Effects of Ga-doping on Structural, Electronic, and Vibrational Properties of NdNiO₃ Thin Films

M.Sc. Thesis

By Satyabrata Mandal



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Effects of Ga-doping on Structural, Electronic, and Vibrational Properties of NdNiO₃ Thin Films A THESIS

Submitted in partial fulfillment of the requirements for the award of the degree

of Master of Science

by

Satyabrata Mandal



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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled Effects of Ga-doping on Structural, Electronic, and Vibrational Properties of NdNiO₃ Thin Films in the partial fulfillment of the requirements for the award of the degree of MASTER OF SCIENCE and submitted in the DISCIPLINE OF PHYSICS, Indian Institute of Technology Indore, is an authentic record of my own work carried out during the time period from August 2021 to June 2023 under the supervision of Prof. Krushna R. Mavani, Discipline 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. Q = 0

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

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Dedicated to my Guardians

and Teachers

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Abstract

The thesis reports on the structural, electronic transport, and vibrational properties of NdNi_{1-x}Ga_xO₃ (x = 0 - 0.2) thin films grown on LaAlO₃ (001)(LAO) substrates using the pulsed laser deposition method. The structural investigations show that the thin films experience compressive in-plane strain. The temperaturedependent resistivity curves indicate that NdNiO₃(NNO) film undergoes an electronic phase transition from metal to insulator, while 20% of Ga doping shows totally insulating behaviour below room temperature. The overall resistivity of the system increases systematically with a gradual increase in Ga doping. The resistivity results exhibit a close agreement with the power law equation with the indication of the non-Fermi liquid state. The Ga doping at Nisite in NdNiO₃ thin films shows a systematic red-shift of Raman modes. These findings provide insights into the properties of NdNi₁₋ $_{x}Ga_{x}O_{3}$ thin films and their potential applications in electronic devices.

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Chapter 1

1.1. Introduction to thin film oxides:

Thin films, nanomaterials, and fabrication processes have attracted a lot of attention from researchers in recent years because of the vast opportunities they present for improving a wide range of technical fields[1]. Researchers have made tremendous strides in shrinking the size of gadgets while increasing their functionality, and thin films have emerged as a viable solution. Thin films are composed of multiple layers of material, each with a thickness typically ranging from a few nanometers to a few micrometers. Thin films have certain distinctive characteristics in the realms of optics, electronics, magnetism, chemistry, and mechanics. They can be used in a wide variety of applications, such as reflective and antireflective coatings, interference filters, compact discs, semiconductor devices, memory discs, gas and liquid sensors, and ultrafast switches[1]. Transition metal oxides, often known as complex oxides, are a subset of thin films that show great potential for future technological advances. The perovskite family of materials has several benefits over the more common siliconbased technology[2]. The concept of Mott Electronics has the potential to enhance current technology by increasing its functionality and laying the groundwork for future breakthroughs in this area. The interplay between lattice, charge, orbital, and spin degrees of freedom gives perovskite oxides their unique and interesting characteristics[3]. Rare earth cuprates (RCuO₃), rare earth nickelates (RNiO₃), and layered rare earth manganates (RMnO₃) are the most studied perovskite oxides due to their high-temperature superconductivity, colossal

magnetoresistance (CM), and giant magnetoresistance (GM), respectively.

1.1.1. Perovskite Oxide:

The first Perovskite substance, CaTiO₃, was found in the Ural Mountains of Russia by Gustav Rose in 1839[4]. Perovskite oxides can be identified by their characteristic chemical formula, ABO₃, in where A denotes a rare earth cation of greater size, B denotes a transition metal cation of lesser size, and O denotes oxygen. As can be seen in Figure 1.1, each A ion is completely surrounded by 8 BO₆ octahedra in this configuration. There are eight octahedra in total; four above and four below. The tolerance factor is the determining factor in the stability of the crystal structures. One can expect that if the tolerance factor value is one then it should be a perfect cubic perovskite structure[5]. Here is an equation that describes the tolerance factor t :

Where R_A , R_B , and R_O are ionic radii of A, B, and O ions respectively. Generally, the tolerance factor(t) lies between 0.75 to 1.



Figure 1.1: Ideal ABO3 cubic perovskite

Also for values from 0.7 to 0.9, the tolerance factor values reflect the orthorhombic/ rhombohedral structure of the Perovskite oxide. To meet the tolerance factor stability criteria, an ion must be sufficiently big. One of the fundamental properties of the stability of perovskite structures is the modification of the radius of the A ion. If the size of the A ions is altered, the BO₆ octahedra will be distorted or tilted, leading to structural instability. The angle between the B-O-B bonds is decreased as distortion increases, leading to a greater tilt. This expands the band gap by decreasing the overlap of d- and p-orbitals in the octahedron. This effect indicates that it is an Orthorhombic distortion. Due to the perovskite structure's high tolerance towards A and B ion radii and the ions' individual degrees of freedom, many oxides display it. Because of their great tolerance, these chemicals can be used as structural modifiers or chemical substitutes[6]. Transition metal oxides undergo both structural and geometrical distortion. When there is more than one degenerate state for an electron, the energy cost of the electronic arrangement increases. A deformation of the structure occurs, leading the system to a less symmetrical and less energetic state, which reduces the overall energy of the system. In an octahedral setting, for instance, the crystal field splits five degenerate d orbitals into three t_{2g} (lower energy) and two e_g (higher energy) orbitals. For the metal ions with d^1 , d^2 , d^4 , d^6 , d^{7} , and d^9 configuration, there are more than one state free for the last electron. By stretching or compressing the BO6 octahedra in such a way that the energy of a few orbital states becomes lower than that of the others, this confused condition at the last electron can be avoided. Z-out distortion refers to an image being stretched out, while z-in distortion refers to an image being compressed. Together, the B-O-B bond length and bond angles determine the electrical and magnetic properties of ABO₃-type perovskite, a phenomenon known as Jahn-Teller distortion. Thus, the Jahn-Teller distortion is crucial in establishing the characteristics of these oxides[7].

1.1.2. Rare earth nickelates (RNiO₃) :

RNiO₃ is their general formula. As a result of their sharp metal-to-insulator transitions (MIT), rare earth nickelates are an interesting and useful material for constructing electronic switches, electronic oscillators, gated devices, thermal and chemical sensors, and so on. Temperature, doping, strain, and the radii of rare earth ions are only some of the characteristics that can be used to fine-tune electronic transitions.



Figure 1.2: Phase diagram of RNiO₃ compounds [8]

The phase diagram (Fig. 1.2) shows that, other than LaNiO₃, all rare earth perovskites exhibit a first-order metal-insulator phase transition, with rare earth ionic radius observed to be a factor affecting T_{MI} . Above room temperatures, all *R*NiO₃ compounds adopt a metallic *Pbnm* orthorhombic phase, while LaNiO₃ always keeps a metallic *R3⁻c* rhombohedral phase at all temperatures. As the size of rare earth ion changes, the packing fraction of the perovskite structure also changes

and it causes phase transitions. Since their metal-to-insulator and magnetic transitions occur at the same temperature, i.e. 135 K for PrNiO₃ and 200 K for NdNiO₃, these two rare earth nickelates have garnered a great deal of attention[9]. The charge, spin, and orbital angular momentum of these two oxides are all highly correlated with one another. PrNiO₃ lies in the category of charge transfer insulator[5]. The degree of overlap between the 3*d* orbitals of nickel and the 2*p* orbitals of oxygen is crucial to the efficient transport of electrons. This shift in local geometry also has an impact on the physical properties of highly linked systems. The electronic transport in strongly correlated oxides is a function of the carrier concentration, which can be modified by doping. Recently, PrNiO₃ has proven to be a platform for studying quantum criticality occurrences in tightly related Mott frameworks.

