Experimental and characterization techniques

2.1 INTRODUCTION

This chapter basically deals with the various experimental techniques used for the present research work. There are two main objectives of the present chapter: the first one is to explain synthesis of the bulk samples/thin films and the other to describe various characterization techniques employed for evaluating different properties of the samples.

2.2 SYNTHESIS OF BULK MATERIALS

The bulk materials can be prepared by various techniques such as solid-state reaction route,\textsuperscript{1-4} sol gel\textsuperscript{5} and coprecipitation.\textsuperscript{6,7} In the present work, the bulk target materials for the thin film deposition of Ni doped LaFeO\textsubscript{3} based materials have been synthesized by solid-state reaction technique. This technique of bulk preparation is also known as ceramic method and it has superiority over other methods such as sol gel or copresipitation technique due to easiness of the process involved. The main steps of solid-state reaction route are (i) mixing the constituent oxide powders in stoichiometric proportion and calcination, (ii) the pelletization and sintering of the polycrystalline bulk.

(i) Mixing/Calcination

We have prepared the LaFe\textsubscript{1-x}Ni\textsubscript{x}O\textsubscript{3} (x=0.1 to 0.6) bulk samples from the mixtures of the high purity (Aldrich/Sigma, 99.999\%) stoichiometric amounts of La\textsubscript{2}O\textsubscript{3}, FeO and NiO in powdered form. The mixtures were ground in an agate mortar with isopropanol to make them homogeneous, as the physical uniformity and the chemical homogeneity of the mixtures are of significant importance for the good quality samples.

The homogeneous mixtures were kept in an alumina crucible and heated in resistive furnace. The powders were calcinated at 1100 °C. This process is repeated 3-4 times with intermediate grinding and every time
keeping the temperature for calcination higher than that in the previous step.

(ii) Pelletization/Sintering

The preheated powder was again ground with a few drops of poly vinyl alcohol (PVA), which acts as a binder in the sample and pelletized by using a rectangular die of dimensions 14mm × 4mm × 2mm. A pressure of the order of 3 tons/cm² was used for making the pellets by hydraulic press. The pellets were sintered at 1300 °C for about 24 hours. The sintering process was followed by slow cooling at a suitable controlled rate (~5 °C per minute), as it favours the required oxygen content in the material.

2.3 THIN FILM DEPOSITION

The importance of coatings and the synthesis of new materials for industry have resulted in a tremendous development of innovative thin film processing technologies. The demand for development of smaller and smaller devices with higher speed especially in the new generation of integrated circuits requires specific materials and new processing techniques suitable for future giga scale integration technology. In this regard, physics and technology of thin films can play an important role in achieving this goal. Therefore, the production of thin films has become very important for device purposes.

There exist a huge variety of thin film deposition processes and technologies, which originate from purely physical or purely chemical processes. Some of the important thin film processes are based on liquid phase chemical techniques, gas phase chemical processes, glow discharge processes and evaporation methods. Recently, a considerable number of novel processes that utilize a combination of different processes have been developed. This combination allows a more defined control and tailoring of the microstructure and properties of thin films. Thin films can be prepared by various deposition techniques such as pulsed laser deposition (PLD), metal organic chemical vapor deposition (MOCVD), DC and RF sputtering, chemical vapour deposition (CVD), molecular beam epitaxy (MBE), thermal deposition and sol gel, etc. The basic process involves the converting materials into an evaporating flux of atomic and molecular species and then transporting them onto a suitably heated substrate in an
appropriate ambient. The choice of substrate for the thin film deposition is guided by the lattice parameter of the compound and substrate as well as the orientation of the substrate. For the present work the films were prepared by PLD and MBE methods.

2.3.1 Pulsed Laser Deposition

Among the large number of processes as mentioned above to grow the thin films, pulsed laser deposition (PLD) has emerged as a unique method to obtain epitaxial and nearly single crystal like thin films of multicomponent oxides. Epitaxial thin films of superconducting high $T_c$ cuprates, metallic, ferroelectric, ferromagnetic, magnetite, manganites, dielectric oxides and their multilayers etc. have been made by this method. Conceptually and operationally, PLD is a simple technique for the thin film deposition.

