make charge carriers shift from the valance band to the conduction band then VRH enables the charge transfer. Phonon in the lattice helps with conduction via hopping. The more closely packed the lattice the higher the probability of hopping of the charge carriers and costs less energy to hop. However, both conditions cannot be satisfied always. The hopping probability at a low temperature is given by:

$$P \propto \exp\left(-\alpha R - \beta \Delta\right) \tag{1.14}$$

where α is localization length, *R* is a spatial separation between two states, β is a constant that is inversely proportional to temperature and Δ is the energy required for hopping.

The energy required for the spatially closer state is more than the one which is far. Hence, the neighbor sites are not only preferable sites for hopping but the sites that are far electron can hop to them. For some optimum values of R and Δ , the hopping probability can be maximum. The relation for temperature-dependent resistivity derived by Mott is as follows [20]:

$$\rho = \rho_0 \exp\left(\frac{T_0}{T}\right)^{\frac{1}{n+1}} \tag{1.15}$$

Here *n* is the dimension of the system and T_0 is the characteristic temperature. The mathematical expression for T_0 is given by:

$$T_0 = \frac{18}{k_B N(E) \alpha^3}$$
(1.16)

Where α is the localization length, for a three-dimensional system ln ρ varies linearly with T^{-1/4}.

1.7. Motivation:

The phase diagram (Figure. 2) of RNiO₃ depicting various structural, magnetic and electronic transitions based on external parameters like temperature, tolerance factor, and Ni-O-Ni angle is shown. In the RNiO₃ family, NdNiO₃ (NNO) and PrNiO₃ (PNO) show metal-to-insulator and antiferromagnetic to paramagnetic transition at the same temperature. These electronic properties in thin films can be manipulated by changing the dimensionality, thickness, doping, oxygen content, and on application of electric field and strain. There are numerous reports of doping at the Nd site in NdNiO₃. Amarasinghe *et al* have studied the doping of Hydrogen ions [21] at the Nd site which leads to a significant increase in room-temperature resistivity. The electrical transport relies on the overlap of 3d and 2p orbitals within the Ni–O–Ni conduction network, these films provide an exciting opportunity to study how strain affects the electrical transport. Strain can induce expansion, compression, or rotation of NiO₆ octahedra in thin films. Consequently, if the strain is coherent across the

thickness, it has the potential to induce substantial modifications in the physical properties of this perovskite system.

In thin films, strain depends on the choice of substrate, i.e., compressive or tensile. It is reported that tensile strain results in the formation of oxygen vacancies in RNiO₃ films. In compressive strain, we get more metallicity. Also, to study the vibrational properties of NdNiO₃ thin films, substrate selection is crucial. SrTiO₃ and NdGaO₃ provide a large background that restricts observing the Raman modes of NdNiO₃ thin film [22]. In the case of LaAlO₃, very few Raman modes are present in the 50 cm⁻¹ to 1000 cm⁻¹ spectral range, making the LAO an ideal candidate to study the Raman spectra of NdNiO₃ thin films. As discussed earlier, there is a scarcity of reports of doping at Ni site in NdNiO₃. Some of us have studied the doping of aliovalent Mn ion at Ni site which changes the electrical properties of NdNiO₃ due to changing the oxidation state of Ni. It would be interesting to see the changes in the physical properties of NdNiO₃ without disturbing the oxidation state at A site, i.e., Nd^{3+} , by doping isovalent Al^{3+} ion at Ni site. As the ionic radii of Al and Ni are similar, Al can be accommodated in the octahedra environment of oxygen ions. Even a small doping of 5% can cause significant changes in transport properties. Considering the above point in mind, we doped 5% Al at the Ni site, deposited NdNi_{0.95}Al_{0.05}O₃ thin films of 10, 20, and 30 nm on LAO (001) substrate, and studied its structural, electrical, and vibrational properties.

Citations:

- [1] M. Zhang, G. Jeerh, P. Zou, R. Lan, M. Wang, H. Wang, and S. Tao, Recent Development of Perovskite Oxide-Based Electrocatalysts and Their Applications in Low to Intermediate Temperature Electrochemical Devices, Materials Today 49, 351 (2021).
- [2] Q. Shen, S. Dong, S. Li, G. Yang, and X. Pan, A Review on the Catalytic Decomposition of NO by Perovskite-Type Oxides, Catalysts 11, 5 (2021).
- J. Zhu, H. Li, L. Zhong, P. Xiao, X. Xu, X. Yang, Z. Zhao, and J.
 Li, Perovskite Oxides: Preparation, Characterizations, and Applications in Heterogeneous Catalysis, ACS Catal. 4, 2917 (2014).
- [4] G. Catalan, *Progress in Perovskite Nickelate Research*, Phase Transitions 81, 729 (2008).
- [5] D. I. Khomskii, *Transition Metal Compounds* (Cambridge University Press, Cambridge, 2014).
- [6] R. Vilarinho, A. Almeida, and J. Moreira, Structural Distortions of Orthorhombic RFeO3 and RMnO3, OAJ Materials and Devices 5, (2021).
- [7] S. Catalano, M. Gibert, J. Fowlie, J. Íñiguez, J. M. Triscone, and
 J. Kreisel, *Rare-Earth Nickelates RNiO3: Thin Films and Heterostructures*, Reports on Progress in Physics 81, 046501 (2018).
- [8] R. C. Advincula and W. Knoll, A Perspective and Introduction to Organic and Polymer Ultrathin Films: Deposition, Nanostructuring, Biological Function, and Surface Analytical Methods, in Functional Polymer Films (John Wiley & Sons, Ltd, 2011), pp. 1–10.
- [9] J. B. Torrance, P. Lacorro, C. Asavaroengchai, and R. M. Metzger, Simple and Perovskite Oxides of Transition-Metals: Why Some Are Metallic, While Most Are Insulating, Journal of Solid State Chemistry 90, 168 (1991).
- [10] N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Holt, Rinehart and Winston, 1976).
- [11] C. Kittel, Introduction to Solid State Physics (Wiley, 2004).

