# Influence of Cu-Doping and Thickness on Metallic Conductance in PrNiO<sub>3</sub> Thin Films

**M.Sc.** Thesis

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# Influence of Cu-Doping and Thickness on Metallic Conductance in PrNiO<sub>3</sub> Thin Films

# A THESIS

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

> by EKTA YADAV



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# DEDICATED TO MY PARENTS AND TEACHERS

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### Abstract

The need of present day technology is exploring new materials with fundamental physics and various technological applications. rich Perovskite oxides, exhibiting lot of practical applications serve as a potential candidate for physics now a days. Rare earth nickelates (RNiO<sub>3</sub>) are abundant with many physical phenomenon of fundamental importance such as phase transition, strongly correlated effects, high temperature superconductivity, Colossal Magnetoresistance (CMR). All these properties are highly controllable in thin film form. We have deposited two series (12 nm and 5 nm) of PrNi<sub>1-x</sub>Cu<sub>x</sub>O<sub>3</sub> (x = 0-0.1) thin films on  $(LaAlO_3)_{0.3}(Sr_2Al-TiO_6)_{0.7} - (LSAT)$  single crystal substrate using pulse laser deposition and studied the effects of Cu-doping and thickness variation on the electronic properties. For series-1 (12 nm), the undoped PrNiO<sub>3</sub> film shows a metal to insulator phase transition and thermal hysteresis around 100 K. A fractional doping of 1.0 atomic percentage of Cu at Ni site is able to supress the insulating phase completely and thereby driving the system towards steady metallicity throughout the temperature range below 300 K. However, at lower dimensions in series-2 with 5 nm thickness, these effects of Cu-doping and metallicity is reduced. Resistivity data of all the films fit to power-law equation show non-Fermi Liquid behaviour (NFL). A switching from one type of NFL to another type has been observed due to both, Cu-doping and thickness variation. Further, the fitting parameters show a systemic variation with increasing Cu content indicating that the carrier injection by even a fractional Cu-doping is highly effective in bringing metallicity in the system due to band-filling effects. We have observed that cu-doping has induced a complete metallic and they can be used for electrode applications.

v

## LIST OF PUBLICATIONS

### A. As first author:

 "Influence of Cu-doping and thickness on non-Fermi liquid behaviour and metallic conductance of PrNiO<sub>3</sub> thin films", <u>Ekta Yadav</u>, Harisankar S, Kavita Soni, K. R. Mavani, *Applied Physics A*, (under review).

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## **ABBRIVIATIONS**

Room Temperature	RT
X- Ray Diffraction	XRD
Reciprocal Space Mapping	RSM
PrNiO <sub>3</sub>	PNO
PrNi <sub>1-x</sub> Cu <sub>x</sub> O <sub>3</sub>	PNCO
LaAlO <sub>3</sub>	LAO
(LaAlO <sub>3</sub> ) <sub>0.3</sub> (Sr <sub>2</sub> AlTaO <sub>6</sub> ) <sub>0.7</sub>	LSAT
Transition Metal	TM
Ferromagnetic	FM
Paramagnetic	PM
Antiferromagnetic	AFM
Pulse laser Deposition	PLD
Physical Vapour Deposition	PVD
Chemical Vapour Deposition	CVD

### **Chapter 1**

## **Introduction to complex oxides:**

The need of present day technology is reduction of size and enhancement of practical applications of appliances so that it can replace the previous silicon based technology. The main focus resides on thin films, nanomaterials and their fabrication techniques and oxides serve as a suitable choice for recent technology. Thin film is a layer of a material having thickness in range of several nanometres. Deposition of thin film is a layer by layer growth of a material on a substrate. It has wide applications in modern day technology due to its various possible applications in electronic devices, switching devices, energy efficient optical electronics, optical coatings and decorative parts etc. [1] [2]. Transition metal oxides, also known as complex oxides, serve as a novel material for these applications. Recently, the most studied complex oxides mainly consist of RCuO<sub>3</sub> (rare earth cuperates) for their high temperature superconductivity, RNiO<sub>3</sub> (rare earth nickelates) for showing Colossal Magnetoresistance (CMR) and RMnO<sub>3</sub> for showing Giant Magnetoresistance [3]. In addition to all this, reduced dimensionality in thin film and hetrostructures have also thrown light in this field.

Gustav Rose discovered CaTiO<sub>3</sub> in the Ural Mountains in 1839 [4]. Perovskite oxides have general formula ABO<sub>3</sub>, where A is a larger cation belonging to rare earths, B is a comparatively smaller cation belonging to transition metal oxides and O is oxygen. In this structure, each A ion is three-dimensionally surrounded by 8 BO<sub>6</sub> octahedra as shown in figure 1.1. Four octahedra are on the above plane and four on below. Stability of the structure is determined by tolerance factor. An ideal cubic perovskite structure has a tolerance factor unity [5]. Tolerance factor is defined by the equation:

$$t = \frac{R_A + R_O}{\sqrt{2(R_B + R_O)}} \quad -----(1.1)$$

Where  $R_A$ ,  $R_B$  and  $R_O$  are ionic radii of A, B and O ions respectively. Generally, tolerance factor(t) lies in between 0.75 to 1[6].



Fig1.1 Ideal cubic perovskite structure.

Basically, A ion should be large enough to satisfy the tolerance factor stability condition. Change in A ion radius is one of the basic feature towards stability of perovskite structure. Any change in A ion size can cause distortion or tilting of  $BO_6$  octahedra and hence causes instability of the structure. This is known as orthorhombic distortion. Many oxides exhibit this perovskite structure because of degree of freedom of each ion and high tolerance of the structure towards A and B ion radii. High tolerance of these compounds makes them useful for structural modification and chemical substitution [7].

Apart from structural distortion, transition metal oxides also experience geometrical distortion. When more than one degenerate state is available for an electron then the energy cost is higher for such electronic configuration. To reduce the overall energy of the system, the structure undergoes a distortion and takes the system to a lower symmetry and lower energy state. For example, in an octahedral environment five degenerate *d* orbitals split in to three  $t^{2g}$  and two  $e^{g}$ orbitals due to crystal field splitting. 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. This state of confusion to the last electron can be avoided by either elongating or compressing the BO<sub>6</sub> octahedra in such a way that energy of few orbital states becomes lower than that of the others. This elongation and compression along *Z*-axis are called z-out distortion and z-in distortion respectively. This combined effect is called **Jahn-Teller distortion** [8]. The electronic and magnetic properties of ABO<sub>3</sub> type perovskite largely depend upon the B-O-B bond length and the bond angles. Therefore, the Jahn-Teller distortion plays an important role in determining the properties of these oxides.

#### Thin films of oxides:

Thin film is a layer of a material having thickness in range of several nanometres. Deposition of thin film is a layer by layer growth of a material on a substrate. For making different devices like, electronic devices, instrument hard coatings, optical coatings, decorative parts etc [9]. thin films have been extensively used for more than a half century. There are several techniques available for thin films deposition on a single crystal substrate like thermal evaporation, chemical decomposition and the evaporation of source materials by the irradiation of energetic species or laser light [10]. In general, the growth process of thin films mainly contains the following features:

- Thin films of materials made by any prescribed method begins with nucleation process followed by development stages.
- Nucleation and growth stages depend upon various deposition conditions, such as growth temperature, growth rate, chemistry and structure of the material as well as substrate.
- 3. The nucleation stage depends significantly on external agencies, such as electron or ion bombardment.
- 4. Phase and orientation of the films are governed by the deposition conditions as well as by the crystal structure of the substrate.

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 [11]. After a continuous film is formed, anisotropic growth takes place normal to the substrate in the form of cylindrical columns. The lateral grain size, or crystallite size can be determined by the initial nucleation density. Thin films can be deposited by various techniques as:

- 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 Pulse laser deposition for thin films synthesis. It is broadly described in chapter 2.