Thin film formation using excimer laser:

A thin film is a material layer with a thickness of just a few nanometers or less. Thin film deposition is the methodical addition of material to a surface in successive layers. Thin films have been widely employed for more than half a century in a variety of applications, including but not limited to electrical devices, instrument hard coatings, optical coatings, decorative parts, etc. Thermal evaporation, chemical decomposition, and the evaporation of source materials by the irradiation of energetic species or laser light are only a few of the methods available for thin film deposition on a single crystal substrate [10]. The following are typical of the thin film growth process in general:

 The first steps in the production of thin films of any material follow a nucleation process, followed by stages of development.

- 2. Conditions during deposition, such as choice of the substrate, growth temperature, growth rate, chemical composition, and background gas pressure, all play a role in nucleation and subsequent development phases.
- 3. External forces, such as electron or ion bombardment, play a crucial role in the nucleation stage.
- 4. The films' phase and orientation are controlled by both the deposition conditions and the substrate's crystal structure.

Film composition, crystal phase and orientation, film thickness, and microstructure are the basic controllable properties of thin films. Many interesting properties are observed in bulk also but a very fine tuning of properties is observed in thin film form. There are different thin film growth techniques:

.

- a) Island growth
- b) Layer-by-layer growth

c) Mixed growth.

In almost all practical cases, the growth takes place by island formation. Once a continuous layer has been established, anisotropic growth occurs normally to the substrate in the shape of cylindrical columns. The initial nucleation density can be used to predict the final crystallite size, also known as the lateral grain size. Many methods exist for depositing thin films.

1) DC sputtering.

- 2) Magnetron sputtering.
- 3) Molecular beam epitaxy.

4) Sol-gel method.

5) Pulse laser deposition.

Out of all these methods, we have opted for Pulse laser deposition for thin film synthesis. It is broadly described in Chapter 2.

1.2. <u>Electrical Transport:</u>

The amount of current that flows through a material when a given voltage is applied is known as the substance's "electrical transport." The contrast in the conductivity range is generally represented by two classes of materials, metals, and insulators. Metals have a conductivity on the order of $10^9 \Omega^{-1} \text{cm}^{-1}$, while for the case of non-metals typically have conductivity in the range of $10^{-18} \Omega^{-1} \text{cm}^{-1}$. According to the textbook definition of metal and insulator, metals have finite conductivity at absolute zero Kelvin (K), while insulators have zero conductivity at the same temperature. Depending on the temperature, RNiO₃ exhibits both metallic and insulating behavior in a particular temperature range. To find the transition from metal to insulator, we can easily focus on the $(d\rho/dT)$ value. In the insulating state, this value is less than zero, i.e., with decreasing temperature, the value of resistivity increases, and contrarily, the metallic state exhibits $(d\rho/dT) > 0$. The evolution of various models to find the exact explanation of the conductivity of RNiO₃ is given below[11].

1.2.1. a) <u>Free Electron Theory:</u>

Paul Drude's "free electron model" was a groundbreaking theory that improved our understanding of electron behavior in materials, especially metals[12]. The conduction electrons in a solid are assumed to operate like gas particles in this model, with no mutual interaction between them. The potential (Fig, 1.3) at the metal's surface is the key factor affecting these electrons. Several underlying assumptions form the basis of the model, which are as follows:

- I. There is no interaction between electrons.
- II. Electrons inside metal are totally unbound.
- III. There is no effect of the positive potential of ions on the lattice.
- Electrons undergo instantaneous, continuous collision among themselves.



Figure. 1.3. Schematic of potential well for free electrons with infinite potential at the surface and zero otherwise.

The electrical resistivity (inverse of conductivity) of a metal in the presence of an external field is given as:

where n is the free electron density, r is known as relaxation time, the average time between two consecutive collisions, e is the charge of an electron, and m is the electron mass.

The Drude model, developed to explain various electrical and thermal phenomena in metals around room temperature, successfully accounted for Ohm's law, DC and AC conductivities, thermal conductivities, the Hall effect, and magnetoresistance. However, it had limitations when it came to explaining certain aspects.

One of the shortcomings of the Drude model was its tendency to overestimate the electronic heat capacity of metals. Additionally, it failed to provide a comprehensive explanation for heat capacity, temperature-dependent resistivity, and the sign of the Hall coefficient observed in certain metals. Another drawback was its inability to distinguish between metals and insulators.

To address these limitations, Arnold Sommerfeld made significant improvements to the Drude model in 1927, resulting in the Drude-Sommerfeld model. In this enhanced model, electrons were treated as quantum particles, incorporating the principles of quantum mechanics and Fermi-Dirac statistics. As a result, Schrödinger's equation could be readily applied within this framework.

The Drude-Sommerfeld model effectively accounted for the Wiedemann-Franz law, which relates electrical and thermal conductivity. It also provided insights into temperature-dependent resistivity, electron heat capacity, the shape of the electronic density of states, and paramagnetic susceptibility. Despite these advancements, however, the model still fell short in distinguishing between metals, semiconductors, and insulators.

In summary, while the Drude model explained several phenomena in metals, it had limitations in terms of accurately predicting heat capacity, temperature-dependent resistivity, and the sign of the Hall coefficient for certain metals, as well as distinguishing between different types of materials. The Drude -Sommerfeld model, with its incorporation of quantum mechanics, addressed some of these issues but still did not fully capture the distinctions between metals, semiconductors, and insulators.

b) **Band Theory for Solids:**

It is also known as the nearly free electron theory. Because of its oversimplification, free electron theory failed because of its premise that the potential field of positive ion cores is constant and, for convenience, was taken as zero. However, in practise, electron mobility in a solid is complicated, and we cannot ignore potential due to the lattice field. The potential field is assumed to be periodic in band theory, with a period equal to the lattice constant. The potential is given as :

$$V(a + x) = V(x)$$
 ------ (1.3)

where a is lattice constant. The actual potential is parabolic but we consider it as pulse by using the Kroning-Penny model. One dimensional Schrödinger equation for a single electron in such periodic potential is given by.

$$\left[\frac{-h^2}{8m\pi^2}\frac{d^2}{dx^2} + V(x)\right]\psi(x) = E\psi(x) \quad -----(1.4)$$

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

$$\psi(x) = e^{ikx}u_k(x) \quad \dots \quad (1.5)$$

 $u_k(x)$ is a periodic function, k is wave vector of electron. After solving the equation, the relation between wave vector k and energy E comes out as:

where, $\alpha^2 = \frac{8\pi^2 mE}{h^2}$ and $P = \frac{4\pi^2 mV ba}{h^2}$, h^2 is constant with b as barrier width and a period of lattice.



Figure 1.4: Schematic of bands in metal, semiconductor and insulator and variation in their band gaps.

The number of occupied energy levels is limited by the equation since $\cos(ka)$ can only take on positive or negative values. This means that the electron wave function cannot be solved in all energy regions. The forbidden energy ranges are referred to as "band gaps." The presence or absence of a band gap characterizes a substance as a metal or an insulator. There is no band gap in metals, therefore insulators have a very band gap measuring several eV in width. In between, semiconductors have a low-energy band gap and conductivity above a certain temperature.

Band gap is shown in Fig. 1.4 to differentiate between metal, semiconductor, and insulator.

C). Mott-Hubbard model:

Band theory fails to describe insulating states of transition metal oxides because it does not account for electron-electron interaction. After Boer and Verwey pointed out the insulating state of NiO and other TM oxides, N.F. Mott first evoked the possibility of electron localization due to large coulomb interactions. Later the theoretical interpretation of this possibility was successfully given by Hubbard, and according to this model, the Hubbard Hamiltonian can be written as:

where, U is the on-site Coulomb interaction energy, t is the hopping integral, $C_{i,\sigma}$, and $C_{j,\sigma}$ are creation and annihilation operators [13]. This Hamiltonian is the convergence of two contrasting terms:

This Hamiltonian consists of two terms: a) Kinetic energy term, the term containing hopping integral and b) Coulomb repulsion term, the term containing coulomb repulsion, which is given by

 $U = E(d^{n+1}) + E(d^{n-1}) - E(d^{2n}) \quad ----- \quad (1.8)$

U is the energy cost of putting two electrons at one site, which is allowed by Pauli Exclusion Principle. This energy cost is large in strongly correlated oxides resulting in the splitting of d orbital in twobands. The lower band is fully filled and called Lower Hubbard band (LHB) whereas the upper band is empty and called Upper Hubbard band (UHB). Here, the strength of electron correlation is given by U/t which is a critical parameter in determining the conducting state of the material [14]. For metals, U/t<<1, i.e. the onsite coulomb repulsion is negligible but for insulators the coulomb repulsion is strong so U/t >>1. Such insulators are called Mott-Hubbard insulators.

