Chapter-2

Materials and Methods

CHAPTER 2: Materials and Methods

2.1 Overview

To achieve the objectives, outlined in chapter 1, it is essential to synthesize and characterize the proposed systems to study their properties and applications. The particulars of synthesis procedures, characterization using various equipment, and applicable experimental methodologies to evaluate the various attributes of the proposed systems are all covered in this chapter The proposed materials in the present work are (a) Samarium strontium Nickelate (SmSr)$NiO_{4-\delta}$ (b) Oxygen deficient (SmSr)$NiO_{4-\delta}$ i.e., $Sm_{2-x}Sr_xNiO_{4-\delta}$ (x = 0.4, 0.6, 0.8, and 1.0) (c) A-site substituted (SmSr)$NiO_{4-\delta}$ i.e., $Sm_{1-x}La_xSr_{1-x}Ca_xNiO_{4-\delta}$ (x = 0.00, 0.05, 0.10, 0.15, and 0.20) (d) NiO thin films. The parent composition and the compositions listed in b and c were prepared was synthesized by solid-state ceramic route method. The thin film of $Sm_{2-x}Sr_xNiO_{4-\delta}$ was prepared by pulse laser deposition technique. Whereas, the thin film of NiO was prepared through sonication method with different depositions. The prepared compositions were characterized for their structural, micro-structural, thermal, and catalytic properties. This chapter consists of three sections. First section deals with the preparation and processing of the compositions. The second section introduces the different characterization techniques which have been implemented in this thesis. Third chapter explore several methods regarding the data analysis techniques.

2.2 Specification of the Materials used

High purity raw materials were used for the synthesis of various compositions. Table 2.1 contain the specifications of these materials.

S. No	Raw Materials	Chemical Formula	Purity	Manufacturer
1.	Samarium oxide	Sm_2O_3	99.9%	Alfa Aesar
2.	Strontium Carbonate	$SrCO_3$	99%	Sigma Aldrich
3.	Nickel Oxide	NiO	99%	Alfa Aesar
4.	Lanthanum Oxide	La_2O_3	99.9%	Alfa Aesar
5.	Calcium Carbonates	$CaCO_3$	99.5%	Alfa Aesar

Table 2.1: Specifications of the materials used along with their chemical formula, purity, and manufacturer used for the preparation of various samples

Some other high-grade chemicals, reagents, and solvents were used to fabricate the samples including ethanol, acetone, nitric acid, deionized water, acetic acid, potassium hydroxide, Sodium sulphate, hydrochloric acid, etc.

2.3 Synthesis of Materials

In order to process the materials, two different synthesis route was adopted, whereas for the fabrication of thin films, Pulse laser deposition and spin coating techniques (PLD) were used. The details of these synthesis techniques are discussed in next section.

2.3.1 Solid-state reaction route (SSR)

Solid state route (SSR) frequently established as ceramic method, is a chemical process which formed a new solid with well-defined structure from solid starting materials. At room temperature, several metal oxides or salt do not react together. Therefore, it is necessary to provide them the extreme conductions, such as high temperature and pressure in order for reaction to occur. Prior to weighing, the reactants are dried in this procedure. After the

weighing out the needed amount, they are thoroughly mixed in agate mortar and pestle (manual mixing of small quantity) with acetone to aid homogenization. This mixing and grinding process normally takes 15-20 minutes, after which acetone has been completely evaporated. To make the desire result, repeat this process 4 to 5 times. This process is also known as “heat and beat” or “shake and bake”. There are several factors which effect the rate of reaction in SSR methods. These factors are shape and surface area of reactants, reaction conditions, structural properties of the reactants, their reactivity, thermodynamic properties of the nucleation and diffusion rate [105], [106]. There are several benefits of this synthesis technique mentioned below:

1. Structurally pure phase.
2. Simplicity in processing and handling.
3. Higher productivity
4. Environment-friendly
5. Low cost