#### **Electrical transport:**

Electrical transport of a material is basically described by its ease to pass current through it. Electrical conductivity( $\sigma$ ) is a key parameter to measure this transport. Typical metals have  $\sigma$  in range of  $10^9 \Omega^{-1}$ cm<sup>-1</sup> and for non-metals, it is  $10^{-18}\Omega^{-1}$ cm<sup>-1</sup>. Materials can be broadly classified into two categories: metals and insulators. The rigorous definition of an insulator is that it is expected to show zero conductivity at 0 K whereas a metal has a finite conductivity. Since experiments are generally preformed at finite temperatures, it is common to define an insulator as a material that exhibits  $(d\rho/dT)<0$ , *i.e.* an increase in resistance with decreasing temperature. Conversely, a metal shows a decrease in resistance with decreasing temperature, hence  $(d\rho/dT)>0$ . There are many theories available to give distinction between conductor, insulator and semiconductor[12]. These are discussed as follows:

#### a) Free electron model:

This model was given by Paul Drude in 1927[13]. In this "Free electron model", electrons are considered as non-interacting free gas particles. The only potential they see is at the surface of the metal. There are many assumptions of free electron model:

- 1) Electrons are non-interacting.
- 2) Inside metal, electrons are completely free.
- 3) Positive ions are immobile.
- Electrons undergo continuous collision irrespective of lattice potential.



Fig. 1.2 Schematic of potential well for free electrons with infinite potential at surface and zero otherwise.

The electric conductivity of a metal in the presence of external field is given as:

$$\sigma = \frac{ne^2\tau}{m} \qquad -----(1.2)$$

where, *n* is free electron density,  $\tau$  is average time between two consecutive collisions known as relaxation time, *e* is charge on electron and *m* is mass of electron.

This model was successfully able to explain ohm's law, electrical and thermal conductivity, metallic lustre and Weideman-Franz law for metals but failed to explain heat capacity, temperature dependent resistivity and sign of Hall coefficient for certain metals. It was also not able to distinguish between metal and insulator. Then came Somerfield theory as a quantum analogue of free electron model. It considered electron as quantum particles and solved Schrödinger's equation for that. Somerfield's theory was able to describe temperature dependent resistivity, heat capacity and paramagnetic susceptibility but it also failed to give distinction between metal, semiconductor and insulator.

#### b) Band Theory for Solids:

It is also known as nearly free electron theory. Failure of free electron theory was due to its over simplified assumption that potential field of positive ion cores is constant and for simplicity it was taken as zero. But in actual, motion of electrons in a solid is complicated and we can't neglect potential because of lattice field. Band theory considered potential field to be periodic with period equal to lattice constant. Potential is given as:

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

where a is lattice constant. Actual potential is parabolic but we consider it as pulse by using 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:

 $u_k(x)$  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:

 $\cos(ka) = \cos(\alpha a) + P \frac{\sin(\alpha a)}{\alpha a} \quad ----(1.6)$ 

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



Fig. 1.3 Schematic of metal, insulator and semiconductor.

The solution of the equation imposes a constraint on the occupancy of energy states as cos(ka) has values between -1 to +1. It means there are energy regions where the solutions for electron wave function are not possible. These forbidden energy regions are called band gaps. This band gap decides whether a material is metal or insulator. Metals don't possess any band gap and insulator have high band gap in the range of several eV. In between these, semiconductors have less band gap at low energy and it behaves as conductor at high temperature. Fig. 1.3 shows distinction between metal, semiconductor and insulator in terms of band gap.

#### c) Mott-Hubbard model:

Band theory was not able to explain the insulating state of some transition metal oxides because it did not consider e<sup>-</sup>-e<sup>-</sup> interaction into account. If this interaction is considered, then Hubbard Hamiltonian can be described as:

$$H = -t \sum_{\langle i,j \rangle,\sigma} (c_{i,\sigma}^+ c_{j,\sigma} + hc) + U \sum_{i=1}^N n_{i\uparrow} n_{j\downarrow} - \dots - (1.7)$$

where U is the on-site coulomb interaction energy, t is the hopping integral,  $c_{i\sigma}$  and  $c_{i\sigma}^+$  are creation and annihilation operators [14] . 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. 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 two bands. 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[15] . For metals, U/t<<1, *i.e.* the onsite coulomb repulsion is strong so U/t >>1. Such insulators are called Mott-Hubbard insulators. It is described in fig 1.4.



Fig 1.4 Band structure for an insulator and a metal. DOS and E stand for density of states and energy respectively.

#### d) Zaanen-Sawatzky-Allen model:

The model is based on three parameters: coulomb repulsion energy (U), band width (W) and charge transfer gap ( $\Delta$ ).  $\Delta$  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. 1.5) [16]. This model shows that the band gap can be either U or  $\Delta$ , depending upon which one has lower size on energy scale. Therefore, there can be two types of insulators:

- a) Mott-Hubbard Insulator.
- b) Charge transfer Insulator.



Fig. 1.5 Schematic for ZSA framework

- 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. RNiO<sub>3</sub>





Fig.1.6 Mott-Hubbard and charge transfer insulator.

#### **Non- Fermi Liquid Theory:**

Resistivity of solids has a strong dependence on temperature and behaves differently for metal and semiconductors (or insulators). In 1956, L.D. Landau introduced the Fermi liquid theory which considers electrons as weakly interacting fermions at sufficiently low temperatures. In metallic state, temperature dependent resistivity may fit to the power law equation [17]:

$$\rho_{\text{NFL}} = \rho_0 + AT^n$$
 - (1)

where,  $\rho_0$  is the residual resistivity, *i.e.* resistivity at absolute zero, which appears because of lattice imperfection, impurities and structural defects *etc.* A is a constant which represents electron-electron scattering strength [16] [18]. If n=2, then it is considered as LFL (Landau Fermi Liquid). It is a semi-classical picture which considers electrons as weakly interacting particles. Here, phase-space arguments apply to low-energy electron–electron scattering around the Fermi energy. However, in some cases, n<2 is also reported which is a deviation to NFL (Non Fermi Liquid) state. The NFL transport

exponents imply the presence of degrees of freedom beyond the electrons themselves and are often associated with quantum critical behaviour [18]. Basically, its three values *i.e.* 1.6, 1.3 and 1 are reported under NFL regime. But, this power law equation fits to a certain temperature range only, so in order to describe resistivity behaviour completely, we account for resistivity saturation in some cases [15, 16,17]. It is described by:

where  $\rho_{SAT}$  acts as a parallel resistor, which is applied to many materials showing resistivity saturation.  $\rho_{SAT}$  is often linked with maximum resistivity that approaches the Mott-Ioffe-Regel (MIR) limit in certain cases. [17].

$$\rho_{\text{MIR}} = \frac{3\pi^2\hbar}{q^2 K_f^2 l_{\text{min}}} \quad -----(3)$$

Where  $l_{min}$  is the minimum mean free path, which equals to the interatomic spacing. If we consider  $K_f = (3\pi^2 N)^{1/3}$ , total carrier density~ $10^{22}$ /cm<sup>3</sup>, a~3.83 A<sup>0</sup>, ħ as reduced Planck's constant and q as elementary charge then  $\rho_{MIR}$  comes out to be 0.716-0.717 m $\Omega$  cm for PrNiO<sub>3</sub> samples.

### **Rare earth nickelates:**

They have general formula RNiO<sub>3</sub>. Rare earth nickelates exhibit very sharp metal to insulator transitions (MIT), which makes them quite fascinating and applicable material in making the electronic switches, electronic oscillators, gated devices, thermal and chemical sensors[19]. Electronic transitions can be tuned by various parameters such as temperature, doping, strain, rare earth ionic radii [20].