- [12] D. B. McWhan, A. Menth, J. P. Remeika, W. F. Brinkman, and T. M. Rice, *Metal-Insulator Transitions in Pure and Doped V₂O₃*, Phys. Rev. B 7, 1920 (1973).
- [13] V. I. Anisimov, J. Zaanen, and O. K. Andersen, *Band Theory and Mott Insulators: Hubbard U Instead of Stoner I*, Phys. Rev. B 44, 943 (1991).
- [14] J. Zaanen, G. A. Sawatzky, and J. W. Allen, Band Gaps and Electronic Structure of Transition-Metal Compounds, Phys. Rev. Lett. 55, 418 (1985).
- [15] F. Gebhard, The Mott Metal-Insulator Transition: Models and Methods (Springer, 1997).
- [16] P. W. Anderson, Absence of Diffusion in Certain Random Lattices, Phys. Rev. 109, 1492 (1958).
- [17] M. L. Medarde, Structural, Magnetic and Electronic Properties of Perovskites (R = Rare Earth), J. Phys.: Condens. Matter 9, 1679 (1997).
- [18] M. A. Omar, Elementary Solid-State Physics: Principles and Applications (Addison-Wesley Pub. Co., Reading, Mass., 1975).
- [19] Y. Chen, W. Yu, and Y. Liu, Effects of Annealing on Structural, Optical and Electrical Properties of Al-Doped ZnO Thin Films, SCI CHINA SER G 47, 588 (2004).
- [20] N. F. Mott, *Conduction in Non-Crystalline Materials*, Philosophical Magazine 19, 835 (1969).
- [21] U. Sidik, A. N. Hattori, R. Rakshit, S. Ramanathan, and H. Tanaka, Catalytic Hydrogen Doping of NdNiO3 Thin Films under Electric Fields, ACS Appl. Mater. Interfaces 12, 54955 (2020).
- [22] MAHESH CHANDRA, "Phase Transitions in NdNiO3 Thin Films and NdNiO3/NdMnO3 Multilayers: Influence of Strain and Dopin" Indian Institute of Technology Indore, SIMROL, INDORE, 2015.

CHAPTER 2 Experimental Techniques

This chapter gives a summary of the methods used to synthesize and characterize the materials in our study. We employed solid-state reaction for bulk pellet synthesis and pulse laser deposition for thin film preparation. For characterization, we utilized X-ray diffraction and Raman spectroscopy for structural analysis and temperature-dependent resistivity measurements to study electronic transport properties.

2.1. Sample Preparation

- a) Bulk synthesis using a solid-state reaction method.
- b) Thin Film synthesis using the PLD method.

2.2. Characterization Techniques

- d) X-ray Diffraction (XRD) techniques
- e) Raman Spectroscopy
- f) Temperature-dependent resistivity measurement

2.1. Sample Preparation:

a) Bulk synthesis by using solid-state reaction method:

Solid-state reaction is a widely used method to prepare bulk samples [1]. In this method, the reaction takes place in powder form, making this a solvent-free approach. We opted for this method to prepare a bulk pellet of NdNi_{0.95}Al_{0.05}O₃.

The first step in this method is mixing the highly pure constituent powders in the appropriate stoichiometric ratio using a high-precision weighing machine. To achieve a homogenous mixture, powders are ground thoroughly using pestle-mortar for 3-4 hours. To ensure thorough mixing, propanol can be added, gradually evaporating as the grinding process continues. The reaction of the powder mixture does not start at room temperature. We calcined the powder mixture in a box furnace for 10 hours to start the reaction. During calcination, volatile gases like CO_2 , NO_2 , and moisture are removed from the bulk sample. The grinding and calcination processes are repeated to ensure uniform particle size and the formation of a single phase in the sample. After the third round of griding, the powder sample is pressed into a pellet using a hydraulic press using a 20 mm die set. Then, the pellet is heated at a high temperature, known as sintering. Sintering is done to enhance the density of the pellet.

Substrate Selection:

Thin films are deposited onto the substrate, making substrate selection crucial in thin film synthesis. We have chosen a LaAlO3 (LAO) single-crystal substrate with (001) orientation. To assess the strain experienced by thin films, we can compare the pseudo-cubic lattice parameters of the NdNiO₃ bulk and the LAO (001) substrate. Upon calculating the lattice mismatch, we find that the film experiences in-plane compressive strain and, therefore, out-of-plane tensile strain.

Synthesis of NdNi0.95Al0.05O3 targets:

We synthesized the NdNi_{0.95}Al_{0.05}O₃ sample by blending high-purity Nd₂O₃, NiO, and Al₂O₃ powders in the appropriate stoichiometric ratios. The reaction can be represented as follows:

$$Nd_2O_3 + NiO + Al_2O_3 \longrightarrow NdNi_{0.95}Al_{0.05}O_3$$

The synthesis process of the bulk sample is shown in the following block diagram:

Highly pure powders of Nd_2O_3 , NiO, and Al_2O_3 were precisely measured using a high-precision electronic weighing machine to achieve the required molar ratio.