The main advantages of PLD systems are in its capability of enabling the fast layer deposition, precise control on stoichiometry and simple implementation of constituents. This is difficult to achieve in other conventional techniques such as evaporation, sputtering, etc. This so called “stoichiometry transfer” between target and substrate has made the PLD technique interesting for the growth of complex systems. Generally, XeF ($\lambda = 352$ nm); XeCl ($\lambda = 308$ nm); KrF ($\lambda = 248$ nm); KrCl ($\lambda = 222$ nm); ArF ($\lambda = 193$ nm); and $F_2$ ($\lambda = 157$ nm) excimer lasers are commercially available and can be used for thin film deposition. It uses a pulsed laser beam, usually but not necessarily, from an ultraviolet excimer laser with pulse energy of about 1 joule. The typical duration of the laser pulse is a few tens of nanosecond. Because of such a short duration of the pulse, tremendous power ($\sim 10-100$ MW/pulse) is delivered to the target. This is because of the nonequilibrium nature of PLD in the sense that the absorption of energy and ablation takes place in a very short time, usually within a nanosecond, before thermodynamic equilibrium is reached. Fig. 2.1 shows the typical schematic of the PLD technique. The system consists of a vacuum chamber, which is evacuated by diffusion and rotary pumps. This assembly is capable of obtaining a base vacuum of the order of $10^{-5}$ to $10^{-6}$ torr in the chamber. The laser beam of the desired energy density incident at an angle of $45^\circ$ at the target surface is focused on to the rotating target, which is a 2.5 cm diameter pellet of the material whose film is to be deposited.
The desired energy density was obtained by focusing the laser beam with the help of a quartz lens to a proper spot size. Laser beams of energy 300 to 400 mJ are focused to a size such that energy density is maintained between 1 to 5 J/cm². Typically, an energy density of ~2 J/cm² was maintained at the target for the present work. The substrate on which film is to be grown is placed opposite the target at a distance of 4-5 cm on a resistive heater (which is capable of achieving temperature upto 850 °C on the surface) with the help of a thin conducting silver layer or clamp. The substrate was ultrasonically cleaned in trichloro-ethylene, acetone and methol. Alumel-Chromel calibrated thermocouple was used to measure the substrate temperature.

Laser processing of materials is a highly non-equilibrium process due to very short pulse width of the beam. When a laser beam of energy density above a material dependent critical value is incident on the target, a large amount of energy is deposited in a few hundred-nanometer depth from the surface over a very short time scale. Due to such a transient energy transfer, the temperature of the surface layers is raised to a sufficiently high value (higher than the melting temperature of the material) and thus the melting
of material starts at the surface. The process takes place in a very short duration of time scale. This causes a rapid ejection of the laser-induced plasma of materials at right angle from the surface of the target in the forward direction towards the substrate. The plasma plume contains various excited atoms, molecules, ions and neutral species. This plasma quickly expands away from the target towards the substrate where the adiabatic expansion of plasma at the surface of the heated substrate takes place leading to development of the desired thin film. While PLD is recognized to transport the stoichiometry from the target to the film, there are several parameters, which immensely influence the growth and properties of thin films. These parameters are laser energy density falling on the surface of the target, the ambient background pressure during and after deposition, the pulse repetition rate, the temperature of the substrate, the choice and the orientation of the substrate itself, the target to substrate distance etc. Laser energy density is a vital factor, which highly affects the properties of films. If the energy density is low, the complex target molecules do not evaporate congruently; if very high, droplet kind of particles are deposited on the substrate. The ambient oxygen partial pressure is vital for the thin film growth of manganites to make up for the loss of oxygen in the ceramic target itself or during the course of transfer of the excited species from the target to the substrate.

There are several limitations of the PLD technique. Firstly, beam scanning and focusing systems are complex and expensive and secondly, it is not always possible to have a laser of wavelength compatible with the absorption characteristics of the material to be evaporated. It is difficult to have large area film deposition due to narrow angular distribution of the plasma plume. To overcome this problem, the substrate can be scanned vertically/horizontally or the laser beam can scan a large area of the target. The system has low energy efficiency and the size of the uniformly deposited film is small (10 to 20 mm) in diameter. The target is scanned during the deposition and sanding done after each deposition in order to reduce roughness to the minimum. To achieve uniformity, the rotation of the target (−10 rpm) is very much desirable. Nevertheless, all the above-mentioned obstacles have been successively overcome in the novel big area deposition PLD systems.
In the present research work the epitaxial thin films of LaFe\(_{1.2}\)Ni\(_x\)O\(_3\) (\(x=0.3, 0.4\) and 0.5) were grown on LaAlO\(_3\) (100) single crystal substrate using PLD technique at University of Pune, Pune-411007, India. A KrF excimer laser (Lambda Physik, LPX200) having wavelength (\(\lambda\)) 248 nm and pulse duration (\(t_p\)) of 20 ns was employed for thin film deposition. The ablation was performed at a laser energy density of 2.1 J/cm\(^2\) on the target surface. The substrate was held at 650 °C, while the oxygen partial pressure of 200 and 300 mtorr was maintained for two separate depositions.

### 2.3.2 Molecular Beam Epitaxy

Molecular beam epitaxy (MBE) was developed in the early 1970s as a means of growing high-purity epitaxial layers of compound semiconductors\(^{23,24}\). Since that time it has evolved into a popular technique for growing III-V compound semiconductors as well as several other materials. MBE can produce high-quality layers with very abrupt interfaces and good control of thickness, doping and composition. Because of the high degree of control possible with MBE, it is a valuable tool in the development of sophisticated electronic and optoelectronic devices.