Figure 2.1: schematic diagram of solid-state route (SSR) method

2.3.2 Sol Gel Method

The sol-gel method is a well-established synthetic approach to prepare metal oxide nanoparticles and mixed oxide composite materials. In this process, monomers are transformed into the colloidal solution called 'sol' which works as the precursor for an integrated network known as 'gel'. Sol-gel method is an easy and straightforward technique for the preparation of advanced ceramics, nanomaterials and catalyst. In sol gel method, metal nitrates or acetates are used as source of metal. In this synthesis technique, all nitrates (or acetates) solutions are mixed well with each other to transform into the final solution. The catalyst can be used in this process as well. The final solution needs to be transparent. Transparency of the solution can be preserved by adding either acidic reagent (i.e., HCl) or basic reagent (i.e., NH_3). The solution was heat up at a constant temperature converted into sol. Structural stability such as grain growth and densification as well as other physical properties can be realized through the final sintering process. This method has a high similarity with the very well-known Pechini process. However, sol gel is differed from Pechini process as nitrates(acetates) are not eliminated but remain in the solution. This method provides the potential control over the textural and surface properties of the materials and the densification frequently occurs at a lower temperature. This technique has numerous benefits listed below:

1. Nanoparticle formation.
2. Dopant can easily be introduced into final products.
3. No need of vacuum.
4. Less time and least cost.
5. Agglomeration of powder remain limited.

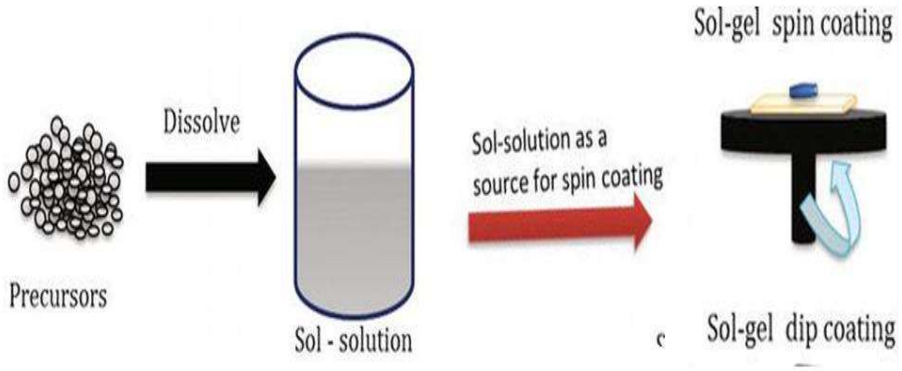

Figure 2.2: schematic diagram of sol gel method

2.3.3 Spin Coating Technique:

Spin coating technique is the most frequently used process to synthesize the uniform and homogeneous thin films over flat substrates. It has wide applications in industries and technology sectors, especially to fabricate the films for semiconducting devices, antireflection coating on solar cells or optical devices, magnetic disk, sensors, detectors and very large-scale integrated circuits (VLSI), etc. The image of the spin coating unit utilized in the present work is displayed in Fig. 2.3 (a). To prepare thin film by a spin coating process, usually, a small amount of depositing solution is dispensed over the flat surface of the substrate. The substrate spins the depositing solution around the axis which is perpendicular to the depositing area. Further, the substrate is rotated at high speed and the excess amount of solution can be eliminated by the help of centrifugal force. In order to form a homogeneous and uniform thin film, the solution gets evenly spread over the surface of the substrate. figure 2.3 (b) represents the scheme of the spin coating process. Several parameters that can affect the deposition process are spin speed, spin time, acceleration and evaporation, homogeneity and viscosity of the solution, etc. All these parameters should be taken into account for uniform thin film formation.