Fig. 1.7 Phase diagram of RNiO<sub>3</sub> compounds.

As we can see from the phase diagram, except LaNiO<sub>3</sub>, all other rare earth perovskites show first order metal to insulator phase transition and it is observed that rare earth ionic radius is a factor that affect  $T_{\rm MI}$ [21]. As the size of rare earth ion changes, packing fraction of the perovskite structure also changes and it causes phase transitions. Among these rare earth nickeltes, PrNiO<sub>3</sub> and NdNiO<sub>3</sub> have gained considerable attention since their Metal to Insulator and Magnetic transition occurs at same temperature i.e. 135 K for PrNiO<sub>3</sub> and 200 K for NdNiO<sub>3</sub> [22]. These two oxides exhibit a strong correlation between charge, spin and orbital degree of freedom. PrNiO<sub>3</sub> lies in the category of charge transfer insulator [5]. Here, electronic transport basically depends on the extent of overlapping of Nickel 3d and oxygen 2p orbitals. Physical properties of strongly correlated systems also get affected by this change in local geometry. Doping can alter the carrier concentration and hence exist as a controllable parameter for electronic transport of strongly correlated oxides. Recently, PrNiO3 has been turned out to be a ground to investigate phenomenon related with quantum criticality in firmly corresponded Mott frameworks.


Fig. 1.8 Resistance versus temperature curve for RNiO<sub>3</sub> compounds.

From fig. 1.8, it is clear that electronic transport of rare earth nickelates is a function of rare earth ion.

## **Motivation:**

The phase diagram of RNiO<sub>3</sub>, enriched with tunable phase gives an opportunity to study the physical properties by modifying various parameters of oxide system. In this family, PrNiO<sub>3</sub> shows MI transition and antiferromagnetic ordering simultaneously at the same temperature around 100 K. The electronic transport of PrNiO<sub>3</sub> largely depends on the presence of oxygen vacancy, strain and doping. There are many reports on the effect of strain in PrNiO<sub>3</sub>, but no effort has been made to investigate doped RNiO<sub>3</sub> thin films.

Earlier reports suggest that Mn doping on Ni-site in NdNiO<sub>3</sub> derives it towards insulating state. A metallic state can be induced by Cu-doping at Ni-site in PrNiO<sub>3</sub> polycrystalline bulk material [6]. Literature suggest that Cu can add extra electrons in *d*-band and can cause metallic state. In order to explore Cu-doping effect in thin film form, we have studied PrNiO<sub>3</sub> thin film samples and Cu doping effects at Ni site.

## **Experimental Techniques:**

This chapter describes basically various synthesis and characterization techniques used during the project work. Synthesis methods involves preparation of bulk pellets using solid state reaction method and thin films using pulse laser deposition. In characterization techniques, we have used X-ray diffraction and RSM for structural analysis followed by temperature dependent resistivity measurement to get an idea about electronic transport. We have opted following experimental techniques in our project:

- 1. Sample preparation process:
- a) Bulk synthesis using Solid State Reaction method.
- b) Thin film synthesis using PLD (pulse laser deposition).
  - 2. Characterization techniques:
- a) X-Ray Diffraction (XRD).
- b) Reciprocal Space Mapping(RSM).
- c) Temperature Dependent Resistivity Measurement using CCR.

## **1.a)** Bulk synthesis by solid state reaction method:

Among various methods, we have opted conventional solid state reaction method for bulk synthesis of PrNiO<sub>3</sub> and PrNi<sub>x</sub>Cu<sub>1-x</sub>O<sub>3</sub> pellets. These pellets were used as a target for thin film deposition under PLD.

Solid state reaction method is one of the most common technique used for bulk synthesis of oxides [22]. It is a solvent free method and hence it is a reaction of powders. It involves weighing and mixing of two or more highly pure powders in appropriate stoichiometric ratio. To ensure homogeneous mixing, it is required that the mixture is thoroughly grinded. It decreases the particle size and increases the surface area and therefore, a high reaction rate is achieved. Generally grinding is done in pestle-mortar for 4-5 hours and in order to ensure homogenous mixing, acetone can be added. As it is volatile organic liquid, it evaporates gradually during the grinding process. Also, these oxides do not react at room temperature, therefore, in order to initialize the reaction, the grinded powder is heated at high temperature. This process is called calcination of grinded mixture and some volatile gases like CO<sub>2</sub> and NO<sub>2</sub> are removed in it. After first heating, second grinding is done for 2-3 hours to maintain uniform particle size. After that, again the powders are calcinated to obtain maintain uniformity and single phase. In order to increase intimate contact between crystallites, the powder is pressed in the form of pellet using a hydraulic press with 15 mm-20mm die set. Then the pellet is heated at high temperature which is higher than calcinations temperature and this process is called sintering. The main purpose of sintering is densification of the compound.

### Synthesis of PrNiO<sub>3</sub> and PrNi<sub>x</sub>Cu<sub>1-x</sub>O<sub>3</sub> targets:

We have prepared  $PrNiO_3$  and  $PrNi_{1-x}Cu_xO_3$  samples by mixing  $Pr_6O_{11}$ , NiO and CuO powders of high purity in proper stoichiometric ratios. The reaction can be written below:

 $Pr_6O_{11}+(1-x) CuO+(x)NiO \longrightarrow PrCu_{(1-x)} Ni_xO_3$ 

The following block diagram includes main steps:

Powders of Pr<sub>6</sub>O<sub>11</sub>, NiO and CuO having very high purity in required stoichiometric ratio were taken using high precision electronic weighing machine

Proper grinding was done for 4-5 hours using pestle mortar for homogenous mixing and calcinated at 800°C for 12 hours so that the powders react properly

Second grinding was done thoroughly for 2-3 hours to maintain uniform particle size and again calcination was done at 800°C for 12 hours to maintain uniformity and single phase

30 minutes grinding was done after second heating

Using Hydraulic press, powders were pressed in form of pellets (diameter=20 mm) and then Pellets were sintered at 1000°C in tube furnace for 12 hours Main involved steps are as follows:

- a) Weighing these oxides was done using high precision electronic weighing machine
- b) Mixing and grinding was done in pestle mortar and for 4-5 hours.
- c) Then heating of sample was done in furnace at 800°C for 12 hours so that powders can react thoroughly.
- d) Second grinding was done thoroughly for 2-3 hours to maintain uniform particle size.
- e) Again calcination was done at 800°C in box furnace for 12 hours to maintain uniformity and single phase.
- f) 30 minutes grinding was done after second heating.
- g) After that the circular pellets of about 20 mm diameter were prepared by applying a high pressure by means of hydraulic pressure pelletizer.
- h) These prepared pellets were finally sintered in tube furnace at 1000°C for 12 hours.

## **Substrate Selection:**

We deposit thin films on single crystal substrates. Therefore, selection of substrate carries an importance in thin film synthesis. In the present study, we have used two substrates LAO(LaAlO<sub>3</sub>) and LSAT((LaAlO<sub>3</sub>)<sub>0.3</sub>(Sr2TiAlO<sub>6</sub>)<sub>0.7</sub>) with (100) orientation and these substrates were cut using diamond cutter. Five such substrates of each type were used in thin film synthesis process. Since, lattice parameter of PrNiO<sub>3</sub> is 3.82A° and that of LAO and LSAT is 3.79A° and 3.86A° respectively. So, both will incorporate different kind of strains because of lattice mismatch.

## **1.b)** Thin Film Synthesis using PLD:

The fabrication of thin films on a single crystal substrate is done by the deposition of individual atoms. For making different devices like, electronic devices, instrument hard coatings, optical coatings, decorative parts etc. thin films have been widely used for more than a half century.

The major steps that constitute a typical thin-film deposition process are:

- (i) production of the appropriate atomic, molecular, or ionic species.
- (ii) transport of these species to the substrate through a medium.
- (iii) condensation on the substrate, either directly or via a chemical and/or electrochemical reaction, to form a solid deposit.