Grinding was done for 3-4 hours using pestle mortar for homogenous mixing then the powder mixture was calcinated at 800°C for 12 hours in a box furnace so that the powder mixture reacts properly.

To ensure uniform particle size, a second round of grinding was done thoroughly for 2-3 hours, and again calcination was done at 800°C for 12 hours in a box furnace to maintain uniformity and single-phase.

After the second heating 30-minute griding was done and then, using a Hydraulic press, the mixture was pressed in the form of pellets (diameter = 20 mm) and then pellets were sintered at 1000° C in a box furnace for 12

b) Thin film synthesis using PLD:

Thin films have been extensively utilized for over half a century in the fabrication of various devices, including electronic devices, instrument hard coatings, optical coatings, decorative parts, enzymatic glucose biosensors, neural circuits, and more. The primary steps involved in depositing thin films are outlined below [2]:

$$Nd_2O_3 + NiO + Al_2O_3 \longrightarrow NdNi_{0.95}Al_{0.05}O_3$$

- Generation of ionic or molecular species.
- Conveyance of these species to the substrate using a medium.
- Condensation of the deposited film onto the substrate, facilitated by cooling or through chemical or electrochemical reactions.

In Broad terms, thin film deposition techniques can be classified into two categories:

(a) Chemical Vapour Deposition (CVD) Techniques:

It is utilized when the material deposited on the film results from a chemical reaction and is employed to create high-quality, highperformance solid materials. It's commonly used in industry to produce high-purity crystalline films of complex oxides, nitrites, and other compounds, and is frequently employed in the semiconductor industry for thin film production.

(b) Physical Vapour Deposition (PVD) Techniques:

It is a method that involves transferring atoms from a solid or molten source to a substrate through physical processes like evaporation, sublimation, or ionic impingement on a target. It includes a range of vacuum deposition techniques used to create thin films and coatings on substrates, including metals, ceramics, glass, and polymers. The most common PVD techniques are Sputtering and Thermal Evaporation [3].

We synthesized our thin films using Pulsed Laser Deposition (PLD) technology, which is the predominant method within the Physical Vapor Deposition (PVD) category.

Experimental design of PLD technique:



Figure 2.1. Schematic diagram of the pulsed laser deposition (PLD) system [2].

The PLD technique is one of the most efficient and versatile methods for depositing thin films onto appropriate substrates. This technique allows for using ultraviolet, visible, and infrared lasers. Q-switched Nd: YAG excimer lasers (with wavelengths at $1.064 \,\mu\text{m}$, second harmonics at $532 \,\text{nm}$, and third harmonics at 266 nm), commonly referred to as solid-state lasers, as well as KrF (λ - 248nm) and ArF (λ - 193nm) excimer lasers, are recognized as some of the most popular types of lasers. We used the KrF excimer laser, which generates ultraviolet pulses, to construct our PLD chamber. The PLD chamber is constructed using stainless steel and includes components such as a target holder, a substrate holder, a heating mechanism, and a process gas intake. To ensure uniform ion ablation from the target, precise raster and rotational motions are programmed into the PLD chamber for the target holder. The substrate holder is positioned at a specific distance from the target holder. The substrate holder is linked to a heater to uphold the necessary deposition temperature during thin film deposition. A rotary pump and a turbomolecular pump are used in the vacuum system. The rotary pump lowers the ambient pressure inside the PLD chamber to approximately 10⁻ ³ Pa. The turbo-molecular pump can attain a base pressure of around 10^{-6} Pa. Figures 2.1. and 2.2. depict the schematic diagram and experimental setup of the PLD chamber.

When a high-energy laser beam impacts the material under vacuum and elevated temperature conditions, plasma plumes emerge [4]. Numerous review publications offer theoretical insights into the formation of plasma plumes [5]. Studies suggest that plasma plume ablation cannot be attributed to a single mechanism but rather to a combination of mechanisms. Ablation occurs when the absorbed laser energy E_{ab} exceeds the binding energy E_b of the atoms on the surface of the target material. This condition is represented as $E_{ab} > E_b$. Upon the target's laser pulse absorption, the energy is initially converted into electronic excitation, then thermal, chemical, and mechanical energy, leading to evaporation, ablation, and plasma formation. Using Excimer Laser technology, the laser ablation and absorption process typically take approximately 30 nanoseconds in PLD chambers. The plasma plume, composed of ablated ions and materials, assumes an elliptical or roughly circular shape, and is directed toward the substrate. Modifying the partial pressure of the inlet gas can alter the shape

and focus of the plasma plume while also regulating the oxygen stoichiometry of the deposited sample. The partial pressure can adjust the plasma plume's kinetic energy and scattering rate, allowing for the regulation of this deposition parameter to achieve optimal growth. Typically, the kinetic energy of ions in the plasma plume ranges from 0.1 eV to 10 eV.



Figure 2.2. Experimental setup of the PLD chamber at Thin Film Lab, IIT INDORE

Thin film growth types:

The growth of certain materials on specific substrates can proceed in various manners following nucleation. We can primarily describe the growth type using the following three models (Figure 2.3):

1. Volmer-Weber growth model (Island growth):

This occurs when the smallest stable clusters form on the substrate and grow into three-dimensional islands. In this growth model, the atoms or molecules being deposited are more strongly bound to each other than to the substrate material. This is frequently observed when the film and substrate are composed of different materials, such as metal and semiconductor films formed on oxide substrates [6].