It is described in fig 1.5.



Figure 1.5: Schematic of energy vs density of states for a metal having half-filled d band caused by weak electron-electron correlation, and splitting of d band into LHB and UHB for an insulator due to strong correlation.

d) Zaanen-Sawatzky-Allen model:

The model relies on the values of the charge transfer gap (Δ), the band width (W), and the coulomb repulsion energy (U). Δ is the energy difference between the anion 2p band and unoccupied 3d band of transition metal, U is the energy difference between LHB and UHB of

Ni and W is the bandwidth of these Hubbard bands (Fig. 1.6) [16]. Band gap in this model is shown to be either U or Δ , depending on which is smaller on the energy scale.

So, there are two possibile types of insulators:

- a) Mott- Hubbard Insulator.
- b) Charge transfer Insulator.
 - a) When W<U< ∆ i.e. energy difference between unoccupied and occupied d bands is less than that of Oxygen p and Nickel upper Hubbard band, then conduction takes place from Nickel LHB to UHB. They are called Mott insulators.
 - b) When W< Δ<U i.e. energy difference between unoccupied and occupied d bands is more than that of Oxygen p and Nickel upper Hubbard band, then conduction takes place between Oxygen 2p to Nickel UHB. They are called charge-transfer insulator. RNiO₃ i.e. rare earth nickelates lie in the category of charge transfer insulator.



Figure 1.6: Schematic for ZSA framework showing two types of insulator, a) Mott insulator, b) charge transfer insulator, and two types of metals c) low U metal and d) low Δ metal.

1.2.2 Conduction Mechanisms:

Temperature has a significant effect on electronic transport in solids like metals and insulators, and the behaviour of temperature dependency varies depending on the types of materials. How metals conduct electricity: From a purely classical viewpoint, the following factors contribute to a metal's resistivity: The defect is caused by either a) phonon-electron interaction or b) impurity, imperfection, or disorder. Considering these factors, we can write down a formula for the resistivity:

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

Resistivity due to disorder does not depend upon temperature, but the resistivity contributed by electron-phonon interaction or phonon scattering linearly depends on temperature that provides the following mathematical expression:

The above expression includes the Boltzmann constant (k), the ion's mass (M), and θ signifies the Debye frequency. As a result, the total resistivity depends linearly on temperature, and the phonon-electron interaction becomes dominant at higher temperatures. However, at the lower temperature, the value of phonon is infinitesimally small, and the phonon defect, which varies continuously with temperature, dominates the overall resistivity.

However, the above theory does not support the experimental results. The reason behind this disagreement is the ignorance of the mutual interaction of electrons. In 1956, Soviet physicist Lev Landau incorporated the concept of mutual interaction of fermions and showed the quadratic dependency of temperature with resistivity. This modified picture of conductivity is known as the classical Landau picture or mostly pronounced as Fermi liquid behavior. The mathematical expression supporting this model is known as power law equation. It can be represented by:

where, ρ_0 is the residual resistivity at absolute zero temperature that occurs due to the lattice - imperfections, grain boundary, dislocations, defects ,and the constant A signifies electron-electron interaction. This model is valid in the low-temperature metallic state [16], [17]. Specifically, the exponent n in this relationship is less than 2. If the value of n =2, then the material shows the behavior of the Landau Fermi liquid state. For some cases, n < 2 which is a deviation to NFL (Non-Fermi Liquid) state. Nickelates are a type of material that exhibits Non-Fermi Liquid (NFL) behavior, which can be characterized by a powerlaw equation between resistivity and temperature.

Conduction mechanism in insulators:

In transition metal oxides, the conductivity of insulating states can be described using a number of different models based on activation energy, hopping energy, etc. Several of these versions are discussed in detail below.

Arrhenius Model:

At high enough temperatures, the most common conduction process in semiconducting materials is thermally stimulated band conduction. At high temperatures, the charge carriers can be shifted from the valence band to the conduction band by the application of thermal energy, and the Arrhenius equation characterises the temperature dependence of resistivity as follows:

$$\rho = \rho_0 \exp\left(\frac{\Delta}{k_B T}\right) \qquad (1.11)$$

where Δ stands for the conduction activation energy and k_B is Boltzmann's constant. If we plot the relationship between lnp and 1/T using the preceding equation, we get a straight line. When the temperature is less than the activation energy, charge carriers can hop from place to place, facilitating conduction. This type of carrier hopping is known as nearest neighbour hopping since it is confined to the closest neighbours. Nearest neighbour hopping requires less activation energy than thermally induced band conduction. This conductance mechanism is typical of disordered materials.

Variable range hopping:

hopping approach conduction Another for mechanism between discrete states is Mott variable range hopping (VRH). Although this Mott VRH conduction mechanism was initially reported in amorphous semiconductors, it was subsequently found in a number of disordered insulators. The VRH facilitates charge transfer at low temperatures when thermal energy is insufficient to activate charge carriers across the gap between the valence and conduction bands. Hopping phonons in the lattice typically aid in conduction in this scenario. When the charge transfer states are closely spaced in the lattice, the hopping of charge carriers is more likely since it requires less energy to do so. However, these two conditions are not always satisfied. Since the hopping energy and the variety of localised states play significant roles in this conduction mechanism, we can express the hopping probability at low temperatures as:

$$P \propto \exp(-\alpha R - \beta \Delta)$$
 ------(1.12)

where β is a constant that is inversely proportional to temperature and Δ is a constant that exhibits hopping energy, and R is the spatial separation between two localized states. The constant α which related to localization length.

When compared to states that are separated by a great distance, the difference in energy that exists between states that are near together in space will be bigger. As a consequence of this, electron hopping is preferred for the sites that are spatially distant from one another in comparison to the sites that are adjacent to one another. The probability of hopping should be set so that it corresponds to the value of R and Δ that gives the best results. Mott's formula for calculating the temperature-dependent resistivity of a material is as follows:

$$\rho = \rho_0 \exp\left(\frac{T_0}{T}\right)^{\frac{1}{n+1}}$$
 (1.13)

In this case, n represents the dimension of the system, and T₀ is the temperature that is characteristic of it. The value of the term T₀ is determined by the density of states N (E) at the Fermi level while preserving the relation $k_B T_0 = \frac{18}{N(E)\alpha^3}$, in which refers to the length of the N(E) localization. In the case of three dimensions (n = 3), it is not difficult to deduce, using the expression for temperature-dependent resistivity, that the value of ln varies in a linear fashion with T ^{-1/4} in accordance with this model.

1.3. Motivation:

As described earlier, the physical properties of RNiO₃ such as electronic, magnetic, and structural properties are strongly correlated and can be varied with various factors such as doping percentage, strain, thickness, oxygen stoichiometry, etc. There are various reports on the hole and electron doping in RNiO₃, which affects the physical properties of these materials via carrier injection. In the present study, we have selected NdNiO₃ as the parent compound due to its strongly correlated nature. We have doped Ga at Ni-site in NdNiO₃ due to the isovalent nature of Ga and Ni ions. This isovalent nature neglects the effect of carrier injection. However, there are no such reports available on the isovalent doping in perovskite nickelates. Therefore, we have studied Ga -doping at the Ni-site in RNiO₃ thin films to investigate the effects of aliovalent dopant. Since the ionic radii of Nd³⁺ and Ni³⁺ ions are 1.27 Å and 0.6 Å, respectively, whereas the ionic radii of Ga³⁺ ions are 0.62 Å, Ga-ion can be easily doped at the Ni-site of NdNiO₃ thin films. We have studied the structural change and transport properties in our current investigation by varying the Ga -ion doping percentage in NdNiO₃ thin films deposited on LaAlO₃ (LAO) single crystal substrates with (001) orientation.