As MBE is a controlled deposition process carried out in a UHV system, there are some basic requirements of such a machine. For generating and maintaining a clean vacuum as high as 10\(^{-10}\)-10\(^{-11}\) torr for the process, the vacuum lock mechanism becomes a basic need. Therefore, a simple MBE system consists of minimum two UHV chambers isolated by a gate valve and pumped by two independent systems. One of them is used as growth chamber while the other one is for sample introduction/preparation. Present day machines have a number of metal chambers with vacuum load locks, which are used for different processings of a wafer before exposure to atmosphere. A schematic of a simple growth chamber is shown in Fig. 2.2. A complex arrangement of various constituent sub-assemblies starting from evaporation sources, growth manipulator to various diagnostic instruments (RHEED, RGA) is seen. With proper design of individual shutter and control of their movements, either manually or through microprocessor, the rate of atomic spray of individual sources may be adjusted to be one monolayer per second. The material sources or effusions cells are independently heated until the desired material flux is achieved. Changes in the temperature of a cell as small as 0.5 °C can lead to flux changes on the order of one percent.
To control thicknesses to about 1%, highly stable control loops with Tungsten-Rhenium thermocouples and proportion, integral and derivative (PID) controllers are used as well as a chilled panel separating the cells to prevent thermal cross talk. Computer controlled shutters are positioned in front of each of the effusion cells in order to shutter the flux reaching the sample within a fraction of a second. Since shutters in front of the effusion cells reflect some of the power back into the cell, opening the shutters is known to cause flux transients of the order of a few percent with a time constant of several minutes. These transients are difficult to measure and depend on cell and system-specific factors such as the shutter type and location, heater element design and thermocouple placement. Although the system provides precise controlled process parameters, it has certain design constraints. Some of them are as follows: It requires a continuous pumping provision. Unlike conventional deposition system, a particular MBE system is restricted for use to a class of materials to avoid contamination even at the level of ppm- ppb. Growth apparatus is not permitted for frequent opening for cleaning purpose as it poses problems to achieve UHV. Whenever a system is opened for repair of any sub-assembly or for loading of evaporation source materials new Ag-plated gaskets are needed and a prolonged baking becomes necessary leading to a long down time.

Fig. 2.2 A schematic view of MBE system.
Alterations and additions to a predesigned chamber is quite difficult due to the precisions involved in achieving deposition uniformity in terms of thickness, composition etc. Since various operations such as transfer of substrates for the desired growth position from loading to growth chamber, movements for flux measurement, rotation of substrates etc. are manipulated from out side, fall of the substrate holder inside the chamber is one of the major set backs at the time of process. MBE operations demand high running cost in terms of power, liquid nitrogen etc.

In the present work we have grown Fe$_3$O$_4$ epitaxial thin films on [100] oriented MgO single crystal substrates using an oxygen plasma assisted MBE system (DCA MBE M600) with a base pressure of $5 \times 10^{-10}$ torr at the Trinity College in Dublin, Ireland.

The M600 MBE is a commercial system supplied by DCA Instruments. It consists of the main growth chamber along with a load lock chamber module. The samples are loaded from the load lock through the UHV gate valve using magnetic coupled transfer arm. The deposition chamber is a vertical 600 mm internal diameter chamber (base pressure $< 5 \times 10^{-10}$ torr), designed for metal or oxide- MBE. The growth chamber has two ports for single or multi-crucible electron guns and up to eight ports for effusion cells or other sources. The system can be configured for 1.5", 2", 3" or 4" max. substrate size. The growth chamber has several ports reserved for precise flux control equipment. In the standard configuration the electron gun fluxes are controlled using quartz crystal film thickness monitors. Ports are reserved for more accurate flux control using either cross beam quadrupole mass spectrometer or atomic absorption spectroscopy. It is equipped with a large volume cryopanel, one single and one multi-heart electron gun, three effusion cells, substrate manipulator, deposition rate monitors and oxygen plasma source. It is also equipped with the state of art Reflection High Energy Electron Diffraction (RHEED) and Residual Gas Analyser (RGA) facilities for in-situ characterization of growth parameters.

2.4 SWIFT HEAVY ION IRRADIATION

The swift heavy ion (SHI) have proven to be versatile tool for processing materials and synthesizing unique structures of interest for a wide variety of applications involving optical materials, magnetic materials, insulators and polymers. Introduction of ion species into the solids can be used to alter and
tailor many material properties like structural, transport, electronic, magnetic and optical etc. Defect generation during ion-solid interactions adds a further dimension to this processing capability enabling kinetic mechanisms to synthesize metastable phases normally unobtainable under equilibrium thermodynamic conditions. Applications of ion beam are modifying materials properties and enhancing the performance of electronic and optical materials, insulators, polymers and metals. Synthesizing new structures and phases and resulting property changes are achieved by ion-beam processing. Controlled introduction of different defect states in solid matrices have been beneficially used in material science for decades to improve the performance of the materials.25-34

First of all, it is essential to understand the basic phenomenon of ion solid interaction. It is well established that when a high-energy heavy ion passes through a material, it suffers energy mainly in two ways:

1. direct nuclear collisions, i.e. nuclear energy loss $S_n$ or $(dE/dx)_n$.
2. inelastic energy loss due to electronic excitation, i.e. electronic energy loss $S_e$ or $(dE/dx)_e$.