2. Frank-van der Merwe growth model (Layer growth):

This process, commonly called the layer-by-layer model, relies on the epitaxial growth of films on the crystal surface. This type of growth is two-dimensional (2D). In this mode, the atoms of thin films are firmly

bonded to the substrate, with each layer successively less strongly bonded than the preceding one. The atoms are deposited in monolayers on the substrate's surface. This model explains the growth of epitaxial and smooth thin films. as exemplified by the epitaxial growth of semiconductors and oxide materials [7].

3. Stranski-Krastanov growth model (Mixed growth):

It combines layer-by-layer and island growth models, known as the 'layerplus-island growth' model. It represents a combination of the twodimensional and three-dimensional growth models. During this growth phase, after forming one or more monolayers layer-by-layer manner, further layer-by-layer growth becomes energetically unfavourable, leading to the emergence of islands. This type of growth has been observed in various metal-metal and metal-semiconductor systems.



Figure 2.3. Schematic diagram illustrating three fundamental growth model: (a) Frank-van der Merwe growth model (b) Frank-van der Merwe growth model (c) Stranski-Krastanov mode.

Parameters of thin film growth:

A plasma plume, generated by a high-energy laser, rapidly expands from the target surface in all directions. Film formation occurs on a substrate, where some of the material from the plume re-condenses. Several external characteristics,

when combined, significantly influence the phase stabilization, quality, and epitaxial nature of the thin film [8].

- 1. Laser energy.
- 2. Process gas partial pressure.
- 3. Substrate temperature.
- 4. Target to substrate distance.

The laser energy regulates the kinetic energy of particles and their growth rate. However, the shape of the plume is influenced by the process gas, which also aids in achieving stoichiometry, especially in the case of complex oxides. The substrate is usually kept at a high temperature throughout the deposition process. The substrate temperature is crucial during thin films' nucleation and growth processes. Additionally, the distance from the target to the substrate is another essential factor determining the plasma plume's angular spread.

Synthesis of NdNi_{0.95}Al_{0.05}O₃ thin films on LAO (001) substrate:

NdNi $_{0.95}$ Al $_{0.05}$ O₃ thin-film depositions are conducted on a single crystal LaAlO₃ (LAO) substrate. Before deposition, the substrates undergo a 10-minute sonication process, first in acetone and then in propanol. The chamber is evacuated before deposition and filled with pure oxygen as the background gas.

Laser Ablation Energy	310 mJ
Laser Wavelength	248 nm
Target	NdNi _{0.95} Al _{0.05} O ₃
Substrate	LaAlO ₃ (LAO) (001)
Target to Substrate Distance	4.5 cm
Base Pressure	1 x 10 ⁻³ Pa
Partial Pressure	40 Pa of O ₂

During the deposition, the following parameters were maintained:

Repetition Rate	4 Hz
No. of shots	700,1400,2100
Estimated Thickness of film	10 nm, 20 nm, 30 nm
Annealing Pressure	1000 Pa of O ₂
Annealing Time	3 minutes

Following deposition, the deposited thin films underwent post-annealing at 720°C while maintaining an oxygen partial pressure of 1000 Pa for 3 minutes.

Advantages of the Pulsed Laser Deposition Method:

- This setup enables greater customization of laser parameters, including laser energy, substrate temperature, target-to-substrate distance, vacuum level, oxygen partial pressure, and other variables.
- Controlling the number of pulses regulates the thickness of the thin films.
- Even when the target is multiphase, PLD can still ensure that their thin films remain pure in phase.
- PLD can also be utilized to create multilayer films and heterostructures. Unlike techniques such as Molecular Beam Epitaxy (MBE), where the composition is adjusted by altering the ratio of the various sources arriving on the substrate, in PLD, the stoichiometry of the film is controlled by the ability to produce a target with the desired composition.

Disadvantages of the Pulsed Laser Deposition Method:

- Due to the narrow size of the plume in PLD, it is challenging to achieve uniform thickness when depositing thin films.
- During rapid heating and cooling, particulates such as micro-sized lumps or droplets can form in the target.
- The PLD technique is most suitable for high-tech applications such as microelectronics, sensor technology, and optical technology rather than large-scale industrial applications.

2.2. Characterization Technique:

Upon completion of synthesis, all thin films undergo examination for phase purity using the X-ray diffraction (XRD) technique. Additionally, Raman spectroscopy is conducted at room temperature. Raman spectroscopy investigates structural changes induced by varying parameters such as thickness or doping levels. The temperaturedependent resistivity of thin films is measured across a wide temperature range, from 300K to 12K, utilizing a closed-cycle refrigerator (CCR). The details of each characterization technique are explained in the following sections.

a) X-ray Diffraction (XRD) techniques:

X-ray diffraction is among the most widely used techniques for characterizing samples, allowing the extraction of atomic-scale information for both crystalline and non-crystalline materials. This is possible because the wavelength of X-rays, which is on the order of Angstroms (Å), matches interatomic distances. When an X-ray beam interacts with a material, it is diffracted by various sets of atomic planes within the crystal structure. Suppose the spacing between these planes (d-spacing) and the angle of incidence concerning the plane satisfy the Bragg relation $2d\sin\theta = n\lambda$. In that case, where d is the interplanar distance, n is an integer, θ is half the angle between the incident and diffracted rays, and λ is the X-ray wavelength. Constructive interference between the diffracted waves occurs. If we consider $\frac{1}{2}$, $\frac{3}{2}$ and so on, the diffracted waves lead to destructive interference. In 1912, Max von Laue ,W. L. Bragg, and his father, W. H. Bragg, discovered this technique, heralding a new material characterization era. This method is commonly employed to probe the internal structure of materials, lattice crystallinity, lattice parameters, lattice strain, etc [9].