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

#### a) Island Growth:

It occurs when the smallest stable clusters nucleate on the substrate and grow with three-dimensional island like features. In this growth mode, the atoms or molecules being deposited are more strongly bonded to each other than to the substrate material. This is often the case when the film and substrate are dissimilar materials. This growth mode is typically observed when metal and semiconductor (i.e., Group IV, III–V, etc.) films are grown on oxide substrates [23].

## b) Layer growth:

It occurs when the extension of the smallest nucleus occurs in two dimensions resulting in the formation of planar sheets. In layerby-layer growth, the depositing atoms or molecules are more strongly bonded to the substrate than each other and each layer is progressively less strongly bonded than the previous layer. This effect extends continuously until the bulk bonding strength is reach. A typical example of this is the epitaxial growth of semiconductors and oxide materials [24].

#### c) Mixed Growth:

It is a combination of the layer-by-layer and island growth. In this growth mode, after forming one or more monolayers in a layerby-layer fashion, continued layer-by-layer growth becomes energetically unfavourable and islands begin to form. This sort of growth is fairly common and has been observed in a number of metalmetal and metal-semiconductor systems.

Thin film deposition is basically divided into two main categories:

- a) Physical Vapour Deposition(PVD).
- b) Chemical Vapour Deposition(CVD).

**Physical vapour deposition** is a technique where by physical processes, such as evaporation, sublimation or ionic impingement on a target, facilitate the transfer of atoms from a solid or molten source onto a substrate. Evaporation and sputtering are the two most widely used PVD methods for depositing films.

If the material deposited on the film is product of a chemical reaction, then the process is called **Chemical Vapour Deposition.** It is widely used in industry to produce high purity crystalline films of complex oxides, nitrites [25, 26].

We have synthesised our thin films using PLD (Pulse Laser Deposition) technique. It is the most commonly used technique which falls in the category of Physical Vapour Deposition.

#### What is Pulse Laser Deposition?

Pulse laser deposition is one of the most efficient techniques employed for thin film synthesis. The PLD system consists of a laser source (Eximer laser  $\lambda$ =248 nm in present work) and a vacuum chamber which contains the target holder, substrate holder, heating element and process gas inlet. Here, a high-power pulsed <u>laser</u> beam is focused inside a <u>vacuum</u> chamber which strikes a target of the material that is to be deposited. This material is vaporized from the target (in form of plasma plume) which deposits it as a <u>thin film</u> on a substrate. This process occurs in <u>high vacuum</u> or in the presence of a background gas, such as oxygen to maintain oxygen stoichiometry.

When the laser pulse is absorbed by the target, energy is first converted to electronic excitation and then into thermal, chemical and mechanical energy resulting in evaporation, <u>ablation</u> and <u>plasma</u> formation. The ejected species expand into the surrounding vacuum in the form of a plume containing many energetic species including <u>atoms</u>, <u>molecules</u>, <u>electrons</u>, <u>ions</u>, clusters and molten globules before depositing on the typically hot substrate.

Detailed mechanism of PLD is broadly divided into two parts:

- a) interaction of laser with material.
- b) thin film growth on to the substrate.

#### a) Interaction of laser with material:

A pulsed beam from a laser is focused by a lens on the target material to be deposited in the form of thin film. The interaction between laser and material takes place in a vacuum chamber where the background vacuum as well as the process gas (Oxygen, Argon *etc.*) pressure can be controlled. When the laser pulse with sufficient energy density hits the target, it ablates the material due to fast heating at the target surface [27]. Absorption of electromagnetic radiation, surface melting, vaporization and plasma emission takes place in less than 30 *ns*. It is **laser ablation of target material**.

The ablated material in form of plasma plume of constituent ions is directed towards the substrate on which the film is to be deposited. Ions in the plasma plume move toward the substrate with very high energies ranging from 0.1 eV to 10 eV [28]. Shape of the plasma plume depends upon the partial pressure of process gas. The partial pressure also influences the kinetic energy as well as the scattering of the particles in the plasma plume. This **dynamics of plasma** has to be maintained inside the PLD chamber.



## a) Thin film growth:

High energy laser-produced plasma plume expands rapidly away from the target surface. Film growth occurs on a substrate upon which some of the plume material recondenses. There are several external parameters which play crucial role in the phase stabilization, quality, and epitaxial nature of the thin film [28, 29].

These parameters are:

- i) laser energy
- j) process gas partial pressure
- k) substrate temperature
- l) target to substrate distance.

Laser energy controls the kinetic energy of the particles as well as the growth rate whereas process gas controls the plume shape and helps in achieving the stoichiometry especially in case of complex oxides. Generally, the substrate is kept at high temperature during deposition. Substrate temperature is critical in nucleation and growth process of thin film. Target to substrate distance is also a crucial parameter which determines the angular spread of the plasma plume.

## Synthesis of PrNi<sub>1-x</sub>Cu<sub>x</sub>O<sub>3</sub> targets:

Thin films deposition is carried out on single crystal substrates LaAlO<sub>3</sub>(LAO) and LSAT substrates having dimensions (2\*5\*0.5) mm respectively. Proper sonication of the substrates was carried out first in acetone and then in propanol for 10 minutes.

Following parameters were maintained during the deposition: Table 1

Parameter	Value
Ablation energy	310 mJ
Base vacuum level	4.5×10 <sup>-4</sup> Pa
Oxygen partial pressure	40 Pa
Target substrate distance	4.5 cm
Deposition temp.	720° C
Deposition time	3.5 min
Thickness of film	12 nm
No. of shots	840
Rep. rate	4 Hz

#### **Advantages of PLD:**

- a) It provides flexibility in laser parameters *i.e.* laser energy, substrate temperature, substrate to target distance, oxygen partial pressure and vacuum level etc.
- b) Even if the target is multiphase, phase purity of thin films is maintained in PLD [9].
- c) In PLD the control of the stoichiometry of the film come from the ability to produce a target with the desired composition, this is compared to techniques such as <u>MBE</u> where the composition has to be produced by controlling the ratio of the different sources arriving on the substrate.
- d) Synthesis of multilayer films and hetrostructures is also possible with PLD.

## 2. Characterization techniques:

It includes structural and electronic property characterization techniques. Structural characterization includes X-Ray Diffraction, Reciprocal Space mapping and XRR *etc.* Electronic property measurement includes temperature dependent resistivity measurement. We have performed these techniques:

- a) X-Ray Diffraction(XRD).
- b) Reciprocal Space Mapping(RSM).
- c) Temperature Dependent Resistivity Measurement.

## 2.a) X-Ray Diffraction:

X-Ray diffraction is one of the most common techniques used for material characterization to obtain information on the atomic scale for both crystalline and non-crystalline materials. It was discovered in 1912 by Max von Laue and W. L. Bragg and his father W. H. Bragg [30]. Since wavelength of X-Ray is of the order of A<sup>o</sup> which is comparable to lattice spacing, so it is a very suitable tool to probe structure of materials. We can get information about crystallite size, lattice parameters, lattice strain, chemical composition, state of ordering, spacing between two crystal planes *etc.* using XRD [31].

## **Working Principle:**

First of all, filament inside the cathode tube is heated by applying the alternating voltage between two electrodes. As the filament gets heated then free electrons travel from cathode to anode with higher velocity and finally strike to the anode surface, this results in creation of X-Rays in the X-ray tube. These X-rays originated from the tube fall on the surface of sample. As the wavelength of these originated X-rays has wavelength

is of order of the lattice parameter which results the diffraction of X-rays in different direction by continuous change in intensity with the incident angle. The X-ray diffraction technique is basically based on the principle of Bragg's law.