The nuclear energy loss is dominant in the low energy region whereas the electronic energy loss dominates in the higher energy region. Depending on the electronic energy loss, various kinds of defect, such as point defects, columnar amorphization are formed in the system.

When energy of the incident ion is small enough (~ keV) so that the ion's velocity is smaller than the Fermi velocity of the electrons of the target material, the incident ion collides and loses its energy directly with the nucleus and looses its energy. In this situation $S_n$ dominates over $S_e$. However, for SHI (energy ~ MeV), the incident ion has velocity of the order of Fermi velocity of the electrons of the target material and suffers collision with the electronic system of the target material. In such a situation, $S_e$ is much higher than the $S_n$ value. Therefore, energy transferred to the materials can be considered to occur mainly because of electronic excitations, provided the thickness of the material is less than the stopping range of the heavy ion. Using the standard transport of ions in matter TRIM95 simulation program,35 we have calculated the $(dE/dx)_e$ and $(dE/dx)_n$ as a function of energy for $^{107}$Ag ion interacting with systems.
It is well established that for the production of columnar defects one requires \((dE/dx)_e\) above a threshold value. Using Szene's model, one can estimate the threshold for the columnar amorphization for oxide magnetic materials.

From the beginning of the 1950s, several theoretical models have been proposed to explain the appearance of tracks induced in matter by the slowing down of energetic ions in the electronic stopping power regime. In the Coulomb spike model, it is assumed that an energetic ion along its path creates a cylindrical region of highly ionized matter. Repulsive electrostatic forces act during the period before electronic neutrality is restored and give rise to a violent explosion. The Coulomb explosion will be significant only if the charge-neutralization time exceeds \(10^{-14}\) s for light target atom. This phenomenon leads to a localized destruction of the lattice. Schiwietz et al. showed that the Coulomb explosion cannot be efficient in such carbon structures as diamond like and graphite like amorphous carbon, because the electronic charge neutralization is too fast in these materials and life of the repulsive states is not long enough to initiate the Coulomb explosion. However, the development of a detailed and quantitative model based on such a mechanism is difficult and has not yet been performed. The thermal-spike model uses a different approach. Here the energy is deposited on the electrons of the target by the projectile. In a first step this energy is shared between electrons and in a second step, is transferred to the lattice atoms by an electron-lattice interaction leading to a large increase of temperature along the ion path. The increase of temperature followed by a rapid quenching (\(10^{13}-10^{14}\) K/sec) results in an amorphised columnar structure when the melt solidifies. Several observations, such as the defect annealing, track formation, the effects of irradiation temperature quantitatively support this description. Track formation in metals and insulators can be explained with thermal spike model. Coulombic explosion and thermal spike can not be separated that means both of the effects are present simultaneously. The cylindrical shock wave generates strain in the lattice around the ion track and presence of thermal spike creates the amorphized columnar tracks. This can be used to create strain in materials by controlling the ion fluence.

In the present work irradiation were carried out at Inter-University Accelerator Centre (IUAC), New Delhi on \(\text{LaFe}_{1-x}\text{Ni}_x\text{O}_3\) (\(x=0.3, 0.4\) and 0.5)
and Fe$_3$O$_4$ thin films at room temperature with 190 MeV $^{107}$Ag ion beam with fluence values $5\times10^{10}$, $1\times10^{11}$, $5\times10^{11}$, $1\times10^{12}$, $5\times10^{12}$ and $1\times10^{13}$ ions/cm$^2$.

The beam current was kept at 0.2 pnA to avoid any heating effect. The ion beam was focussed to a spot of 1x1 mm$^2$ size and scanned over an area of 10x10 mm$^2$ using magnetic scanner to irradiate the whole sample uniformly. The fluence values were measured by collecting the charge falling on the sample mounted on an electrically insulated sample ladder placed in secondary electron suppressed geometry. The ladder current was integrated with a digital current integrator and charged pulses were counted using a scalar counter in order to observe modification in its structural, electrical transport and magnetic properties. The schematic of 15UD pelletron accelerator is shown in Fig. 2.3.

![Fig. 2.3 The schematic of 15UD pelletron accelerator.](image-url)
The 15UD pelletron is a versatile, heavy ion tandem type of electrostatic accelerator. In this pelletron, negative ions are produced and preaccelerated to ~ 400 keV and injected into a strong electric field inside an accelerator tank filled with SF₆ insulating gas. At the center of the tank there is a terminal shell that is maintained at a high voltage (~16 MV). The negative ions on traversing through the accelerating tubes from the top of the tank to the positive terminal are accelerated. On reaching the terminal they pass through a stripper, which strips the electrons from the negative ions, thus transforming the negative ions into positive ions. These positive ions are then repelled away from the positively charged terminal and are accelerated to ground potential to the bottom of the tank. In this manner, same terminal potential is used twice to accelerate the ions. On exiting from the tank the ions are bent onto a horizontal plane by an analyzing magnet, which also selects a particular beam of ions. The switching magnet diverts the high-energy ion beam into the different experimental areas of the beam hall. The entire machine is computer controlled and is operated from a centralized control room.