Working Principle:

X-ray diffraction relies on using an X-ray tube, which functions through the acceleration and collision of electrons. When an alternating voltage is applied to the X-ray tube's electrodes, the filament within the cathode heats up. This heat causes the cathode to emit free electrons, moving towards the anode. The accelerated free electrons gain significant speed and energy as they move towards the anode. These high-energy collisions generate X-rays within the X-ray tube when they collide with the anode's surface. The X-rays produced have a wavelength that matches the size of the lattice parameter, which is the distance between atoms within a crystal structure. After these X-rays leave the tube, they meet the sample being examined. When the X-rays hit the sample, they experience a process called diffraction. This event occurs when the X-rays engage with the atoms in the crystalline structure of the sample, causing the Xrays to scatter in different directions. During this diffraction event, the X-ray intensity varies as their incidence angle changes. The interaction between the Xrays and the crystal structure leads to both constructive and destructive interference, which in turn creates fluctuations in the intensity of the scattered Xrays. The principle of X-ray diffraction fundamentally relies on Bragg's law.



Figure 2.4. X-ray diffraction through Bragg's reflection in the atomic plane.

This concept involves two X-ray beams striking two adjacent atomic planes in parallel, resulting in a path difference for the two beams of $2dSin\theta$. Constructive and destructive interferences occur under two conditions dictated by Bragg's law.

$$2d\,\sin\theta = n\lambda\tag{2.1}$$

Where d represents the spacing between planes, n is an integer, and θ is half the angle between the incident and diffracted rays, constructive interference between the diffracted waves occurs. The constructive interference occurs if the path difference (d Sin θ) equals an integer (n =1,2,3...). Destructive interference occurs when the path difference is equal to half of the odd multiples (n = $\frac{1}{2}, \frac{3}{2}$...).



Figure 2.5. Schematic of X-Ray diffraction.

Substrate-induced strain:

Upon deposition of a film onto a substrate, the film experiences two distinct types of strain arising from the lattice mismatch. Depending on the sign of the lattice mismatch, determined by the simple lattice parameters of both the film and the substrate, strains can be classified into one of two categories:

A. Compressive strain:

When the lattice parameter of the thin film is greater than that of the substrate, it experiences compressive strain (Figure 2.6.). Consequently, the film tends to compress itself, leading to an increase in the out-of-plane lattice parameter. As a result, to comply with Bragg's law, the diffraction angle in the XRD pattern shifts

towards lower values, indicating that the film is experiencing compressive strain due to the substrate



Figure 2.6. Thin film showing compressive strain on the substrate.

B. Tensile strain:

In the case of tensile strain (Figure 2.6), the lattice parameter of the thin film is smaller than that of the substrate. Consequently, the film naturally expands and adjusts its lattice to match the substrate's. This expansion results in a decrease in the out-of-plane lattice parameter of the film. Therefore, the peaks of the XRD pattern shift towards the right in accordance with Bragg's law.



Figure 2.7. Thin film showing tensile strain on the substrate.

b) Raman Spectroscopy:

When monochromatic light or light with a very narrow frequency range is incident on a medium, the frequency of the scattered light from the medium may be identical to the frequency of the incident light. Moreover, the frequency of the scattered light and the corresponding energy can either be higher or lower than the frequency of the incident light. When the scattered radiation closely matches the energy of the incident radiation, it is termed Rayleigh scattering. Conversely, if the scattered radiation exhibits discrete frequencies both above and below the frequency of the incident radiation, the process is referred to as Raman scattering. This phenomenon was first identified by C. V. Raman and K. S. Krishnan in 1928. A. V. Raman was honored with the Nobel Prize in 1930 for his pioneering work on Raman spectroscopy. [10].

The classical theory of the Raman effect:

The classical theory of the Raman effect provides insights into a fundamental concept known as the polarizability of a molecule. When a positively charged molecule is subjected to a static electric field, the positively charged nuclei of the molecule are attracted to the negative pole of the field, while the positively charged electrons are attracted to the positive pole of the field. This results in the polarization of the molecule due to the separation of charge centers. The separation of charge centers induces an electric dipole moment in the molecule. The magnitude of the applied field, denoted by E, and the molecule's susceptibility to deformation both contribute to the value of the induced dipole, denoted by μ .

$$\mu = \alpha E \tag{2.2}$$

where α is known as the polarizability of the molecule. When a sample containing these molecules is exposed to a radiation beam with a frequency v, the electric field experienced by each molecule fluctuates, as expressed in the following equation:

$$\mathbf{E} = \mathbf{E}_0 \sin 2\pi \mathbf{v} \mathbf{t} \tag{2.3}$$

Therefore, the induced dipole moment also oscillates at the frequency v according to the following expression:

$$\mu = \alpha E = \alpha E_0 \sin 2\pi v t \tag{2.4}$$

According to the classical theory of Rayleigh scattering, an oscillating dipole emits radiation that matches its own frequency. Hence, the frequency of the radiation coming in and being scattered away is the same. Moreover, due to certain internal activities like rotation and vibration, the polarizability of the molecule undergoes periodic changes. Specifically focusing on vibrational movements with a frequency denoted as v_{vib} , which influences the molecule's polarizability, the resultant induced dipole moment can be described as:

$$\mu = \alpha E = (\alpha_0 + \beta \sin 2\pi v_{vib} t) E_0 \sin 2\pi v t$$
(2.5)