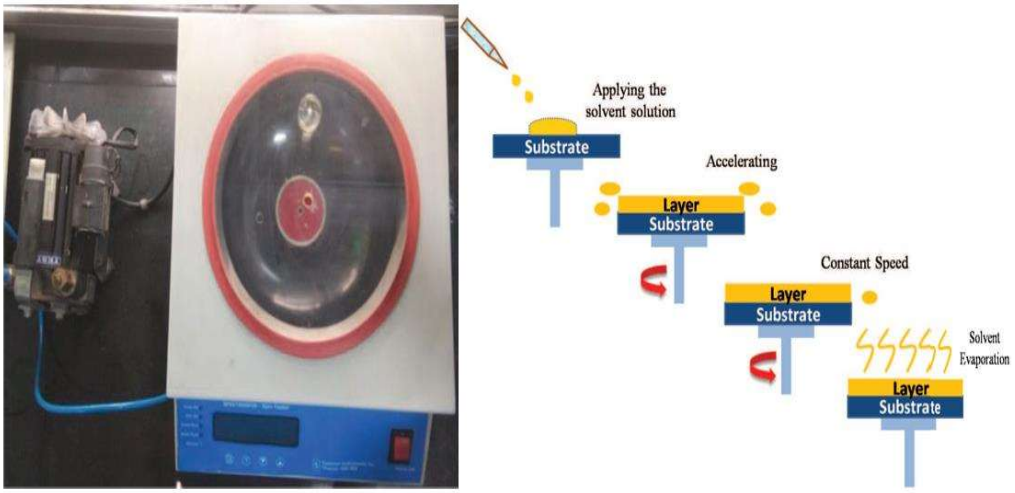

Figure 2.3: (a) Spin coating system used in present work (b) schematic diagram of thin film formation by spin coating technique

2.3.4 Pulse Laser Deposition Technique (PLD)

Pulse laser deposition (PLD) is a very easy and uncomplicated technique for thin film deposition. This technique used high-power pulsed laser beam as an external energy source to hit the target with the material that needs to be deposited. It consists of a vacuum chamber housing a target holder and a substrate holder. The pulsed laser beam makes a 45^0 angle with the target holder The target material absorbs the laser beam, which interacts with the surface of materials and generates a colorful plasma plume. The plume is made up of electrons, atoms, ions and molecules. The extracted substance is then steadily deposited on the substrate, where it forms a uniform film Either a vacuum or a low gas pressure environment is used for the deposition process. During PLD, many experimental conditions can be changed, which have a huge influence in the properties of film. For multi-element materials, PLD is often easier to

achieve the necessary film stoichiometry than other deposition processes. The process of PLD can be classified into four steps:

- Laser absorption on the target surface and laser ablation of the target material and plasma creation
- Plasma Dynamics
- Deposition of the ablation material on the substrate
- The film's nucleation and growth on the substrate's surface.

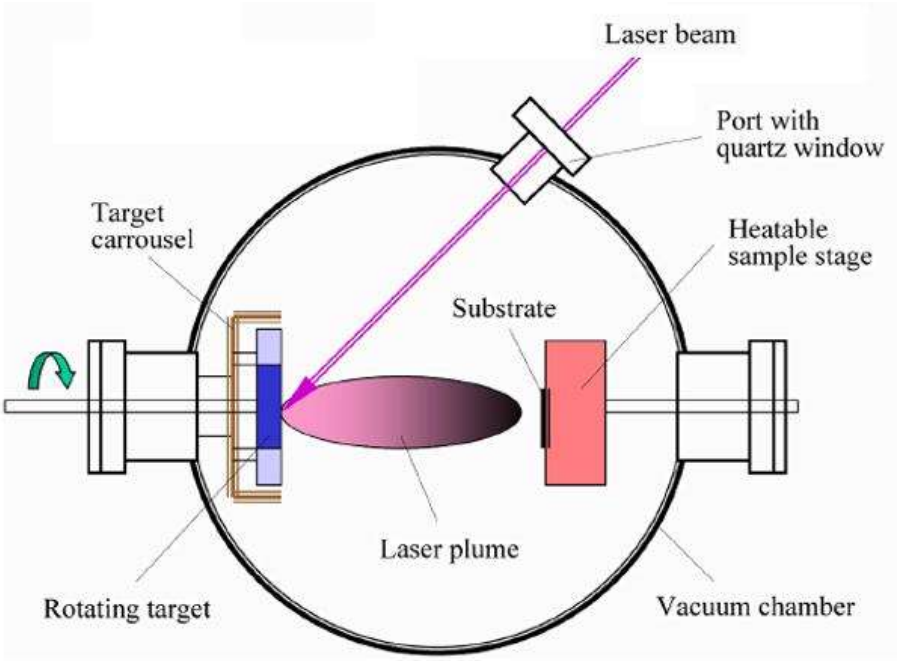

Figure 2.4: Schematic diagram of pulse laser deposition technique[107]