2.5 SAMPLE CHARACTERIZATION TECHNIQUES

The development of materials, processes and advanced devices for microelectronics and microsystems requires a huge effort in the field of the characterization techniques. We have used various experimental techniques to characterize structural, electrical and magnetic properties of our samples.

2.5.1 X-ray Diffraction

X-ray diffraction (XRD) provides a fast and reliable tool for routine mineral identification. XRD is particularly useful for identifying fine-grained minerals and mixtures or intergrowths of minerals that may not lend themselves to analysis by other techniques. XRD can provide additional information beyond basic identification. If the sample is a mixture, XRD data can be analyzed to determine the proportion of the different minerals present. Other information obtained can include the degree of crystallinity of the minerals present, possible deviations of the materials from their ideal compositions (i.e. presence of other elements) and the structural state of the materials. This technique is suitable for both forms of samples i.e. bulk as well as thin film and can yield the information regarding the crystallinity of the material,
nature of the phase present, lattice parameter, grain size, out of plane orientation and relative in plane orientation between the film and substrate. In case of thin film, the change in lattice parameter with respect to the bulk gives the idea of nature of strain present in the film.

X-rays are energetic enough to penetrate into the material and their wavelengths are of the same order of magnitude as interatomic distances in solids. Thus, a collimated beam of x-rays is diffracted by the crystalline phases in the sample according to Bragg’s Law

\[ n\lambda = 2dsin\theta, \quad \text{with } \lambda \leq 2d \]

where \( \lambda \) is the wavelength of the x-rays, \( d \) is the interplanar spacing for a family of planes; \( n \) is the order of the diffraction and \( \theta \) the incoming diffraction angle.

The above relation shows that the diffraction effects cannot be observed from a family of planes for any arbitrary angle of incidence. Even if monochromatic x-rays are used, the match amid \( d, \theta \) and \( \lambda \) has to be sought to satisfy the above relation and get the diffraction. So, it is clear that Bragg diffraction is very different from ordinary diffraction, which generally puts no restriction on the incident angle.

2.5.2 Diffraction Techniques

There are various techniques, which are used to x-ray diffraction patterns. The three main techniques are the Laue method, the Rotating crystal method and the Debye-Scherrer method. Debye-Scherrer method is also known as the powder diffraction method. It is fast and very accurate for the determination of lattice constants. In view of this fact we are describing here Debye-Scherrer method.

The Debye-Scherrer Method

Polycrystalline or powdered sample can be used in the present model. Each grain of the sample has a random orientation; therefore, this method is equivalent to the rotating crystal method in which the sample is rotated over all possible orientations. Each reciprocal lattice point will generate a sphere of radius equal to the magnitude of the reciprocal lattice vector. If this spherical shell of reciprocal lattice vectors intersects with the Ewald sphere, it produces Bragg reflections. Each lattice vector of length less than 2 \( k \) will
produce a cone of Bragg reflections, with an angle $\theta$ relative to the un-scattered beam. The magnitude of the reciprocal lattice vector is given by $Q=2k \sin(\theta/2)$. Thus a measurement of $\theta$ will give the lengths of the smallest reciprocal lattice vectors. The another important use of this method is in the study of phase diagrams of alloys systems. Since lattice constant are unique for a materials, this method is widely used for the identification of materials. Further, it is the only method which works for all crystalline materials.

The diffraction pattern can be used to determine the reciprocal lattice vectors and hence the Bravais lattice associated with the crystal. In order to completely determine the crystal structure, one must determine the basis. This can be done by examining the structure and form factors. In thin films, x-rays are diffracted by the oriented crystallites at a particular angle to satisfy the Bragg's condition. Having known the values of $\theta$ and $\lambda$, one can calculate the interplaner spacing. Schematic view of XRD is shown in Fig. 2.4.

![Diagram of X-ray diffractometer](image)

**Fig. 2.4** A schematic of x-ray diffractometer.

The XRD can be taken in various modes such as $\theta$-$2\theta$ scan mode, $\theta$-$2\theta$ rocking curve, and $\phi$ scan. In the $\theta$-$2\theta$ scan mode, a monochromatic beam of x-ray is incident on the sample at an angle of $\theta$ with the sample surface. The detector motion is coupled with the x-ray source in such a way that it always makes an angle $2\theta$ with the incident direction of the x-ray
beam. The resulting spectrum is a plot between the intensity recorded by the detector and $2\theta$.

The crystalline quality of the oriented samples can be estimated by using it in rocking curve mode wherein a single Bragg peak is measured as the sample is tilted within the diffraction plane. In this arrangement the position of the detector is kept fixed at $2\theta$ value corresponding to a particular $d$ value and the sample is rocked around the $\theta$ value. The resulting spectrum is a plot between the intensity and $\theta$. The full width at half maximum (FWHM) of the plot estimates the misorientation of the grains in the film with respect to the sample normal.