Equation 2.5 can be rewritten using the trigonometric formula:

$$\mu = \alpha_0 E_0 \sin 2\pi v t + 1/2 \beta E_0 \{ \cos 2\pi (v - v_{vib}) t - \cos 2\pi (v + 2 v_{vib}) \\ t \}$$
(2.6)

The first term in equation (2.6) corresponds to the frequency of the incident radiation, reflecting the Rayleigh scattering phenomenon. In the second and third terms, two frequencies emerge: one is lower than the frequency of the incident beam, while the other is higher. Thus, the term with frequency $(v - v_{vib})$ arises from Stokes' radiation, while the term with frequency $(v + v_{vib})$ arises from anti-Stokes' radiation.

The quantum theory of the Raman effect:

In the quantum theory of the Raman effect, we examine the interaction between photons with a frequency v and molecules within the sample. These interactions can be categorized as elastic or inelastic collisions. In an elastic collision, photons are deflected without any energy loss. However, the energy exchange between

the photon and molecule can occur in an inelastic collision. According to quantum laws, only molecules can gain or lose energy, with the energy change ΔE representing the difference between two permissible states. This vibrational



Figure 2.8. Schematic of energy level diagram showing various types of emissions.

and rotational energy change must be denoted by ΔE . If the molecule gains energy ΔE , the dispersed photon will carry energy $hv - \Delta E$, resulting in radiation with a frequency $v - \Delta E/h$. Conversely, if the molecule loses energy ΔE , the scattered frequency will be $v + \Delta E/h$ [11]. Therefore, radiation with a frequency $v - \Delta E/h$ is termed Stokes' radiation, while radiation with a higher frequency is termed anti-Stokes' radiation. Due to the higher population of lower energy states compared to higher energy states and the fact that Stokes' radiation results from transitions from lower to higher energy states, while anti-Stokes' radiation results from transitions from higher to lower energy states, the intensity of Stokes' radiation is typically greater than that of anti-Stokes' radiation (Figure 2.8.).

C. Temperature-dependent resistivity measurement:

The resistivity of a material refers to its ability to delay the movement of charge carriers within its lattice, resulting in resistance. Temperaturedependent resistivity measurement, also known as electrical resistivity measurement, is a technique employed to investigate the electrical properties of materials in relation to temperature. This technique involves measuring the electrical resistance of a material across a range of temperatures to assess its conductivity and to observe how temperature affects its electrical behavior. The resistivity of insulating materials tends to decrease as temperature rises, while that of metals increases. This contrast makes resistivity measurements particularly useful for studying structural phase transitions in metal-insulator systems, which often involve electronic transitions. Resistivity can be calculated using the following formula:

$$\rho = \frac{RA}{l} \tag{2.7}$$

Where R is the sample's resistance, the probes' shortest distance in measurement system 1 and cross-section area A is kept.

The temperature coefficient of resistivity (α) represents the change in resistivity with respect to a change in temperature. It quantifies the impact of temperature on electrical resistivity. The formula to calculate the temperature coefficient of electrical resistivity (α) is given by:

$$\alpha = \frac{1}{\rho_0} \frac{d\rho}{dT}$$
(2.8)

 ρ_0 represents the residual resistivity, $\frac{d\rho}{dT}$ denotes the rate of change of resistivity with temperature, and α is the temperature coefficient of electrical resistivity, measured in units of K⁻¹. Metals typically show a positive value for the temperature coefficient (α), indicating increased electrical resistivity with rising temperature. Conversely, insulators demonstrate a negative α value, suggesting a decrease in electrical resistivity with increasing temperature.

The two-probe or four-point probe methods can determine the electrical resistivity (ρ). The two-probe method is suitable for highly resistive samples, while the four-point probe method is preferred for samples with low resistance.

Four-probe method:

The four-probe method is widely utilized and versatile for accurately measuring resistivity, particularly for low-resistance samples. This method eliminates contact resistance by employing separate probes for the source and measurement, enhancing measurement accuracy compared to the two-probe method.

The four-probe method is employed to find the resistance of a single crystal or thin film. Current flows through the outer contacts near the sample edges, while the potential difference between the inner contacts is measured (Figure 2.9.) [12]. This method is beneficial when the distance between the probes is minimal relative to the sample's smaller dimension.



Figure 2.9. Schematic of Four Probe method.

Advantages of the Four-Probe method over the Two-Probe method:

- (i) It eliminates contact resistances, which can lead to measurement errors.
- (ii) This method proves highly advantageous when sample have low resistance and contact resistance might impact the measurement [13].
- (iii) We are measuring the voltage and current difference across two probes; there is a reduced chance of error in the data.

The four-probe method was employed to determine the resistivity of $RNiO_3$ thin films. Typically, the samples exhibit a long, thin, rectangular shape with 5 x 2 mm dimensions. Four collinear connections were established on the thin film's surface using conductive silver paste (EPO-TEK EE 129-4), applied with Epoxy technology. Subsequently, the samples were heated for 10-15 minutes before insertion into the measurement chamber.