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Chapter 2

Experimental Techniques:

This chapter provides overview of the synthesis and characterization techniques used perform the reported study. Synthesis methods includes the solid-state reaction approach for preparing bulk pellets and the pulse laser deposition technique for preparing thin films. In characterization techniques, we have employed X-ray diffraction and Raman spectroscopy for structural analysis and to investigate electronic transport properties we have followed the temperaturedependent resistivity measurement. We have opted following experimental techniques in our project:

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) technique
- b) Raman Spectroscopy
- c) Temperature-dependent resistivity measurement

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

We have chosen the conventional solid-state reaction method as our preferred technique for synthesizing bulk NdNiO₃ and NdNi_{1-x}Ga_{xO3} pellets. This method is widely used for oxide synthesis and offers several advantages [9]. One of its key benefits is that it is a solvent-free process, involving the reaction of powders.

The process begins with weighing and carefully mixing highly pure powders in the appropriate stoichiometric ratio. Achieving a homogeneous mixture is crucial, so the powders are thoroughly ground. This grinding step serves multiple purposes: it reduces particle size, increases surface area, and promotes a higher reaction rate. Typically, grinding is performed using a pestle and mortar for approximately 4-5 hours. To ensure proper mixing, acetone can be added, which gradually evaporates during the grinding process.

Since these oxides do not react at room temperature, the grinded powder needs to be initiated for the reaction to occur. This is achieved through a process called calcination, where the powder is heated at high temperatures. During calcination, volatile gases such as CO₂ and NO₂ are eliminated. After the initial heating, a second grinding step lasting 2-3 hours is performed to maintain uniform particle size. Subsequently, the powders are calcinated again to achieve uniformity and a single phase.

To enhance the intimate contact between crystallites, the powder is pressed into pellet form using a hydraulic press with a 15 mm-20 mm die set. The resulting pellet is then subjected to hightemperature heating, a process known as sintering. The primary objective of sintering is to densify the compound, creating a solid, compact structure. By employing the conventional solid-state reaction method, we capitalize on its solvent-free nature and leverage the reaction of powders to synthesize NdNiO₃ and NdNi_{1-x}Ga_xO₃ pellets. This approach involves precise weighing, thorough grinding, controlled heating through calcination, and final sintering to achieve the desired densification of the compound.

Synthesis of NdNiO₃ and NdNi_{1-x}Ga_xO₃ targets:

We have prepared NdNiO₃ and NdNi_{1-x}Ga_xO₃ samples by mixing Nd₂O₃, Ga₂O₃, and NiO powders of high purity in proper stoichiometric ratios. For PLD, a target material is required in a large pellet form. The pellet will be synthesized using Solid State Reaction as shown in the chart below:

$$Nd_2O_3 + (1-x)NiO + (\frac{x}{2})Ga_2O_3 \longrightarrow NdNi_{1-x}Ga_xO_3$$

The following block diagram includes main steps:

Very high-purity powders of Nd_2O_3 , NiO, and Ga_2O_3 were measured out using a high-precision electronic weighing machine to ensure the correct stoichiometric ratio.

In order to get the right reaction out of the powders, they were first ground for 4-5 hours in a pestle mortar to ensure uniform mixing, and then calcinated at 800°C for 12 hours.

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Particle size uniformity was maintained by re-grinding for another two to three hours, then calcination at 800°C for another 12 hours.

After a second heating, the mixture was ground for 30 minutes before being crushed into pellets (diameter=20 mm) using a Hydraulic press and then sintered at 1000°C in a tube furnace for 12 hours.

Substrate selection:

The selection of the substrate upon which thin films are to be deposited is an extremely important step in the production of the films. In our particular instance, we have decided to go with a LaAlO₃ (LAO) single-crystal substrate oriented in the (001) direction. It is possible to investigate the pseudo-cubic lattice characteristics of the NdNiO₃ bulk material and the LAO (001) substrate in order to determine the amount of strain that was experienced by the thin films. We have determined that the thin film undergoes compressive strain in the inplane direction and, as a result, experiences tensile strain in the out-ofplane direction.

2.1.2. Thin film synthesis using PLD method:

Thin films have been widely employed for more than a halfcentury to make various devices such as electronic devices, instrument hard coatings, optical coatings, decorative parts, enzymatic glucose biosensors, neural circuits, and so on. The major steps followed to deposit thin films are given below:

- Production of the appropriate atomic, molecular, or ionic species.
- Transport of these species to the substrate through a medium.
- Condensation on the substrate, either directly or via a chemical and/or electrochemical reaction, to form a solid deposit.

We can easily classify the thin film deposition techniques into two categories:

a) Physical Vapour Deposition (PVD):

In the process of physical vapour deposition, atoms are transferred from a solid or molten source to a substrate by use of various physical processes such as evaporation, sublimation, or ionic impingement on a target. Evaporation and sputtering are the two most prevalent techniques for depositing films using the PVD technique.

b) Chemical Vapour Deposition (CVD):

When the material that is deposited on the film is the result of a chemical reaction, the technique known as chemical vapour deposition is utilised. It is widely utilised in industrial settings for the production of high-purity crystalline films of various chemicals, including complicated oxides, nitrites, and others[10].

The method known as Pulsed Laser Deposition (PLD) was utilised in the production of our thin films. Within the realm of Physical Vapour Deposition (PVD), it is the technology that sees the most widespread application.

Experimental design of PLD technique:



Figure 2.1: Schematic diagram of the pulsed laser deposition (PLD) system.

One of the most effective and versatile methods for depositing thin films on suitable substrates is the PLD method. Various

kinds of lasers, including UV, visible, and infrared light, can be used in this method. O switched Nd:YAG excimer laser (λ - 1.064 µm, second harmonics - 532 nm, third harmonics - 266 nm) which is also called solid-state laser, KrF (λ - 248nm), and ArF (λ - 193nm) excimer lasers, etc., are among the most popular types of lasers. The KrF excimer laser, which produces ultraviolet pulses, was the type of laser we employed to create our PLD chamber. Stainless steel is used for the PLD chamber's construction, and its components include a target holder, a substrate holder, a heating instrument, and a process gas intake. In the PLD chamber, the raster and rotational motion of the target holder are precisely set to ensure that the ions are ablated equally from the target. The target holder is fixed at a specific distance from the substrate holder. To keep the substrate holder at the correct temperature during thin film deposition, a heater is connected to it. The vacuum system makes use of a rotary pump in addition to a turbomolecular pump. The rotary pump brings the ambient pressure in the PLD chamber down to around 10⁻³ Pa, which is the target pressure. The turbomolecular pump has the capability of reaching base pressures of less than 10⁻⁶ Pa. Diagrammatic representation of the PLD chamber may be found in Figure 2.1.

When a high-energy laser beam strikes the material at a vacuum and temperature, a plasma plume emerges [18]. Many review publications provide theoretical explanations for the formation of plasma plumes[4], [5]. Plasma plume ablation cannot be explained by a single mechanism, according to studies, but rather by a combination of mechanisms. Ablation occurs when the absorbed laser energy E_{ab} is larger than the binding energy E_b of the atoms on the target materials' surface. The following is a representation of the condition: $E_{ab} > E_b$. When a laser pulse is absorbed by the target, the energy is transformed first into electronic excitation, then into thermal, chemical, and mechanical energy, causing evaporation, ablation, and plasma production. The laser ablation and absorption process take about 30 nanoseconds. Plasma plume made up of the ablated ions and materials take an elliptical or roughly circular shape and are directed towards the

substrate. Adjusting the partial pressure of the inlet gas can change the shape and focus of the plasma plume and also balances the oxygen stoichiometry of the depositing sample.