The in-plane orientation of the film is determined by using XRD in $\phi$ scan mode (Fig. 2.5). In this mode, the sample is rotated about the surface normal from $0^\circ$ to $360^\circ$ while keeping $\theta$, $2\theta$ and $\chi$ fixed where Bragg condition is satisfied. Here $\chi$ is the angle between planes $(h_1 k_1 l_1)$ (which is different from the oriented direction $(h k l)$ of the film and is in the horizontal direction to face the x-ray beam) and $(h k l)$. If the crystal has n fold symmetry, it will satisfy the Bragg’s condition n times during the $0^\circ$ to $360^\circ$ rotation about the surface normal and hence n peaks are observed during the $\phi$ scan with peaks separated at angle of $(360/n)^\circ$.

![Fig. 2.5 An illustration of $\phi$-scan x-ray diffraction, where, $\omega$ - angle between incident x-rays and sample surface, $2\theta$ - angle between incident x-rays and detector, $\psi$ - sample tilt, $\phi$ - in-plane sample rotation, $x, y$ - in-plane displacement of sample, $z$ - vertical displacement of sample.](image)

In the present work, the XRD pattern for the bulk and thin films of Ni doped LaFeO$_3$ and Fe$_3$O$_4$ were recorded at Inter-University Accelerator Centre (IUAC), New Delhi using D8 Advanced Bruker diffractometer with Cu-K$_{\alpha}$ radiation ($\lambda=1.541838\text{Å}$) at room temperature by taking 0.020 step size. The cathode was maintained at 30 kV. Diffraction patterns were recorded in the range $20^\circ \leq 2\theta \leq 80^\circ$. 
2.5.3 X-ray Absorption Spectroscopy

X-ray absorption spectroscopy (XAS) is a powerful tool to study the local electronic and atomic structure of solids, liquids and gases in a wide range of external conditions defined by temperature, pressure etc. The information on the local electronic structure can be extracted from x-ray absorption spectrum in the vicinity of an absorption edge of an atom (XANES), whereas structural information can be determined from the extended x-ray absorption fine structure (EXAFS), having an oscillating character and located beyond the absorption edge. The EXAFS range extends usually to about 500-1000 eV above the edge due to limitations caused by the experimental noise and/or by the presence of another absorption edge. The x-ray absorption spectrum has been recorded using an x-ray source. Historically, first an x-ray tube was used; but at present most experiments are performed using synchrotron radiation. A typical synchrotron radiation source consists of two accelerators (a linear accelerator called LINAC, and a booster) and a storage ring. The charged particles (electrons or positrons) are accelerated within the LINAC and the booster up to operating energy and are injected into the storage ring, where a radially accelerated charged particle emits electromagnetic radiation, including x-rays, in the tangent direction to their orbit. This radiation is utilized by experimental stations located at beamlines in the Experimental Hall. The synchrotron radiation has several advantages due to unique characteristics, which include

1. Wavelength tunability from the infrared (IR) to the hard x-rays.
2. Polarisation selectability (both linear and circularly polarized lights are available).
3. Extremely high brilliance.
4. A pulsed radiation structure of high stability, enabling measurements to be made at very short time intervals (down to $10^{-11}$ seconds).

The x-ray absorption measurements on the samples along with Fe$_2$O$_3$ and NiO at O $K$, Fe L$_{2,3}$ and La M$_{4,5}$ edges were made using the high-energy spherical grating monochromator (HSGM) beam line of the National Synchrotron Radiation Research Center (SRRC), Taiwan operating at 1.5 GeV with a maximum storage current of 200 mA. The spectra were
measured using the sample drain current mode at room temperature and the vacuum in the experimental chamber was in low range of $10^{-9}$ torr. The resolution of the spectra was better than 0.2 eV.

2.5.4 Atomic Force Microscopy

The Atomic Force Microscopy (AFM), invented by Binnig, Quate and Gerber in 1986,\(^4\) is a very powerful technique for studying the surface morphology. The microscope consists of a cantilever with a sharp tip at its end, typically composed of silicon (Si) or silicon nitride ($\text{Si}_3\text{N}_4$) with tip sizes of the order of nanometers. The tip is brought into close proximity of a sample surface. A representative view of the function of an atomic force microscope is shown in Fig. 2.6.

The van der Waals force between the tip and the sample leads to a deflection of the cantilever according to Hooke's law, where the spring constant of the cantilever is known. Typically, the deflection is measured using a laser spot reflected from the top of the cantilever into an array of photodiodes.

![Fig. 2.6 Schematic diagram of an Atomic Force Microscopy.](image)
However a laser detection system can be expensive and bulky; an alternative method in determining cantilever deflection is by using piezoresistive AFM probes. These probes are fabricated with piezoresistive elements that act as a strain gage. Using a Wheatstone's bridge, strain in the AFM probe due to deflection can be measured, but this method is not as sensitive as the laser deflection method. If the tip were scanned at constant height, there would be a risk that the tip would collide with the surface, causing damage. Hence, in most cases a feedback mechanism is employed to adjust the tip-to-sample distance to keep the force between the tip and the sample constant. Generally, the sample is mounted on a piezoelectric tube, which can move the sample in the $z$ direction for maintaining a constant force, and the $x$ and $y$ directions for scanning the sample. The resulting map of $s(x,y)$ represents the topography of the sample.