In our project, we utilized a JANIS RESEARCH CCR cryostat to evaluate the temperature-dependent resistivity of the samples. This system can measure the resistivity of two samples simultaneously, facilitating a comparative analysis between them. We employed a temperature controller manufactured by Lakeshore to control and monitor the temperature. Voltage measurements were conducted by applying a specific current using the KEITHLEY-2612 A Source Meter. Once a satisfactory vacuum level was achieved, measurements were performed using LABVIEW RT-5d within the 300K to 12K temperature range. Figure 2.10. depicts an image of the experimental setup for temperature-dependent resistivity measurements.



Figure 2.10. The setup for temperature-dependent resistivity measurement in the thin film laboratory at IIT Indore.

Citations:

[1] A. Venimadhav, I. Chaitanya Lakshmi, and M. S. Hegde, Strain-Induced Metallic Behavior in PrNiO3 Epitaxial Thin Films, Materials Research Bulletin 37, 201 (2002).

[2] Introduction To Pulsed Laser Deposition (PLD):8 Applications, https://vaccoat.com/blog/what-is-pulsed-laser-deposition-pld/.

[3] H. Usui, Preparation of Polymer Thin Films by Physical Vapor Deposition, in Functional Polymer Films (John Wiley & Sons, Ltd, 2011), pp. 287–318.

[4] K. Wang, G. Tai, K. H. Wong, S. P. Lau, and W. Guo, Ni Induced Few-Layer Graphene Growth at Low Temperature by Pulsed Laser Deposition, AIP Advances 1, 022141 (2011).

[5] M. Henini, Handbook of Thin-Film Deposition Processes and Techniques, Microelectronics Journal 31, 219 (2000).

[6] Solid State Chemistry and Its Applications, 2nd Edition, Student Edition | Wiley

[7] F. C. Frank, J. H. van der Merwe, and N. F. Mott, One-Dimensional Dislocations. I. Static Theory, Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences 198, 205 (1997).

[8] H.-U. Krebs et al., Pulsed Laser Deposition (PLD) -- A Versatile Thin Film Technique, Advances in Solid State Physics 505 (2003).

[9] D. B. Chrisey and G. K. Hubler, Pulsed Laser Deposition of Thin Films (John Wiley & Sons, New York, 1994).

[10] Introductory Raman Spectroscopy. John R. Ferraro, Kazuo Nakamoto and Chris
W. Brown. Academic Press, Amsterdam, Second Edition, 2003. Xiii + 434 - Long - 2005
- Journal of Raman Spectroscopy - Wiley Online Library

[11] C. N. Banwell, A. Elaine, and M. Mccash, "FUNDAMENTALS OF MOLECULAR SPECTROSCOPY FOURTH EDITION."

[12] G. Catalan, Progress in Perovskite Nickelate Research, Phase Transitions 81, 729 (2008).

[13] "Resistivity by Four Probe Method (Theory) : Solid State Physics,"Virtual Lab: Physical Sciences: Amrita Vishwa Vidyapeetham Virtual Lab.

Chapter 3 Result and Discussion

3.1. X-ray diffraction:

The phase purity and out-of-plane lattice parameters were assessed using Xray diffraction (XRD) analysis conducted with the Rigaku Smart Lab Automated Multipurpose X-ray diffractometer. No undesired peaks were observed in the XRD patterns of the films, as depicted in Figure 3.1., indicating highly oriented growth without any impurities. This confirms that the NdNiO₃ films maintain phase purity and structure after 5% Al doping with varying thickness. The lattice mismatch can be calculated using the following mathematical expression:

Lattice mismatch (%) =
$$\frac{a_{sub} - a_{film}}{a_{sub}} \times 100$$
 (3.1)

Where a_{sub} and a_{film} are the pseudocubic lattice parameters of the substrate and thin film, respectively.



Figure 3.1. Full-scale XRD Patterns of 10,20, and 30 nm NdNi_{0.95}Al_{0.05}O₃ thin films on LAO (001) substrate.

The value of 3.86 Å for the out-of-plane parameter (c) was determined from the (002) peak of the X-ray diffraction pattern obtained for the NdNi_{0.95}Al_{0.05}O₃ thin film grown on the LAO (001) substrate. The pseudocubic lattice parameter of LaAlO₃ and NdNi_{0.95}Al_{0.05}O₃ are 3.79Å and 3.807 Å, respectively. Using equation 3.1, the lattice mismatch was calculated to be approximately -0.44%. The negative value of the lattice mismatch confirms that the NdNiO₃ thin film experiences an in-plane compressive strain, corresponding to an out-of-plane tensile strain. The out-of-plane parameter of the NdNi_{0.95}Al_{0.05}O₃ thin film exceeds the value of the pseudocubic lattice parameters ($a_{pc} = 3.807$ Å) of polycrystalline NdNi_{0.95}Al_{0.05}O₃ bulk, indicating that the film experiences out-of-plane tensile strain.

3.2. Temperature-dependent resistivity measurement:

We conducted experimental measurements to explore the temperature-dependent electronic transport properties of all the NdNi_{0.95}Al_{0.05}O₃ thin films below room temperature. As the thickness of thin films increases, resistivity increases in the metallic region due to partial relaxation of the strain. Below T_{MI} resistivity increases with an increase in thickness. The Insulting region has the highest resistivity for the lowest thickness thin film as shown in figure 3.2. The T_{MI} is determined by the temperature at which the slope of the resistivity curve changes. The temperature coefficient of resistivity (α) measures the change in resistivity with temperature. The influence of temperature on electrical resistivity was analyzed by determining the temperature coefficient (α) for all the thin films. Metals typically exhibit a positive α , signifying increased resistivity with rising temperate, whereas insulators typically display a negative α , indicating a decrease in resistivity with increasing temperature. As a result, when the phase transition occurs, the sign of α changes. The metal-to-insulator phase transition for 10, 20, and 30nm occurs at 128, 97, and 114 K, respectively.