The partial pressure can be altered to change the kinetic energy and scattering rate of the plasma plume; as a result, this deposition parameter can be managed to provide the best possible growth. Ions in the plasma plume have been measured to have kinetic energies ranging from 0.1 to 10 eV in general. The partial pressure has an effect, not only on the kinetic energy of the particles in the plasma plume, but also on their scattering. This dynamics of plasma has to be maintained inside the PLD chamber.

Based on the various experimental and theoretical studies, there are three main growth types:

- a) Island Growth
- b) Layer growth
- c) Mixed Growth

a) Island Growth:

When the tiniest clusters to remain stable nucleate on the substrate and expand into three dimensions, they exhibit morphologies reminiscent to islands. The atoms or molecules being deposited in this method of development form stronger bonds with one another than they do with the substrate. This occurs frequently when the film and substrate are made of different materials. Metal and semiconductor (i.e. Group IV, III-V, etc.) films commonly grow in this mode when they are produced on oxide substrates [6].

b) Layer growth:

It happens when the smallest nucleus extends in two dimensions, producing planer sheets. When a material is grown layer by layer, the atoms or molecules that are deposited initially have stronger bonds to the substrate than to one other. Until the bulk bonding strength is achieved, this effect will persist indefinitely. Epitaxial development of semiconductors and oxide materials is a common example[7].

c) Mixed Growth:

It combines aspects of both island expansion and layering. After a certain number of monolayers have been formed, further layer-by-layer growth becomes energetically unfavourable, and islands begin to form in this growth phase. In some metal-metal and metal-semiconductor systems, this type of development has been observed and is relatively common.

Thin film growth:

A plasma plume created by a high-energy laser quickly extends in all directions away from the target surface. The formation of a film takes place on a substrate, upon which some of the material that was in the plume re-condenses. There are a few different external characteristics that, when combined, have a significant impact on 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 kinetic energy of the particles and their growth rate are both under the control of the laser energy, however, the morphology of the plume is under the control of the process gas, which also assists in achieving the stoichiometry, particularly in the case of complicated oxides. During the deposition process, the substrate is typically maintained at a high temperature. During the nucleation and growth processes of thin films, the temperature of the substrate is an extremely important factor. The distance from the target to the substrate is another important factor that plays a role in determining the angular spread of the plasma plume.

Synthesis of NdNi_{1-x}Ga_xO₃ (x=0-0.2) thin films on LAO (100) substrate:

NdNi_{1-x}Ga_xO₃ (x=0-0.2) thin-film depositions are carried out on a single crystal LaAlO₃ (LAO) substrate with dimensions of $(2 \times 5 \times 0.5)$ mm. The substrates were properly sonicated for 10 minutes, first in acetone and subsequently in propanol. Before deposition, the chamber was evacuated and then filled with pure oxygen as background gas. During the deposition, the following parameters were maintained.

Parameter	Value
Ablation energy	310 mJ
Laser Wavelength	248 nm
Target	$NdNi_{1-x}Ga_xO_3(x=0-0.2)$
Substrate	LAO (100)
Base vacuum level	1.3 ×10 ⁻³ Pa
Oxygen partial pressure	40 Pa
Target substrate distance	4.5 cm
Deposition temp.	720° C
No. of shots	1400
Estimated Thickness of film	20 nm
Rep. rate	4 Hz
Annealing Pressure	1000 Pa

Table- 1.1

After deposition, the deposited thin films were post-annealed at 720 °C keeping 1000 Pa oxygen partial pressure for 3 minutes.

Advantages of PLD:

- It allows for more customization of laser parameters such as laser energy, substrate temperature, target-to-substrate distance, order of vacuum, oxygen partial pressure, and others.
- 2. Even when the target is multiphase, PLD may keep the thin films they produce pure in terms of phase.
- 3. Regulating the number of pulses controls the thickness of the thin films.
- 4. PLD may also be used to make multilayer films and heterostructures. Unlike techniques like Molecular Beam Epitaxy (MBE), where the composition is regulated by modifying the ratio of the various sources arriving on the substrate, in PLD the stoichiometry of the film is controlled by the capacity to produce a target with the desired composition.

Disadvantages of PLD:

- 1) As the plume size in PLD is narrow enough, it is very difficult to deposit thin films with uniform thickness.
- During the fast heating and cooling process, particulates such as micro-size lumps or droplets are formed in the target.

2.2. Characterization Technique:

After synthesis, all thin films are examined for phase purity by implementing the X-ray diffraction (XRD) technique. Raman spectroscopy at room temperature and temperature-dependent Raman spectroscopy is used to probe structural changes brought on by varying any given parameter, like temperature or doping levels. The temperature-dependent resistivity of thin films is measured over a broad temperature range, from 300K to 12K, using a closed-cycle refrigerator (CCR).

Each characterization technique's specifics are explained in the sections below.

2.2.1 X-ray Diffraction (XRD) :

X-ray diffraction is a method that is utilised in the process of analysing the structure of crystalline substances. It is predicated on the idea that when a beam of X-rays interacts with a crystal, the X-rays are either diffracted or scattered in different directions by the atoms in the crystal lattice. This idea underpins the concept of x-ray diffraction. By analysing the angles and intensities of the X-rays that are diffracted by the crystal, one can acquire significant insight into the manner in which the atoms are arranged within the crystal. The X-rays have an effect on the atoms that make up the crystal lattice, and this has the effect of producing both constructive and destructive interference in the scattered waves. This interference pattern is recorded by the detector, and the results are often presented in diffraction pattern form. The diffraction pattern is made up of a succession of spots or peaks, and each one of these spots or peaks corresponds to a unique configuration of atoms contained within the crystal.

Max von Laue, W. L. Bragg, and W. H. Bragg, the son of W. L. Bragg, made the discovery in 1912 that led to the beginning of a new era in the field of material characterization. This method is frequently applied in the process of investigating the internal structure of the material, as well as the lattice crystallinity, lattice parameters, strain on the lattice, etc.

Working Principle:

The process of X-ray diffraction involves the utilization of an X-ray tube, which operates based on the principles of electron acceleration and impact. Initially, an alternating voltage is applied to the electrodes of the X-ray tube, causing the filament inside the cathode to

heat up. This heating process leads to the emission of free electrons from the cathode towards the anode.

The accelerated free electrons travel with increased speed and energy towards the anode, ultimately colliding with its surface. These highenergy collisions generate X-rays within the X-ray tube. These X-rays



Figure 2.2: X-ray diffraction through Bragg's reflection in the atomic planes.

possess a wavelength that corresponds to the order of the lattice parameter, which is the characteristic distance between atoms in a crystal lattice.

The generated X-rays then exit the X-ray tube and interact with the surface of the sample under investigation. Upon striking the sample, the X-rays undergo a phenomenon known as diffraction. This diffraction process involves the X-rays interacting with the atoms in the sample's crystal lattice, leading to the scattering of the X-rays in various directions. During diffraction, the intensity of the X-rays continuously changes as they adopt different incident angles. The interaction between the X-rays and the crystal lattice results in constructive and destructive interference, causing variations in the intensity of the diffracted X-rays.

The concept of X-ray diffraction is totally based on the condition of Bragg's law (Figure 2.2). If we take two parallel X-ray beams falling on two consecutive atomic planes, then the path difference between the two beam paths becomes $2d\sin\theta$.

The constructive and destructive interferences happen in two different situations of the following condition, called Bragg's law.[Equation 2.1]

 $2d\sin\theta = n\lambda$ ----- (2.1)

Where d is spacing (the spacing between the planes), n is an integer, and θ is the half of the angle between the incident and diffracted rays, then constructive interference between the diffracted waves occurs. If we consider n = 1/2, 3/2, and so on, then the diffracted waves result in destructive interference.