Schemes for non-contact and dynamic contact mode operation include frequency modulation and the more common amplitude modulation. In frequency modulation, changes in the oscillation frequency provide information about a sample's characteristics. In amplitude modulation (better known as intermittent contact or tapping mode), changes in the oscillation amplitude yield topographic information about the sample. Additionally, changes in the phase of oscillation under tapping mode can be used to discriminate between different types of materials on the surface.

### 2.5.5 Magnetic Force Microscopy

In a Magnetic Force Microscope (MFM) a magnetic tip is used to probe the magnetic stray field above the sample surface. The magnetic tip is mounted on a small cantilever that translates the force into a deflection, which can be measured. The microscope can sense the deflection of the cantilever that will result in a force image (static mode) or the resonance frequency change of the cantilever, which will result in a force gradient image. The sample is scanned under the tip that results in a mapping of the magnetic forces or force gradients above the surface.

The facts that no sample preparation is necessary and that a lateral resolution below 50 nm can be reached make it a powerful tool for investigation of submicron magnetization patterns. Since it is possible to apply external magnetic fields during the measurement, the field dependence of domain structures and magnetic reversal processes can be
observed. Methods to separate topography and magnetic features allow pure magnetic images to be achieved. Topographic and magnetic details from the same scan can be related to each other.

We recorded AFM and MFM images in the present work at Inter-University Accelerator Centre (IUAC), New Delhi-110067, India.

2.6 MEASUREMENT OF ELECTRICAL AND MAGNETIC PROPERTIES

2.6.1 Electrical Resistivity Measurement

The dc electrical resistivity measurements are generally made by four-probe technique. When the sample resistance is measured by two probes using a multimeter, the contact and lead wire resistances cannot be avoided. The four-probe method is a simple technique to overcome this limitation. In the present study the electrical resistivity measurement is performed using four-probe technique, in the temperature range 77-300 K in a home built cryostat. A constant current in the range μA to mA drawn from a Keithley constant current source (Model 220) was passed through the outer contacts. The voltage across the inner contacts was measured using a Keithley nanovoltmeter (Model 2001). The resistivity as a function of temperature was measured during the warming up cycle. The temperature was controlled with the help of a Lakeshore temperature controller (Model DRC-93CA).

2.6.2 Noise Measurement

While trying to handle small signals electronically, one ultimately comes to the point where the incoming signal drowns in the random current or voltage fluctuations generated in the electronic systems. These fluctuations are usually called noise. Noise is always present in real devices and is often a practical limit to the performance of a device. The measurement of signal to noise ratio is, therefore, an important activity which can be advanced by an understanding of the details of the operation of the device and improvement of the quality of the materials. Four types of noise are important for any device.

(I) Thermal or White Noise: Any resistance R shows spontaneous current or voltage fluctuations according to the following equation:

\[ S_v = 4k_B T R \]

and \[ S_I = 4k_B T / R \]
where, \( S_v \) and \( S_i \) represent the spectral power densities of voltage and current fluctuations respectively. \( k_b \) is the Boltzmann constant and \( T \) is the absolute temperature.

White noise was found to be independent of frequency. Therefore, this noise is independent of the conduction process and nature of the mobile charge carriers.

(ii) Shot Noise: A second type noise, always present in the diode type devices, is the shot noise. This noise is the result of the corpuscular nature of electricity and the random emission of charge carriers across a potential barrier. The spectrum of the current fluctuation is proportional to the elementary charge \( q \) of the carriers and the average current \( I \)

\[ S_i = 2qI \]

(iii) Generation-recombination Noise: The number of free electrons in the conduction band may fluctuate due to generation and recombination processes between the band and traps. Due to this there is a fluctuation in the conductance \( G \) and therefore, in the resistance \( R \).

(iv) \( 1/f \) or Flicker Noise: A fourth type noise is the \( 1/f \) noise proposed by Schottky. It was observed practically in all cases that an increase of the spectral density of current noise \( (S_v \propto f^{-\alpha}; \; \alpha \text{ varying in between } 0.8 \text{ and } 1.2) \) with decreasing frequency \( f \) is approximately proportional to \( 1/f \). Therefore, this current noise is usually called \( 1/f \) or flicker or pink noise. This noise is observed in various materials such as semiconductors, superconductors, semimetals, CMR materials, etc.

The great interest in studies of \( 1/f \) noise stems from the fact that this problem is very general and to a considerable degree unsolved. The great importance of these studies also plays a significant role, since \( 1/f \) noise is a serious interference that limits the parameters of many electronic devices at low frequencies. \( 1/f \) noise is known to be very susceptible to any fluctuation or transition whether electrical or magnetic. In uniform conductors the spectral density of \( 1/f \) noise is proportional to the square of the mean voltage or the mean current throughout the voltage region in which ohm's law is obeyed.
The spectral density of $1/f$ noise follows a power law $1/f^\alpha$, with the exponent $\alpha$ very close to unity, and is proportional to $V^2$. In this case one can represent the spectral density of fractional fluctuations in the form

$$
\frac{S_r(f)}{V^2} = \frac{\gamma}{N_c f}
$$

where coefficient $\gamma$ is called the Hooge parameter. It is a dimensionless coefficient and widely used to compare the $1/f$ noise magnitude in different samples materials.