The main advantages of PLD are as:

1. Effective method of synthesizing the thin film of complex compositions.
2. Versatile method.

3. Cost effective.
4. Ability to preserve the stoichiometry of compound materials.
5. Fast: high quality samples can be grown reliably in 10 or 15 minutes.

2.4 Characterization Techniques

2.4.1 Thermogravimetric Analysis (TGA)

The concept of TGA was proposed by a physicist from Japan, Honda[108]. Thermogravimetric analysis (TGA) is a method for finding out how significantly a sample's mass changes over time or as a function of temperature in a controlled environment. It is used to establish the thermal stability and calcination temperature of a material. The sample is said to be thermally stable in that particular temperature range if its mass remained stable over the course of the specified temperature range.

Working Principle: In TGA, a solid reactant when heated, it produces some product and the gas is emitted out. This modification entails a lowering of mass or weight. This mass loss may be caused by the gas formed during the reaction between the reactants by heat, or it may be induced by the presence of water in the reactants. This change the result from a thermogravimetric run may be presented by either weight vs temperature or weight loss vs temperature. The obtained graph is known as thermogram. The plateau in thermogram curve indicates no change in weight while the curved portion indicates the weight loss. The measured weight loss curve provides details on kinetic parameter, thermal stability and changes in sample compositions. Derivative of weight loss curve can deduce the point where weight loss is more noticeable. TGA can also provide the information about the second order transition, vaporization, absorption, adsorption, oxidation and reduction[109].