The constructive interference occurs if the path difference is equal to the integer number of the X-ray wavelength. Similarly, in the case of the path difference equal to half of the odd integers, the interference is destructive.



Figure. 2.3 Schematic of X-Ray diffraction.

Figure 2.3, shows a schematic representation of XRD. The angle 2θ represents the angle θ between the incident and diffracted rays, and the angle denotes the angle of rotation about the direction of the surface.

When a film is deposited onto a substrate, the film itself experiences two different kinds of strain as a result of the lattice mismatch. In accordance with the sign of the lattice mismatch, that is, the simple lattice parameters of both the film and the substrate, we are able to classify the strains into one of two categories:

A. Tensile strain:



Figure 2.4: Thin film showing tensile strain on the substrate

In the case of tensile strain (Figure 2.4), the lattice parameter of the thin film is smaller than that of the substrate. As a result, the film undergoes a natural tendency to expand and adjust its lattice to match that of the substrate. This expansion leads to a decrease in the out-of-plane lattice parameter of the film. so the peaks of the XRD pattern shift towards the right in accordance with Bragg's law.

B. Compressive strain:



Figure 2.5: Thin film showing compressive strain on the substrate

The lattice parameter of the thin film is greater than that of the substrate when subjected to a compressive strain, as shown in Figure 2.5. Because of this, the film exerts an effort to compress itself, which causes an increase in the value of an out-of-plane lattice parameter. In order to obey the Bragg's law, the diffraction angle in the XRD pattern shifts in the direction of a lower value, which is indicates that the film is experiencing compressive strain as a result of the substrate.

2.2.2 <u>Raman Spectroscopy:</u>

When a monochromatic light or a light with a very narrow frequency range is incident on a medium, the frequency of the light that is scattered off of the medium may be the same as the frequency of the light that was incident on the medium. In addition, the frequency of the scattered light and the energy that corresponds to it can either be higher or lower than the frequency of the light that originally hit the object. If the scattered radiation possesses almost entirely the energy of incident radiation, the scattering is called Rayleigh scattering. In addition, the scattering process is referred to as Raman scattering if the scattered radiation achieves discrete frequencies above and below the frequency of the incident radiation. C. V. Raman and K. S. Krishnan were the ones who first identified this phenomenon in 1928 [9]. A. V. Raman was honoured with the Nobel Prize in 1930 for his creation of Raman spectroscopy, which created a new route of progress in the new generation of scientists [10].

The classical theory of the Raman effect:

In the form of spectroscopy, the classical theory of the Raman effect can lead to an understanding of a fundamental concept known as the polarizability of a molecule. When a positively charged molecule is placed in the presence of a static electric field, the positively charged nuclei of the molecule are pulled to the negative pole of the field, while the positively charged electrons are drawn to the positive pole of the field. It is because of the separation of charge centres in the molecule that it is thought to be polarised. This is because the separation of charge centres causes an induced electric dipole moment in the molecule. The magnitude of the applied field, denoted by E, and the molecule's susceptibility to being deformed both contribute to the value of the induced dipole, denoted by μ . The following expression can be written out by us:

$$\mu = \alpha E$$
 ------ (2.2)

where α denotes the molecule's polarizability. When a sample of these molecules is subjected to a beam of radiation with a frequency of v, the electric field that each molecule is immersed in fluctuates as a result, as denoted by the equation that is shown in equation(2.3):

$$E = E_0 \sin 2\pi v t$$
 -----(2.3)

Thus, the induced dipole moment also undergoes the oscillation of frequency v by the following expression:

$$\mu = \alpha E = \alpha E_0 \sin 2\pi v t - (2.4)$$

As an oscillating dipole emits radiation of its own oscillating frequency, the frequency of incident and scattered radiation is equal. This is the classical explanation of Rayleigh scattering. In addition, due to some internal motions such as rotation and vibration, the polarizability changes periodically. If we consider only the vibrational motion with frequency v_{vib} which changes the polarizability of the molecule, then the induced dipole moment will be:

$$\mu = \alpha \mathbf{E} = (\alpha_0 + \beta \sin 2\pi v_{\text{vib}} t) \mathbf{E}_0 \sin 2\pi v t \dots (2.5)$$

which corresponds the following expression (using 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) has the frequency same as the frequency of incident radiation which corresponds to the Rayleigh scattering phenomena. In the second and third terms, two frequencies arise: one has a frequency less than the incident beam frequency and another has a greater one. Therefore, the term having $(v - v_{vib})$ frequency arises due to Stokes' radiation and another one (having $(v + v_{vib})$ frequency) arises due to anti-Stokes' radiation.

The quantum theory of the Raman effect:

The quantum theory of radiation provides a natural framework for comprehending Raman scattering. The molecules in the quantum model have quantized energy levels that correspond to several possible stationary states. It is assumed that photons with energy hv_0 collide with molecules when this radiation is incident on a sample. Collisions can be elastic, in which case the photons are merely deflected without changing their kinetic energy, or inelastic, in which case the photon and molecule exchange energy, leading to a change in the molecule's vibrational or rotational energy levels.

A change in the molecule's vibrational and/or rotational energy must be represented by ΔE ($\Delta E = h v_{vib}$). In quantum mechanics, the phenomenon of scattering can be understood as the excitation of a virtual state that possesses lower energy compared to a real electronic state. The energy of the scattered radiation is influenced by the energy of the incident radiation. The scattered radiation has the same energy as the incident radiation is known as Rayleigh scattering, which does not involve any energy loss. When a molecule absorbs energy ΔE , a photon is scattered with an energy of $hv_0 - \Delta E$, which is known as Stokes' scattering. On the other hand, when a molecule loses energy ΔE , the scattered photon carries an energy of $hv_0 + \Delta E$, and this type of scattering is referred to as anti-Stokes' scattering [11]. The strength of Stokes' radiation is typically greater than that of anti-Stokes' radiation.



Figure 2.6: Schematic of energy level diagram showing various types of emissions

2.2.3. Temperature-dependent resistivity measurement:

A material is said to have a certain resistivity if there is a resistance formed when there is a barrier in the movement of charge carriers in a lattice. Temperature-dependent resistivity measurement, which is also known as electrical resistivity measurement, is a technique that is used to explore the electrical behaviour of materials as a function of temperature. It requires taking readings of a material's electrical resistance at a range of temperatures in order to gain an understanding of the material's electrical conductivity as well as the influence of temperature on the electrical characteristics of the material.

However, the resistivity of insulating materials will decrease as the temperature increases, but the resistivity of metals will increase. As a consequence of this, measurements of resistivity have developed into an extremely helpful tool for the investigation of structural phase shifts in metal-insulator systems, which are accompanied by electronic transitions.

The resistivity of a sample can be calculated by:

$$\rho = \frac{RA}{l} \qquad ----- (2.7)$$

where R is the resistance of the sample keeping the shortest distance of the probes in measurement system 1 and cross-section area A. This R-value can be calculated by Ohm's law: R = V, where V is the potential *I* difference of the probes at a particular current I.

The temperature coefficient of resistivity (α) can be generally defined as the amount of change in resistivity with a particular temperature change. The effect of temperature on electrical resistivity was examined by calculating the temperature coefficient of electrical resistivity (α) of all the thin films. The temperature coefficient of electrical resistivity (α) is a measure of the rate of change of electrical resistivity with temperature and is given by the formula [equation(2.8)]:

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

where ρ_0 is the residual resistivity, $\frac{d\rho}{dT}$ is the rate of change of resistivity with temperature, and α has units of K⁻¹. Metals exhibit a positive value of the temperature coefficient of electrical resistivity (α), indicating that their electrical resistivity increases as temperature increases. On the other hand, insulators exhibit a negative value of α , meaning that their electrical resistivity decreases as temperature increases.

The electrical resistivity (ρ) can be measured using either the two-probe method or the four-point probe method. For extremely resistive samples, the two-probe approach is appropriate. The four-probe approach, on the other hand, is best for conducting samples with low resistance.