Fig 2.2 Diffraction of X-Ray by Crystal

## Here, Path difference= $2dSin\theta$

For constructive interference, path difference should be integer multiple of wavelength  $\lambda$ . So the Bragg's condition for constructive interference,

 $2dSin\theta = n\lambda$ , where n is an integer.

Whenever this condition is satisfied a diffraction peak will occur in the diffraction pattern. So, Bragg's law states that only for the angle  $\theta$  satisfying Brag's law  $2d\sin\theta = \lambda$  there is constructive interference. For all other angles, the intensity of peaks should cancel out.

The intensity of these X-rays diffracted peaks depends on the electron density across that miller plane. So, the intensity distribution

varies with the angle between incident and diffracted beam. By knowing those plane, we can calculate the structure of sample, composition of the crystal, spacing between two planes, and lattice constant etc.

Schematic of a typical XRD set up is shown in figure. Here,  $\omega$  is the angle between incident X-ray beam and sample surface,  $2\theta$  is angle between incident beam and diffracted beam,  $\varphi$  is angle of rotation about a plane perpendicular to the surface and  $\psi$  is angle about the line parallel to the surface. Different types of scan are possible using XRD depending upon the type of information to be extracted.



Fig 2.3 Schematic of X-Ray diffraction.

In case of thin films, there is always a lattice mismatch between the substrate and film due to which film experiences a strain. It will try to attain the same lattice parameter as that of the substrate. There are two type of strains:

- 1. Tensile strain.
- 2. Compressive strain.

## 1. Tensile stain $(a_{thin film} < a_{substrate})$ :



In tensile strain, lattice parameter of thin film is less than that of bulk. So, the film tries to expand itself resulting in decrease of out of plane lattice parameter and hence diffraction angle in XRD pattern shifts towards right in accordance with Bragg's law.

Fig 2.4 Film showing tensile strain.

## 2. Compressive strain (athin film > a substrate):



In compressive strain, lattice parameter of thin film is more than that of bulk. So, film tries to compress itself which results in increase of out of plane lattice parameter. This causes in a backward shift of diffraction angle in XRD pattern.

Fig 2.5 Film showing compressive strain.

## 2.b) Reciprocal Space Mapping (RSM):

#### What is Reciprocal Space?

Fourier transform of a real periodic space is known as reciprocal space. It is an imaginary space in which a single point represents family of parallel planes. The diffraction pattern of a crystal can be used to determine reciprocal vectors of a lattice.

#### Why we use it?

Since in a direct lattice, it is very difficult to deal with very large number of planes. But in reciprocal space, set of parallel planes are described by a point. It can be used to determine lattice mismatch, strain relaxation, mosaicity and supperlattice periods.

Crystals that are highly perfect can diffract over a very small angular range and therefore require very high angular resolution x-ray techniques to extract detailed structural information. As a solution to it, RSM can be used as route to extract detailed structural information of some materials[32].

The RSM scan is a collection of several  $2\theta$  scans at different  $\omega$  values around a Bragg peak.



Fig 2.6 Schematic of Reciprocal space coordinates

There can be two types of scans:

*i*) symmetric scan: when  $\omega = \theta$  and no tilting of sample is done so it can give information about the planes parallel to the substrate,

*ii*) **asymmetric scans**: here a tilting of sample is done for each scan and it gives information about the in-plane crystal structure.

When a beam of X-ray is scattered from a periodic structure, momentum remains conserved and the conservation of momentum is given as scattering vector:

$$Q = k_f - k_i$$

where  $k_i$  and  $k_f$  are wave vectors of incident and scattered beam. For coplanar scattering, the incident wave, the scattered wave and the normal to the surface lie in the same plane [33]. If the reciprocal space axis  $Q_z$  is taken parallel to the normal and  $Q_x$  parallel to the surface sample, then the relations between instrumental coordinates  $2\theta$ ,

 $\omega$  and components of scattering vector Q are represented as [34]:

$$Q_{x} = K [cos\omega - cos (2\theta - \omega)]$$
$$Q_{z} = K [sin\omega + sin (2\theta - \omega)]$$

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

For recording the RSMs of various thin films, a diffractometer with 5-axes cradle (Emperean, PanAlytical) (Cu-K $\alpha$ ) was used.

## **2.c)** Electronic Property Measurement:

It includes temperature dependent resistivity measurement of different thin film samples. As we know, resistivity is a measure of resistance of a given size of a specific material in path of electrical conduction. It indicates charge carrier density and mobility in a material. Determination of the temperature dependent electrical resistance is a very important tool to explain the nature of ground state, phase diagrams, electrical, electronic and magnetic properties and instabilities observed of the studied materials [35].

Various models have been suggested for electrical resistivity measurement. Temperature dependent resistivity measurements have been carried out in Closed Cycle Refrigerator (CCR) Cryostat using four probe point method in a temperature range of 300K-10K.

## Four probe setup:

Four probe apparatus is one of the standard and most widely used apparatus for the measurement of electrical resistivity. It is also known as potential probe setup. It is basically preferred for low resistive samples. In this method, the potential drop is measured across two probes and distance between these probes D is used as sample length[36].



Fig 2.7 Four-point probe setup

When the probes are not point contacts, in that case, the most accurate value for the probe distance is the distance between the centres rather than the closest distance between the probes.

Fig. 2.7 shows the schematically arrangement for four probe method. Resistivity of the sample is given by:

$$\rho = \frac{VA}{DI}$$

Detailed description of this method is given by **L. Valdes**[37]. This gives the functional relationship between the resistivity ' $\rho$ ' and the voltage and current ratio for various geometries. The arrangement of probes is shown in fig.

Four probe method can be used to determine the resistance of the single crystal as well as thin film. Here current passes through the outer contacts which are close to the edges of the sample and potential difference is measured across the inner contacts. This method can eliminate the effects of contact resistance between the sample and electrical contacts and therefore is most suitable for low and accurate resistance measurements.

This method is applicable when the distance between the probes is small compared to the smaller dimension of the sample, and provided none of the probe is too close to an edge of the sample. It has various advantages over two probe method:

- 1. It avoids contact resistances which can cause error in measurements.
- Since we are taking difference of voltage and current between two probes, so it reduces error.
- 3. This is extremely useful where actual sample resistance is low so contact resistance can change this value[38].

Four-Probe method has been used for resistivity measurements. The ohmic contact between the sample surface and metallic wire were made by silver paste of Epoxy technology (EPO-TEK EE 129-4). As in RNiO<sub>3</sub> compounds, the thermal hysteresis in temperature dependent resistivity is observed which is a manifestation of a first order metal to insulator transition. Therefore, the resistivity of thin films was recorded with heating and cooling of the sample with a constant rate of 5 K/ min. However, for checking the effect of heating and cooling rate on the hysteresis loop, different cooling and heating rates were also used for few selected thin films.

Resistivity measurement was performed in a **JANIS RESEARCH** CCR cryostat. **Keithely 2612A** was used as source meter as well as voltage meter. After achieving good vacuum, measurement was performed with the help of **LABVIEW RT-5d** in a temperature range of 300k-10K. Liquid He was used in CCR cryostat.