If the Hooge relationship were exact, and this implies universal, it would be a convincing argument in favour of one universal mechanism of $1/f$ noise. Therefore, $1/f$ noise measurement also provides the useful information about various kinds of defects on the charge transport process in thin films. The effect of irradiation can also be seen by the measurement of $1/f$ noise.

In the present work we have measured the spectral density of voltage noise $S_v$ by four-probe method for frequencies from 1 to 50 Hz. The sample is biased with direct current generated by a constant current source (battery) and the voltage across the sample is ac coupled to a low noise preamplifier of gain 100 (SR-552, Stanford). The preamplifier blocks the dc component of voltage and allows only the ac component to pass through it. The amplified signal was then fed to a fast Fourier transform based spectrum analyzer (HP356565A, Hewlett Packard), which measures the spectral density of voltage noise and its frequency spectrum. A schematic diagram of noise measurement is shown in Fig. 2.7.

![Fig. 2.7 A representation of the noise measurement setup.](image-url)
The excess noise arising due to conductance fluctuations was extracted from the observed noise spectrum by subtracting the background noise, which is the sum of the preamplifier and thermal noise (4k_BT). Furthermore, to make sure that the contacts did not contribute to the noise, we checked the linearity of the current-voltage characteristics at several temperatures during the noise measurements. The current-voltage characteristics were found to be linear within the range of current values employed in the measurements.

We studied 1/f noise on pristine and irradiated (190 MeV Ag ion) of LaFe_{1-x}Ni_xO_3 (x=0.3, 0.4 and 0.5) and Fe_3O_4 thin films at Inter-University Accelerator Center (IUAC), New Delhi, India.

2.6.3 Measurement of Magnetic Properties

Magnetic properties of the materials can be measured using several techniques such as Vibrating Sample Magnetometer (VSM),^48 Superconducting Quantum Interference Device (SQUID),^49,50 the Hysteresis Meter (HM) and the Alternating Gradient Field Magnetometer (AGFM). VSM is the most common instrument because it offers the best combination of performance capabilities and can accommodate a large range of samples with widely different properties.

In this research work, Alternating Gradient Field Magnetometer (AGFM) (Micromag-3900, Princeton Measurements, USA) with a sensitivity of 10^-8 emu has been employed to measure the magnetic property of all studied samples at Trinity College, Dublin, Ireland.

2.6.3.1 Alternating Gradient Field Magnetometer

The Alternating Gradient Force Magnetometer (AGFM or AGM) is a highly sensitive measurement system, capable of measuring hysteresis properties on a wide range of sample types and strengths. Because of its high sensitivity, great caution must be exercised in its use to avoid large errors in the measurement results. It uses a modified technique to conventional vibrating sample magnetometry. Traditionally, a sample placed in a magnetic field is vibrated at a fixed frequency via an electro-mechanical transducer. However, in AGFM an alternating gradient field is utilized to exert a periodic force on a sample placed within a variable or static dc field of an electromagnet, as shown schematically in Fig. 2.8. The force is
proportional to the magnitude of the gradient field and the magnetic moment of the sample. The force deflects the sample and this deflection is measured by a piezoelectric sensing element mounted on the probe arm. The output signal from the piezoelectric element\textsuperscript{51,52} is synchronously detected at the operating frequency of the gradient field. Operating near the mechanical resonant frequency of the assembly enhances the signal from the piezoelectric element. The AGFM has a noise floor of $10^{-8}$ emu compared with $10^{-6}$ emu for the VSM.

AGFM is highly sensitive and applicable for the present application purpose. However, it has some misleading information in most cases due to the following:

1. The piezoelectric reed sample holder of AGFM which is fragile and expensive, must operate at the resonance frequency of the sample holder which depends on the mass of the sample/substrate combination. A new sample requires re-tuning to its resonance frequency and if its magnetic moment is low, automatic tuning does not work and the user has to do it manually.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure.png}
\caption{An illustration of Alternating Gradient Force Magnetometer.}
\end{figure}
2. For AGFM the measured moment is very sensitive to sample placement due to the gradient field. To obtain a calibrated reading, the sample and the calibration standard must be identical in mass and size.

3. When measuring low coercivity samples (~100 Oe or smaller) it is necessary to reduce the magnitude of the gradient field in order to maintain accuracy. This reduces the sensitivity of the AGFM. This severely limits the capability of AGFM to measure low coercivities, since the alternating field cycles through part of the hysteresis loop. Similarly, the gradient field limits the accuracy of remanence measurements since the field is cycling through a minor loop around remanence.

4. The AGFM has limitation in measuring samples with large magnetic moments.
REFERENCES

A study of the effect of SHI irradiation on Experimental and...