Four-probe method:

Due to the fact that it provides accurate readings, the fourprobe method is one of the most used methods that is also extremely versatile. It is used to determine the sample's resistivity. Therefore, it works best with samples that have a low resistance.. The use of separate probes for the source and measurement eliminates contact resistance, making this approach superior to the two-probe method. To assess the resistance of a single crystal or a thin film, four probe approaches can be utilized. Current flows via the outer contacts, which are near the sample's edges, and the potential difference between the inner contacts is measured (Figure 2.7) [12]. Furthermore, this approach may be used when the distance between the probes is minimal in comparison to the sample's smaller dimension.



Figure. 2.7. Four-point probe setup

Therefore, it provides a number of benefits over the two-probe approach:

- 1. This eliminates contact resistances, which are known to introduce error into measurement processes.
- 2. Because we are measuring the difference in voltage and current between the two probes, this method will reduces its error.
- 3. This is of tremendous use in situations in which the real sample resistance is low and the contact resistance has the potential to alter this value.

The four-probe approach was used to measure the resistivity of RNiO₃ thin films. Four collinear connections were created on the surface of the thin film with Epoxy technology's conductive silver paste (EPO-TEK EE 129-4), and the samples were heated under the for 1 hour before being placed in the measurement chamber. In our project work a JANIS RESEARCH CCR cryostat was utilised in order to determine the temperature dependant resistivity of the samples. The system can detect the resistivity of two samples at the same time, which is useful for a

comparative examination of two samples. The voltage was measured by providing a certain amount of current using the KEITHLEY-2612 A Source Meter. Following the achievement of a good vacuum, measurements were made using the LABVIEW RT-5d in the temperature range of 300K-12K.

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Chapter 3

Effects of Ga-doping on Structural, Electronic, and Vibrational Properties of NdNiO₃ Thin Films

Introduction:

The most significant part of NdNiO₃ is its perovskite structure with unique electronic properties and potential applications in electronics, making it of deep interest to the scientific community. For PrNiO₃ and NdNiO₃, there is a correlation between structural (orthorhombic to monoclinic), electronic (from metal to insulator), and magnetic (paramagnetic to antiferromagnetic) transitions occurring at the same temperature. Despite having a 3d⁷ configuration, Ni³⁺ does not show Jahn-teller distortion; however, charge disproportionation has been suggested for NdNiO₃. The origin of MIT has been widely interpreted as a charge disproportionation at the Ni site,(Ni³⁺ - $Ni^{(3+\delta)}/Ni^{(3-\delta)}$). It is reported that this charge disproportionation exists in the insulating state at low temperatures in NdNiO₃. According to Zaanen Sawatzky- Allen framework, the low-temperature state of NdNiO₃ lies in the class of low- Δ charge-transfer insulators. The metallic phase is observed at high temperatures due to the closing of the bandgap between nickel 3d- and oxygen 2p- orbitals across the fermi level, and the metallic conduction occurs according to the electronic state transformations $d_i^{3+}p_j^{2-} - d_i^{2+}p_j^{-}$. There have been numerous investigations on doping in NdNiO₃, among them some are doping at the Nd-site, and others doping at Ni-site.

Doping at Nd-site has a greater effect on the tolerance factor and the Ni–O–Ni bond angle. The change in Ni-O-Ni bond angle is very sensitive to tuning their physical properties. At Ni-site there are lots of aliovalent doping has been observed, which indicated the effect of carrier injection. But also there are few that have focused specifically on iso-valent doping at the Ni site. It should be noted that iso-valent doping does not take into account the impact of carrier injection on the system. As such, further studies are needed to fully elucidate the effects of isovalent doping on the electronic and structural properties of NdNiO₃.

We have successfully synthesized Ga-doped NdNiO₃ targets via a solid-state reaction method. We have maintained the percentages of doping at 0%, 5%, 10%, and 20%. Each doped sample was deposited as a 20 nm thick film using the PLD method on a single crystal substrate of LaAlO₃ (LAO). The properties of the produced thin films were studied using extensive measurements of X-ray diffraction (XRD), Raman scattering (Raman), and temperature-dependent resistivity. The experimental data provides vividly specificity in describing the physical characteristics of thin films. Experimental techniques are more specifically described in Chapter 2.

Results and Discussions:

3.1. X-ray diffraction:

X-ray diffraction (XRD), carried out on an Empyrean-DY2528, Malvern Panalytical X-ray diffractometer, was used to examine the phase purity and out-of-plane lattice parameter.



Figure 3.1: Full-scale XRD Patterns of NdNi_{1-x} Ga_x O₃ (x= 0- 0.2) films on LAO (001) substrate.

As you can be seen in Figure 3.1, the XRD patterns of the films do not contain any unwanted peaks. This indicates that all of the grown films have no traces of impurities and are orientated in the direction of the LAO (100) substrate. Even after doping the Ga with NdNiO₃ at a doping of 20%, phase purity is not affected. The value of 3.86 Å for the out-of-plane parameter (c) was taken from the (002) peak of the X-ray diffraction pattern and was obtained for the NdNiO₃ thin film that was produced on the LAO (001) substrate. The pseudocubic lattice parameter of LAO and NdNiO₃ are 3.79Å and 3.807 Å, respectively. The lattice mismatch can be calculated as:

Lattice mismatch (%) =
$$\frac{a_{sub} - a_{film}}{a_{sub}} \times 100 = -0.44\%$$
 ----- (3.1)

Where a_{sub} and a_{film} are the pseudocubic lattice parameters of the substrate and thin film. Since the lattice mismatch comes out to be negative, LAO provides compressive strain to the films.



Figure 3.2. Magnified view of the (200) peak of XRD Patterns of NdNi_{1-x}Ga_xO₃ (x = 0-0.2) films on the LAO (001) substrate.

Due to in-plane compressive strain, the value d will increase, and consequently, θ will decrease to satisfy Bragg's Law i.e. $2d Sin(\theta) = n\lambda$. From Fig.2, We have found that the Ga content of NNO thin films on LAO substrate faces compressive strain. The corresponding FWHM value of the (200) peaks and out-of-plane lattice parameters (cparameter) of the thin film is shown in Table 3.1.

Sample	20	C- parameter	FWHM (Å)
	(degree)	(Å)	
NdNiO ₃	47.40	3.83	0.31
NdNi0.95Ga0.05O3	47.52	3.82	0.21
NdNi0.90Ga0.10O3	47.48	3.82	0.20
NdNi0.80Ga0.20O3	47.28	3.84	0.32

Table 3.1

3.2 Temperature-dependent resistivity measurement:

We have investigated experimentally the temperaturedependent electronic transport properties measurements of all NdNiO₃ (NNO) thin films below room temperature. When the doping percentage is increased, the T_{MI} occurs at a higher temperature, and the insulating phase shows a wide temperature range as a result. The 20% Ga-doped NNO film exhibits insulating behavior in the room temperature range (12 K to 300 K) because there is no electronic phase transition. The T_{MI} is determined by the temperature at which the slope of the resistivity curve changes.

The temperature coefficient of resistivity (a) can be generally defined as the amount of change in resistivity with a particular temperature change. The effect of temperature on electrical resistivity was examined by calculating the temperature coefficient of electrical resistivity (α) of all the thin films. Metals exhibit a positive value of the temperature coefficient of electrical resistivity (α), indicating that their electrical resistivity increases as temperature increases. On the other hand, insulators exhibit a negative value of α , meaning that their electrical resistivity decreases as temperature increases. As a result, whenever the transition happens, the sign of ' α ' is altered. Thin film with x=0 shows MI transition at 79 K which is lower than T_{MI} of bulk. This lowering of T_{MI} clearly shows the effect of compressive strain occurs on NNO thin films due to LAO substrate. The doped samples with x = 0.05, and 0.10 have T_{MI} of around 82 K, and 112K, respectively. It shows that with increasing Ga-doping, the T_{MI} systematically increases. Except for NdNi_{0.8}Ga_{0.2}O₃, which shows a negative value of ' α ' in this temperature range. The temperature coefficient of resistivity has a positive value for other samples at higher temperatures in metallic states. As a result, in the case of NdNi_{0.8}Ga_{0.2}O₃ film, no transition in the resistivity data, and the negative value of ' α ' confirms the insulating phase throughout a wide temperature range. The low-temperature region of the undoped sample shows a clear hysteresis loop, indicating a first-order phase transition with the coexistence of metallic and insulating phases.