## **Results and discussion:**

We have prepared three series of Cu-doped PrNiO<sub>3</sub> samples named  $S_1$ ,  $S_2$  and  $S_3$  on two different substrates LaAlO<sub>3</sub> (LAO) and (LaAlO<sub>3</sub>)<sub>0.3</sub>(Sr<sub>2</sub>TaAlO<sub>6</sub>)<sub>0.7</sub> (LSAT) using Pulse Laser Deposition technique. Cu-doping content in all series is 1%, 2%, 5% and 10% at Nisite. Series  $S_1$  and  $S_2$  contains 12 nm and 5 nm films on LSAT substrate respectively. Series  $S_3$  contains 12 nm films on LAO substrate. After that, we have characterized these samples using XRD, RSM and temperature dependent resistivity measurements as described in chapter 2. Complete analysis of these thin films is given as:

- a) Series S<sub>1</sub>: PrNi<sub>1-x</sub>Cu<sub>x</sub>O<sub>3</sub> (*x*=0-0.10) thin films (PNCO/LSAT) under tensile strain (12 nm).
- **b**) Series S<sub>2</sub>:  $PrNi_{1-x}Cu_xO_3$  (*x*=0-0.10) thin films (PNCO/LSAT) under tensile strain (5 nm).
- **c)** Series S<sub>3</sub>: PrNi<sub>1-x</sub>Cu<sub>x</sub>O<sub>3</sub> (*x*=0-0.10) thin films (PNCO/LAO) under compressive strain (12nm).

The structural and electrical transport properties of these thin films are described in this chapter by various characterization techniques.

## 1) PrNi<sub>1-x</sub>Cu<sub>x</sub>O<sub>3</sub> (*x*=0-0.10) thin films (PNCO/LSAT) under tensile strain:

## **1.a) X-Ray Diffraction:**

X-Ray diffraction is a kind of non-destructive scattering technique which gives information about crystal structure, chemical composition, and physical properties of bulk materials as well as thin films. In order to examine phase purity and epitaxial strain in Cu-doped PrNiO<sub>3</sub> thin films (12 nm), we have done XRD (X-Ray diffraction) measurement using PanAlytical made setup.



Fig. 3.1 XRD patterns of  $PrNi_{1-x}Cu_xO_3(x=0-0.1)$  thin films on LSAT (100) substrate.

Fig. 3.1 shows XRD patterns of  $S_1$  series films on LSAT substrate. This shows that all the films are free from any impurity and are grown towards (100) crystallographic axis. As we know, pseudo-cubic lattice parameter of bulk PrNiO<sub>3</sub> is 3.83A<sup>o</sup> and that of LSAT substrate is 3.86 A<sup>o</sup> [40]. So, when a thin film of PrNiO<sub>3</sub> is deposited on LSAT, then because of lattice mismatch between film and substrate, unit cell of thin film material expands. As a

result of that, in-plane lattice parameter of thin film increases which causes a decrease in out-of-plane lattice parameter in order to keep the unit cell volume constant.



Fig.3.2 XRD patterns of PrNi<sub>1-x</sub>Cu<sub>x</sub>O<sub>3</sub>(x=0-0.1) films on LSAT (100) substrate.

The Bragg's law is given by:

$$2 \operatorname{dsin} \Theta = n \lambda \quad \dots \quad (3.1)$$

where d is the interatomic spacing which is equivalent to out-ofplane lattice parameter,  $\Theta$  is the diffraction angle, n is the order of diffraction and  $\lambda$  is the wavelength of light used *i.e.* 1.54A<sup>o</sup> for Cu-K<sub>a</sub>. So, with decrease in *d*, diffraction angle increases. There is an increase observed in diffraction angle  $\Theta$ . As shown in fig. 3.2, (200) peak of all films shows a systematic shift towards right side of the graph with increasing Cu content. This is generally termed as tensile strain. It means unit cell of thin film is trying to expand itself in order to maintain same lattice spacing as that of substrate. This is the reason of tensile strain. In fig. 3.2, all the substrate peaks lie along the same position and all the films have peak towards right side. 1% film peak is broadest out of all and after that with increase in Cu-doping the broadening of peak decreases. This can be because of decrease in unit cell volume. There is no systematic shifting in thin film peaks with Cu doping and they mostly lie around the same position.

## **1.b) Reciprocal Space Mapping:**

Reciprocal space mapping is a tool which gives information about in-plane strain coherency and in-plane lattice parameters in some cases [41]. It is a kind of 3-D plot of wave vectors along x and y axis. We have performed RSM (Reciprocal Space Mapping) measurements of  $PrNi_{1-x}Cu_xO_3(x = 0 \& 0.10)$  *i.e.* lowest and highest doping thin films around asymmetric (301) Bragg's peak. Fig. 3.3 shows RSM images of  $PrNi_{1-x}Cu_xO_3(x=0 \& 0.1)$  thin films on LSAT (100) substrate.



Fig. 3.3 RSM of  $PrNi_{1-x}Cu_xO_3(x=0 \& 10)$  thin films around (301) Bragg's peak on LSAT(100).

The thin film and substrate peak lie along the same pseudomorphic line indicating that the strain coherency is maintained along thickness of the films. Both the films are coherently strained and there is no relaxation in films with Cu-doping at Ni-site in PrNiO<sub>3</sub>. Film peak lies above that of substrate in the given figure, which indicates that wave vector in y-direction is more for thin films as compared to that of bare substrate. As wave vector is inversely proportional to the lattice constant in out of plane direction and hence lattice parameter in in-plane is less for thin film. It clearly shows that tensile strain is present in the films. No systematic and significant change in the lattice parameter was observed with doping which is similar to observed in the bulk Cu-doped NdNiO<sub>3</sub> system [42].

## 1.c) Temperature dependent resistivity measurement:

All the above discussed characterization were carried out in order to examine structural purity. These measurements don't tell anything about electrical conduction of material. We have also performed temperature dependent resistivity measurements of all PrNi1-<sub>x</sub>Cu<sub>x</sub>O<sub>3</sub>(x=0-0.10) films on LSAT in order to get idea about electrical transport. This was done by using four-probe resistivity setup in **JANIS** made Close Cycle Refrigerator (CCR) cryostat. Four-probe method is mostly used in case of thin films and wafers [43]. Here, current passes through the outer contacts which are close to the edges of the sample and potential difference is measured across the inner contacts. It gives us an idea whether given sample is metallic or insulating and how this effect evolves with temperature. Fig. 3.4 shows resistivity vs temperature plots for all PrNi<sub>1-x</sub>Cu<sub>x</sub>O<sub>3</sub> (PNCO) films. It is clear that thin film with x=0 *i.e.* undoped film shows metal to insulator phase transition at around 100K. All the other films show a complete metallic state with a suppression of MIT. For x=0.01 and 0.02, thin films tend to show metallic state at lower temperatures. Except undoped film, all the other films are showing completely metallic behaviour with different slopes.



Fig. 3.4 Temperature dependent resistivity curves for  $PrNi_{1-x}Cu_xO_3(x=0-0.10)$  thin film on LSAT (001) substrate.

It is important to note that as we increase Cu-doping content, resistivity of thin films is decreasing that means they are going towards more conducting or metallic state. Cu can add extra electron to d-band and hence increases conductivity. The metallicity may be influenced by modification in band structure of PrNiO<sub>3</sub> due to Cu-doping. The PNCO film with x = 0.10 shows a complete metallic state with lower resistivity and the curve seems to be more straight than other films at lower temperatures.

As discussed earlier, the RNiO<sub>3</sub> compounds lies in the category of charge transfer gap insulators according to the Zaanen, Sawatzky and Allen (ZSA) frame work [44] where the energy difference ( $\Delta$ ) between the O 2p band and unoccupied Ni 3d band is smaller than the d-d coulomb interaction energy (U) *i.e.* gap between upper and lower Hubbard band. Recent studies in RNiO<sub>3</sub> show that this charge transfer gap ( $\Delta$ ) is very small or it can even be negative [45]. Because of this small gap, the ground state of the RNiO<sub>3</sub> may be considered as a mixture of 3d<sup>7</sup>2p<sup>6</sup>and 3d<sup>8</sup>L configuration, where L is a legend hole in the oxygen 2p band [46]. It is well known that the relative amount of Ni<sup>2+</sup> and Ni<sup>3+</sup> ions in PrNiO<sub>3</sub> affects the electronic transport in PrNiO<sub>3</sub> and presence of Ni<sup>2+</sup> decreases the band width [47] and favors the insulating state. Cu acquires 2+ oxidation state in oxides, such as in high temperature superconductors and also in doped RNiO<sub>3</sub> [48]. In view of these arguments, Cu<sup>2+</sup> may replace the Ni<sup>2+</sup> and this not only increases the carrier density in *d* band but also increases the bandwidth (decrease in charge transfer gap) resulting in overlapping of orbitals and a complete metallic state is observed.