Nickelates are a class of materials recognized for their Non-Fermi Liquid (NFL) properties, characterized by a power-law relationship between resistivity and temperature. In our study, we derived the value of n for thin films of NdNi_{0.95}Al_{0.05}O₃, as presented in Table 3.1, indicating that our films exhibit a non-Fermi liquid state. The plotted fit for the metallic state of NdNi_{0.95}Al_{0.05}O₃ films is illustrated in Fig. 3.3.



Figure 3.2. Resistivity vs Temperature behavior of 10,20 and 30 nm NdNi_{0.95}Al_{0.05}O₃ thin films on LaAlO3 (LAO) (001) substrate.



Figure 3.3. Fitting of Resistivity data of NdNi_{0.95}Al_{0.05}O₃ (a) 10 nm, (b) 20nm, and (c) 30 nm thin films grown on LAO (001) Substrate.

Га	ble	2 3	.1

Thickness	Temperature range	Fitting parameter
nm	(K)	(n)
10	150 - 300	1.6
20	150 - 300	1.6
30	150 - 300	1.3

3.3. Raman Spectroscopy:

Raman spectroscopy is a highly effective and versatile technique for studying phase and phonon modes. It is sensitive to variations in the local geometry, making it a valuable tool for in-depth structural analysis. So, to study the structural properties of 10, 20, and 30 nm NdNi_{0.95}Al_{0.05}O₃ thin film, roomtemperature Raman spectra have been recorded (shown in Fig. 3.4.). NdNiO₃ have an orthorhombically distorted structure within the Pbnm space group at room temperature. This structural distortion arises from the anti-phase tilting of adjacent NiO₆ octahedra ($a^{-}a^{-}c^{+}$ in Glazer's notation). In the bulk polycrystalline form, the primitive unit cell contains 20 ions with 60 vibrational modes $(7A_{1g} +$ $7B_{1g} + 5B_{2g} + 5B_{3g} + 8A_u + 8B_{1u} + 10B_{2u} + 10B_{3u}$) exhibited at the center of the Brillouin zone. Out of these modes, 24 Raman modes $(7A_{1g} + 7B_{1g} + 5B_{2g} + 5B_{3g})$ have been identified. From the Raman spectra obtained at room temperature, we found 5 Raman modes $(A_g + 2B_{1g} + 1B_{2g} + B_{3g})$ for 10, 20, and 30 nm NdNi_{0.95}Al_{0.05}O₃ thin films, with the LAO (001) substrate serving as a background, across the spectral range of 150-1000 cm⁻¹. The B_{2g} mode at 440 cm⁻¹ 1 and B_{1g} mode at 249, 300, and 566 cm⁻¹ appear due to the tilting of NiO₆ octahedra [1] and phase oscillation of NiO₆ octahedra [2] [3]. On Aluminium doping at the Nickel site, we have observed B_{3g} mode at 691 cm⁻¹. This mode represents the breathing motion of oxygen ions surrounding nickel ions. The variation of B_{1g} and B_{3g} mode with the thickness (Figure 3.5.) shows the redshift, indicating the partial strain relaxation in thin films.



Figure 3.4. Room temperature Raman spectra of 10,20 and 30 nm $NdNi_{0.95}Al_{0.05}O_3$ thin films.



Figure 3.5. Variation of Raman shift with thickness (a) B_{1g} mode and (b) B_{3g} mode.

3.4 Conclusion:

The effects of thickness variations on the physical properties of 5% Al-doped NdNiO₃ thin films were studied. The XRD peaks of all synthesized thin films shift on the 2θ -axis, indicating a variation in lattice parameter that shows the compressive strain on the LAO substrate. The red shifting of the B_{1g} and $B_{3g}\,Raman$ modes at 298 and 691 cm⁻¹ with thickness indicates the partial relaxation of strain in thin films. Substitution of nickel (Ni) with Al ions in NdNiO3 can induce distortions and in-phase rotations of the octahedra formed by the nickel and oxygen ions. These distortions and rotations can lead to changes in the Raman spectra, including the appearance of the B_{3g} mode at higher frequencies. Temperature-dependent resistivity data confirms the metal-to-insulator phase transition. As the thickness of thin films increases, resistivity increases in the metallic region due to partial relaxation of the strain. Resistivity increases with thickness below T_{MI}, with the highest resistivity observed in the insulating region for the lowest-thickness film.

Citations:

[1] C. Girardot, J. Kreisel, S. Pignard, N. Caillault, and F. Weiss, Raman Scattering Investigation across the Magnetic and Metal-Insulator Transition in Rare Earth Nickelate RNiO₃ (R = Sm,Nd) Thin Films, Phys. Rev. B 78, 104101 (2008).

[2] H. C. Gupta, M. K. Singh, and L. M. Tiwari, A Lattice Dynamical Investigation of Raman and Infrared Wavenumbers at the Zone Center of the Orthorhombic NdNiO₃ Perovskite, Journal of Physics and Chemistry of Solids 64, 531 (2003).

[3] M. Zaghrioui, A. Bulou, P. Lacorre, and P. Laffez, Electron Diffraction and Raman Scattering Evidence of a Symmetry Breaking at the Metal-Insulator Transition of NdNiO₃ Phys. Rev. B 64, 081102 (2001).