Nickelates are a class of materials known for their Non-Fermi Liquid (NFL) properties, which are characterized by a power-law equation between resistivity and temperature.



Figure. 3.3. Resistivity vs Temperature behavior of NdNi_{1-x}Ga_xO₃ (x = 0-0.2) thin films grown on LAO (001) Substrate. Inset shows the temperature coefficient of resistivity (α) vs Doping percentage.

In our case, we obtained the value of n of thin films of NdNi_{1-x}Ga_xO₃ (x = 0-0.1) which is shown in Table 3.2, i.e. indicates that our grown films are showing Non-Fermi liquid state. The fitted plot for the metallic state of NdNi_{1-x}Ga_xO₃ (x = 0-0.1) films are shown in Fig.3.4. The thin film of 20% Ga-doped NdNiO₃ shows the insulating state at high temperatures. For this insulating state activation type conduction dominates, which can be expressed by using the Arrhenius model.



Figure. 3.4. Fitting of Resistivity data of NdNi_{1-x}Ga_xO₃ (x = 0-0.2) thin films grown on LAO (001) Substrate.

Sample	Temperature	Fitting parameter n
	range (K)	
NdNiO3	150 - 300	1.61
NdNi0.95Ga0.05O3	150- 300	1.34
NdNi0.90Ga0.10O3	150- 300	1.43

Table 3.2

3.3 <u>Raman spectroscopy:</u>

To observe the structural and vibrational properties of nickelates thin films, Raman spectroscopy is very effectively used. It is susceptible to any change in the local geometry. So, to demonstrate the doping-dependent structural properties of NdNiO₃ thin films, roomtemperature Raman spectra have been recorded, which are shown in Fig. 3.5. According to crystal symmetry analysis, at room temperature NdNiO₃ exhibits orthorhombic distortion with a crystal structure similar to that of GdFeO₃, which is classified under the *Pbnm* space group. This structural distortion occurs due to the anti-phase tilting of adjacent NiO₆ octahedra (a-a-c+ in Glazer's notation). In the polycrystalline bulk form, the primitive unit cell consists of 20 ions and exhibits a total of 60 vibrational modes $(7A_{1g} + 7B_{1g} + 5B_{2g} + 5B_{3g} +$ $8A_u + 8B_{1u} + 10B_{2u} + 10B_{3g} + 8A_u + 8B_{1u} + 10B_{2u} + 10B_{3g}$). These modes are located in the centre of the Brillouin zone. 24 Raman modes have been determined, which are comprised of these modes (7A1g + $7B_{1g} + 5B_{2g} + 5B_{3g}$). From the Raman spectra obtained at ambient temperature, we are able to observe seven Raman modes $(A_g + 3B_{1g} +$ $2B_{2g} + B_{3g}$) for NdNi_{1-x}Ga_xO₃ thin films while maintaining the LAO (001)substrate as the background in the spectral range of 150-800cm⁻¹

(Fig.3.5). The lack of other Raman modes in thin films may be explained by the presence of highly orientated planes within the film. The B_{2g} mode at 440 cm⁻¹ appears due to the tilting of NiO₆ octahedra



and, consequently, the change in the Ni-O-Ni bond angle.

Figure. 3.5 Room temperature Raman spectra of NdNi_{1-x}Ga_xO₃ (x = 0-0.2) films on LAO (001) substrate. Inset it shows that The variation of FWHM and Raman shift of B_{3g} mode at 696 cm⁻¹ with doping percentages of NdNi_{1-x}Ga_xO₃ (x = 0-0.2) films.

We have observed from Fig.3.5, that significant B_{3g} Raman mode at 696 cm⁻¹ starts appearing with an increase in doping percentage in NNO thin films. This B_{3g} Raman mode is absent in undoped NNO film and starts occurring at 5% Ga doping and it becomes very

prominent in 20% Ga-doped NNO film. Also, this B_{3g} mode doesn't belong to *Pbnm* space group nickelates. The variation of Raman shift of B_{3g} mode has shown in Fig.3.5(Inset plot), with doping percentages of NdNi_{1-x}Ga_xO₃(x = 0-0.2) films. Furthermore, the observed red shift of the mode with increasing doping fraction implies an increase in the bond length of Ni/Ga-O. The FWHM and peak position variations of this B_{3g} mode are tabulated in Table 3.4.

	r	Fable 3.3	
Sample	FV	WHM peak of B _{2g}	Peak Position of
	m	ode	B _{2g} mode
	(ci	m ⁻¹)	(cm ⁻¹)
NdNiO ₃		24.27	442.15
NdNi0.95Gao.0	5 O 3	67.71	433.23
NdNi0.90Ga0.1	0 O 3	42.06	439.26
NdNi0.80Ga0.2	0 O 3	37.56	437.26

Table 3.4

Sample	FWHM peak of B3g mode (cm ⁻¹)	Peak Position B _{3g} mode (cm ⁻¹)
NdNiO ₃	-	-
NdNi0.95Ga0.05O3	96.68	698
NdNi0.90Ga0.10O3	69.08	686
NdNi0.80Ga0.20O3	73.61	671

The results of temperature-dependent Raman spectroscopy of NdNiO₃ thin films, which was conducted to investigate the thermal evolution of vibrational modes and the strain state in each film (Fig.3.6). The peaks of B_{2g} mode at 447cm⁻¹ shift towards lower wave numbers as the temperature increases. The Raman peak position and FWHM get affected by the temperature. As the temperature increases, the thermal energy of the system increases as well, leading to increased motion of the atoms and molecules in the material. It causes the vibrational modes of the material, corresponding to bond stretching or bending to become broader and the frequencies of these modes can shift to lower values. This indicates the expected red-shift in Raman mode.



Figure. 3.6 . Temperature-dependent Raman spectra of NdNiO₃ thin films on LAO (001) substrate.
3.4. Conclusion:

The physical properties of Ga -doped NNO thin films have been investigated with varying doping percentages. The XRD peaks of all synthesized thin films shift on the 2θ -axis indicating a variation in lattice parameter that is showing the compressive strain on the LAO substrate. The red shifting of the B_{2g} Raman mode at 440 cm⁻¹ carries the information of enhancement of octahedral tilt angle with doping percentages. Also at 696 cm⁻¹ another vibrational distortion Raman mode was observed, which showed systematic red shifts with increasing doping. When NdNiO₃ is doped with Ga, such as by substituting nickel (Ni) with Ga ions, it 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[1],[2]. The temperature-dependent Raman of NNO shows the red-shift of Raman mode at 447 cm⁻¹, which is the indication of thermal expansion and bond lengthening of inter-atomic bonds. The metal-to-insulator phase transition has been confirmed by temperature-dependent resistivity measurements, with the exception of the NdNi_{0.8}Ga_{0.2}O₃ sample. The $T_{\mbox{\scriptsize MI}}$ increases systematically as the doping percentages increase, which indicates the occurrence of charge disproportion below room temperature. In contrast to the other samples, the thin film of NdNi_{0.80}Ga_{0.20}O₃ demonstrates insulating behavior that is unaltered across the whole temperature range. The substitution of Ga for a fraction of the Ni-ions in NdNiO₃ can modify the electronic band structure. The presence of Ga may introduce additional energy levels or modify the bandgap, leading to an increased bandgap or a localized state within the band gap. We have calculated the band gap from the fitting of the Arrhenius equation for NdNi_{0.80}Ga_{0.20}O₃ is 18.29 meV.

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