In order to understand metallic behavior completely, we have fitted some theoretical equation on temperature dependent resistivity curves. As we have already discussed in chapter 1, in metallic cases resistivity may fit to the power law equation given by:

$$\rho_{\rm NFL} = \rho_0 + AT^n$$
 - (3.2)

where,  $\rho_0$  is the residual resistivity, *i.e.* resistivity at absolute zero, which appears because of lattice imperfection, impurities and structural defects *etc* [49]. A is a constant which represents electron-electron scattering strength. If in this equation n=2 is observed, then it is considered as LFL (Landau Fermi Liquid). However, in some cases, n<2 is also reported which is a deviation to NFL (Non Fermi Liquid) state. In certain cases, n=1.6 and n=1.3 are observed. It means that our system is going away from classical fermi transport and heading towards semi-classical regime.

Since, this power law equation fits to a certain temperature range only, in order to describe resistivity behaviour completely, we account for resistivity saturation [50, 51, 52]. Thus the above equation modifies as:

$$\rho^{-1}(T) = \rho^{-1}_{NFL}(T) + \rho^{-1}_{SAT} \qquad (3.3)$$

where  $\rho_{SAT}$  acts as a parallel resistor, which is applied to many materials showing resistivity saturation at higher temperature.



Fig. 3.5 Inverse of resistivity( $\rho^1$ ) versus temperature for PrNi<sub>1-x</sub>Cu<sub>x</sub>O<sub>3</sub> (x= 0 - 0.10) on LSAT(100).

Fig. 3.5 (a-e) shows inverse of resistivity with temperature plots for  $PrNi_{1-x}Cu_xO_3$  (x= 0 – 0.10) on LSAT (100). All the curves fit very well with equation 3.3. In Fig. 3.5(a) Pure  $PrNiO_3$  on LSAT shows a metal to insulator phase transition at ~100K and its fit converges very well with n=1.6, indicates a Non-Fermi Liquid behaviour.  $PrNi_{1-x}Cu_xO_3$ (x= 0.01 – 0.10) remain metallic in the entire temperature range as shown in fig. 3.5(b-e). These films fit with NFL exponent 1.3, which is also a Non-Fermi Liquid. We have got values of fitting parameters. Table 1 lists all the fitting parameters:

x	п	$A( imes 10^{-7})\ (\Omega.cm(K^n)^1)$	$ ho_0( imes 10^4) \ (\Omega.cm)$	$ ho_{SAT}( imes 10^4) \ (\Omega.cm)$
0	1.6	0.16	0.612	2.04
0.01	1.3	1.24	0.795	6.52
0.02	1.3	1.23	0.655	5.85
0.05	1.3	0.87	0.567	3.87
0.10	1.3	0.49	0.503	1.59

Table 1: Transport properties of  $PrNi_{1-x}Cu_xO_3$  (x = 0.01 – 0.10) thin films

It is clear from table 1 that all the fitting parameters have a trend with Cu-doping. Although n is an adjustable parameter in fitting,

its two values *i.e.* 1.6 and 1.3 are obtained from the fitting of equation 3.3 on all the inverse resistivity plots, indicating NFL behaviour. For the pure film NFL behaviour with n = 1.6 is observed, but for the Cu-doped films, n changes to 1.3. It indicates Cu doping is deriving system towards more metallic state. The parameter representing residual resistivity,  $\rho_0$ , decreases linearly with increasing Cu doping. The Cu-doping imposes short-range ordering in the system and hence it decreases the scattering rate [14].  $\rho_{SAT}$  is often linked with maximum resistivity that approaches the Mott-Ioffe-Regel limit [53].

$$\rho_{\text{MIR}} = \frac{3\pi^2\hbar}{q^2 K_f^2 l_{min}} \qquad ----(3.3)$$

where  $l_{min}$  is the minimum mean free path, which equals to the interatomic spacing. If we consider  $K_f = (3\pi^2 N)^{1/3}$ , total carrier density~ $10^{22}$ /cm<sup>3</sup>, *a*~3.83 Å *i.e.* lattice constant of PrNiO<sub>3</sub>, ħ as reduced Planck's constant and q as elementary charge then  $\rho_{MIR}$  comes out to be 0.716-0.717 mΩ.cm. Replacement of Cu in place of Ni causes a change in lattice parameter of the corresponding unit cell which also changes its  $\rho_{MIR}$ . Therefore, resistivity saturation value changes systematically with Cu-doping. We observe a decrease in electron-electron interaction factor with increasing Cu-doping. Cu is providing extra electron in *d*-band, so the number of charge carriers increases.

In order to investigate the effect of Cu doping on metallic nature of the films in detail, we have calculated temperature coefficient of resistivity ( $\alpha$ ) for all the thin films in metallic state. The temperature coefficient of resistivity is given as:

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

where,  $\rho_0$  is residual resistivity, is a measure of how resistivity of a material changes with temperature and it has a positive value for metals whereas negative value for insulators. Figure 3.6 shows variation  $\alpha$  with doping content. The rate of change in resistance with temperature is determined by  $\alpha$ . It can be seen that  $\alpha$  initially increases with Cudoping up to 2% and then linearly decreases up to 10%. From this inset figure, it can be seen that the 2% Cu-doping seems to be an optimal doping for highest  $\alpha$  and metallicity.



Fig. 3.6 Temperature coefficient of resistivity versus x.

We conclude that for series  $S_1$  films, Cu-doping is changing the non-fermi liquid behaviour. NFL exponent is changing from n=1.6 to n=1.3 just by fractional doping, that means it is going towards more metallic side. Cu-doping can be an effective tool to describe conduction behaviour of these PrNiO<sub>3</sub> films. We have also varied thickness of these thin films.

# 2) PrNi<sub>1-x</sub>Cu<sub>x</sub>O<sub>3</sub> (*x*=0-0.10) thin films (PNCO/LSAT) under tensile strain (5 nm):

## 2.a) X-Ray Diffraction:

In order to examine phase purity and epitaxial strain in the films, we have performed XRD (X-Ray diffraction) measurement using PanAlytical made setup. Fig. 3.7 shows XRD patterns of series S<sub>3</sub> films on LSAT substrate.



Fig. 3.7 XRD patterns of PrNi<sub>1-x</sub>Cu<sub>x</sub>O<sub>3</sub>(x=0.01-0.10) films on LSAT.

The pseudo-cubic lattice parameter of bulk PrNiO<sub>3</sub> is 3.83A<sup>o</sup> and that of LSAT substrate is 3.86 A<sup>o</sup>. When a thin film of PrNiO<sub>3</sub> is deposited on LSAT, then because of this in-plane lattice mismatch unit cell of thin film material tries to expand itself. As a result of that, inplane lattice parameter of thin film increases which causes a decrease in out of plane lattice parameter in order to keep unit cell volume constant. The Bragg's law is given by:

$$2dsin\Theta = n\lambda$$
 -----(3.1)

where d is the interatomic spacing which is equivalent of out of plane lattice parameter,  $\Theta$  is the diffraction angle, n is the order of diffraction and  $\lambda$  is the wavelength of light used. So, with decrease in *d*, diffraction angle increases. There is an increase in diffraction angle  $\Theta$ . This is an indication of tensile strain present in the thin films. As shown in fig. 3.7, (200) peak of all films shows a shift towards right side of the graph. This is generally attributed as tensile strain. It means unit cell of film is trying to expand itself in order to maintain same lattice spacing as that of substrate. This is the reason of tensile strain. In fig. 3.7, all the substrate peaks lie along the same line and all the films have peak towards right side.

## 2.b) Temperature dependent resistivity measurement:





Fig. 3.8 Temperature dependent resistivity curves for  $PrNi_{1-x}Cu_xO_3$ (x=0 - 0.10) thin film on LSAT (001) substrate of series S<sub>2</sub>.

Temperature dependent resistivity measurements of all PNCO films on LSAT were carried out using four-probe resistivity setup in **JANIS** made Close Cycle Refrigerator (CCR) cryostat. Fig. 3.8 shows resistivity vs temperature plots for all PNCO films. From this resistivity plot, we can see that for x=0 and x=0.01 films shows insulating behaviour for the complete temperature range (300-10K). For all remaining doping percentage, metallic state is observed. So, only by a fractional change in Cu-doping content, electrical conduction behaviour changes completely. As discussed earlier, in metallic state, we can fit resistivity curve to a power law equation given by:

$$\rho^{-1}(T) = \rho^{-1}_{NFL}(T) + \rho^{-1}_{SAT} \qquad (3.3)$$

where  $\rho_{SAT}$  acts as a parallel resistor, which is applied to many materials showing resistivity saturation.



Fig. 3.9 Inverse of resistivity( $\rho^1$ ) with Temperature for PrNi<sub>1-x</sub>Cu<sub>x</sub>O<sub>3</sub> (x=0.02-0.10) on LSAT.

Fig. 3.9 shows inverse of resistivity with temperature for  $PrNi_{1-x}Cu_xO_3$  (x=0.02-0.10) thin films belonging to series S<sub>3</sub>. All data fit with NFL exponent 1.6 and remain metallic for entire temperature range. It is important to note that at lower temperature (10-50K) resistivity saturation is observed. It is an indication that two contrasting factors are playing role in resistance. This effect is observed in semi-metals where carrier density and mobility show opposite trend with temperature and hence the resultant effect is neglected. As Cu doping content is increased, this saturation region is resistance is decreasing.

Thickness	x	n	$\begin{array}{l} A(\times 10^{-7}) \\ (\Omega.cm(K^n)^{-1}) \end{array}$	$ ho_0( imes 10^{-4})$ ( $\Omega.cm$ )	$ ho_{SAT}( imes 10^4) \ (\Omega.cm)$
5 nm					
Series 2	0.02	1.6	0.89	8.2	20.28
	0.05	1.6	0.48	3.88	7.21
	0.10	1.6	0.40	2.51	4.17

Table 2 lists all fitting parameters:

It is clear from table 2 that all the fitting parameters have a trend with Cu-doping. Although *n* is an adjustable parameter in fitting, its two values *i.e.*1.6 and 1.3 are obtained from the fittings of equation 3.3 in inverse resistivity data of metallic region, indicating NFL behaviour. For x=0.02, 0.05 and 0.10, NFL exponent comes out to be 1.6. The parameter representing residual resistivity,  $\rho_0$ , decreases linearly with increasing Cu content. Cu-doping imposes short-range ordering in the system and hence it decreases the scattering rate.  $\rho_{SAT}$  is often linked with maximum resistivity that approaches the Mott-Ioffe-Regel limit [52]:

$$\rho_{\text{MIR}} = \frac{3\pi^2\hbar}{q^2 K_f^2 l_{min}} \qquad ----(3.4)$$

where  $l_{min}$  is the minimum mean free path, which equals to the interatomic spacing. If we consider  $K_f = (3\pi^2 N)^{1/3}$ , total carrier

density~ $10^{22}$ /cm<sup>3</sup>, *a*~3.83 Å for PrNiO<sub>3</sub>, ħ as reduced Planck's constant and q as elementary charge then  $\rho_{MIR}$  comes out to be 0.716-0.717 mΩ.cm. Replacement of Cu in place of Ni causes a change in lattice parameter of the corresponding unit cell which also changes its  $\rho_{MIR}$ . Therefore, resistivity saturation value changes systematically with Cudoping. We observe a decrease in electron-electron interaction factor with increasing Cu-doping. Cu is providing extra electron in *d*-band, so the number of charge carriers increases and it may be the cause of increase in electron interaction. All parameters are showing continuous trend with change in Cu content.
# 3) PrNi<sub>1-x</sub>Cu<sub>x</sub>O<sub>3</sub> (*x*=0-0.10) thin films (PNCO/LAO) under compressive strain (12nm):

#### **3.a) X-Ray Diffraction:**

In order to examine phase purity and nature of strain present in the films, we have done X-Ray diffraction measurement of 12 nm Cudoped films on LAO substrate. 12 nm thickness of films was approximated by adjusting total number of laser shots. As the pseudocubic lattice parameter of bulk PrNiO<sub>3</sub> is  $3.83A^{\circ}$  and that of LaAlO<sub>3</sub> (LAO) substrate is  $3.79A^{\circ}$ , so there is -1% lattice mismatch between thin films and substrate. Fig. 3.10 shows the XRD patterns of all the films on LAO.



Fig. 3.11 XRD patterns of  $PrNi_{1-x}Cu_xO_3(x=0-0.1)$  thin films on LAO (100).

When a thin film of PNCO is deposited on LAO, then unit cell of film will try to compress itself in order to fit in lattice spacing of substrate. As a result of it, in-plane lattice parameter decrease which causes increase in out of plane lattice parameter to conserve overall volume of unit cell. Using Bragg's law, we can infer that diffraction angle is decreasing and that's why we observe a leftward shift in XRD patterns. This is called compressive strain. From fig. 3.10, we can say that thin films are impurity free with compressive strain. They are highly oriented towards crystallographic axis (100). There is no systematic shift in film peaks with Cu-doping content. But we can say that films are having compressive strain. There is no broadening of films peaks observed with Cu-doping.

#### 3.b) Temperature dependent resistivity measurements:

Temperature dependent resistivity measurements of all PNCO films on LAO were carried out using 4-probe resistivity setup in **JANIS** made Close Cycle Refrigerator (CCR) cryostat.



Fig. 3.11 Temperature dependent resistivity curves for  $PrNi_{1-x}Cu_xO_3$ (x=0 - 0.10) thin film on LAO (001) substrate.

Fig. 3.12 shows resistivity vs temperature plots for all  $PrNi_{1-x}Cu_xO_3$  (x=0 - 0.10) films. Resistivity data is not smooth and it seems to be rough. We did not fit any power law equation on the plots. Only one thing we can infer from this data is that resistivity is increasing with increasing Cu content. Since LAO is offering compressive strain to the Cu doped thin films, combined effect of electronically active ion doping and compressive strain is making this data rough.

## **Conclusion:**

In conclusion, we can say that the divalent Cu ion doping at trivalent Ni-site in PrNi<sub>1-x</sub>Cu<sub>x</sub>O<sub>3</sub> films strongly influences the electronic properties due to injection of charge carriers in *3d* band.

Several systematic changes are observed with increasing Cu-doping:

- the XRD peaks of films of all series shift on 2θ-axis indicating a variation in lattice parameters *i.e.* showing tensile strain on LSAT and compressive strain on LAO substrates.
- ii) In series A, NFL behaviour is modified by Cu-doping as indicated by a change of parameters in power-law equation with n=1.6 for undoped film to n=1.3 for doped films.
- iii) In series C, reduced thickness causes a transformation in NFL from n=1.3 to n=1.6 as seen from Table-2.
- iv) Both,  $\rho_0$  and  $\rho_{SAT}$  decrease smoothly indicating enhanced metallicity by Cu-doping in both the series.

The present results clearly suggest that the thickness variation and Cu-doping affects the metallicity and NFL state in a controllable manner in PrNiO<sub>3</sub> thin films.

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