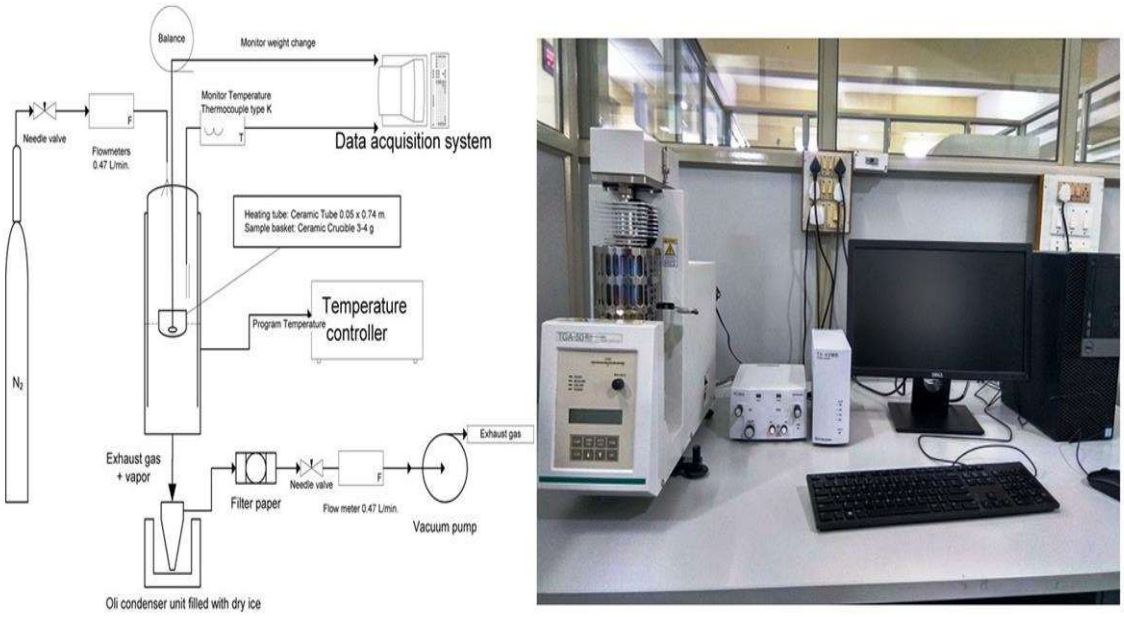

Figure 2.5: (a) Schematic diagram of TGA[110] (b) Experimental setup of TGA at Central instrument facility (CIF) IIT (BHU)

A precision balance and a sample pan are the components of a TGA. That pan is heated or cooled in a furnace throughout the experiment. The mass of the sample is gauged throughout the experiment. A sample purge gas regulates the sample environment. This gas, which passes the sample and is ejected through an exhaust, could be reactive or inert.

The main component of a TGA apparatus is a high precision thermobalance, Furnace with temperature, programming facility and facility to provide inert atmosphere or oxidizing environment. In the present thesis work, TGA measurement was recorded by SHIMADZU TGA-50.

2.4.2 Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry (DSC) is the measurement of the difference rate of heat transfer between a sample and a reference sample while they are both subjected to a controlled temperature programme. DSCs provide fast measurements of reaction and transition heats, as

well as heat flow rates and variations at particular temperatures, on small sample masses across a broad temperature range with typically adequate precision[111].

There are two basic types of DSC, which are, heat flux DSC and Power compensation DSC. In heat flux DSC, the heat to be measured is exchanged with the environment along a well-defined heat conduction route with a preset thermal resistance. In the case of power compensation DSC, the heat to be measured is (almost entirely) compensated by electric energy by raising or reducing the heat of an adjustable Joule. A common feature of both forms of DSC is that the measured signal is proportional to a heat flow rate (ϕ), rather than a heat, as is the case with most traditional calorimeters. On the basis of the $\phi(t)$ curve, time dependences of a transition may be detected. Because of this characteristic (directly measured heat flow rates) all DSCs may address difficulties in a wide range of applications[111].

Figure 2.6: Experimental setup of DSC at Central instrument facility (CIF) IIT (BHU)

Working principle: A temperature differential (in the form of a voltage) and the specified value of the furnace (or sample support) temperature are the original quantities measured in a DSC. Internally, the temperature difference is converted into a differential heat flow rate. This raw collected data generates the DSC curve and serve as a basis for all further investigation. The DSC curve may be used to rapidly ascertain precise heat changes, transitions, and reactions. The output from DSC may be used to solve many different problems. It can be used to measure the heat capacity, determination of heat of reaction, kinetic investigation, the glass transition process, the phase behavior and determination of phase diagram.

2.4.3 Bench-Top X-Ray Diffraction (BT-XRD)

X-ray diffraction (XRD) is a one of the most potential characterization tools and nondestructive technique for characterizing crystalline materials. It is used to identify the type and phase of material, preferred orientation, and other structural parameter (crystallinity, average grain size, crystal defect). The fundamental components of an X-ray diffractometer are an X-ray tube, a sample holder, and an X-ray detector.

Working Principle: This analytic technique is based on the diffraction of X-ray by matter. The most frequent used target material for single-crystal diffraction is copper and the analysis is carried out using X-ray source that emits Cu Kα radiation (λ= 1.5406 Å). In a cathode ray tube, X-rays are produced by heating a filament to produce electrons, subsequently applying a voltage to accelerate the electrons toward a target and bombarding the target material with electrons. In diffractometer, sample is positioned in instrument's center and illuminated by an X-rays beam. The motion of the X-ray tube and detector is synchronized. A special interference effect known as "diffraction" is used to measure the distance between the atoms because of

wavelength of X-rays is comparable to the separation between atoms in a crystal. Bragg's diffraction is the most common type of diffraction in X-ray crystallography. Incident X-rays are scattered by interacting with the electrons of the atoms. This phenomenon is known as elastic scattering and the scatterer in this phenomenon is electron. Spherical waves are produced by these scatterers in a regular array. Due to destructive interference, these waves cancel each other out in the majority of directions, but they contribute constructively in a small number in specific directions, as indicated by Bragg's law[112]. The condition for the constructive diffraction according to Bragg's law is:

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

Where, d represent the distance between lattice plane and θ is the angle of diffracted wave and n is the order of diffraction. When the incident X-rays collide with the sample in a manner that confirms to the Bragg Equation, constructive interference occurs, generating a sharp peak. The sample's signal is captured and graphed, and a peak corresponding to the sample's atomic structure may be observed[113].

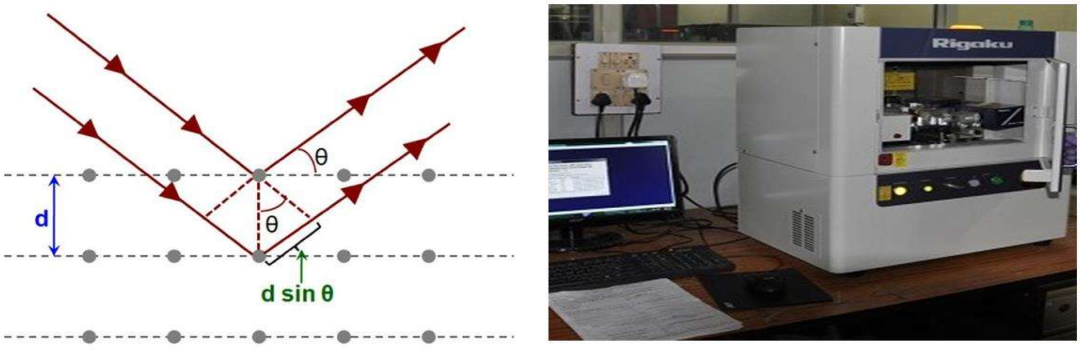

Figure 2.7: (a) Interpretation of Bragg's law in 2-dimensional crystal lattice (b) Experimental set-up of BT-XRD at Central instrumentation facility CIF IIT(BHU)

Most common application of X-ray diffraction is the identification of unknown crystallite materials. Other application includes the measurement of sample purity, determination of unit cell dimensions. XRD can also be used to determine the crystal structural with the help of specialized technique 'Rietveld Refinement'. The details of Rietveld refinement will be discussed later in this chapter. In this thesis, BT-XRD is performed using the instrument RIGAKU Miniflex 600 Desktop X-ray Diffraction system.

2.4.4 Fourier-Transform Infrared Spectroscopy (FTIR)

The term Fourier-transform infrared spectroscopy (FTIR) coined from a mathematical process Fourier transform, which is required in this process to convert the raw data into the real spectrum. FTIR is the most popular form of infrared spectroscopy. For a number of reasons, FTIR is the favored approach for infrared spectroscopy. First, the sample doesn't contaminate in this technique. Second, it is far quicker than earlier techniques and thirdly, it is far more accurate and sensitive. Polymer science, pharmaceutical industry, food analysis, organic synthesis and petrochemical engineering all use FTIR spectroscopy. In other words, it has variety of applications, including monitoring processes, identifying molecules, and figuring out the constituents of a combination[114].

Working Principle: All infrared spectroscopies (including FTIR) operate under the premise that some IR energy is absorbed when it passes through a material. The radiation that passes through the sample is recorded. The spectra can be used to recognize and differentiate between molecules, since different molecules produce different spectra because of their different structures. Covalent bonds in a molecule will selectively absorb radiation of particular wavelengths during FTIR. It will change the vibrational energy of that particular bond.

The atoms present in covalent bond will determine the kind of vibration (stretching or bending) caused by the infrared radiation. The transmittance pattern varies for different molecules because different bonds and functional groups absorb different frequencies. Wavenumber (cm^{-1}) is plotted on the X-axis and transmittance is plotted on the Y-axis to represent the spectrum.

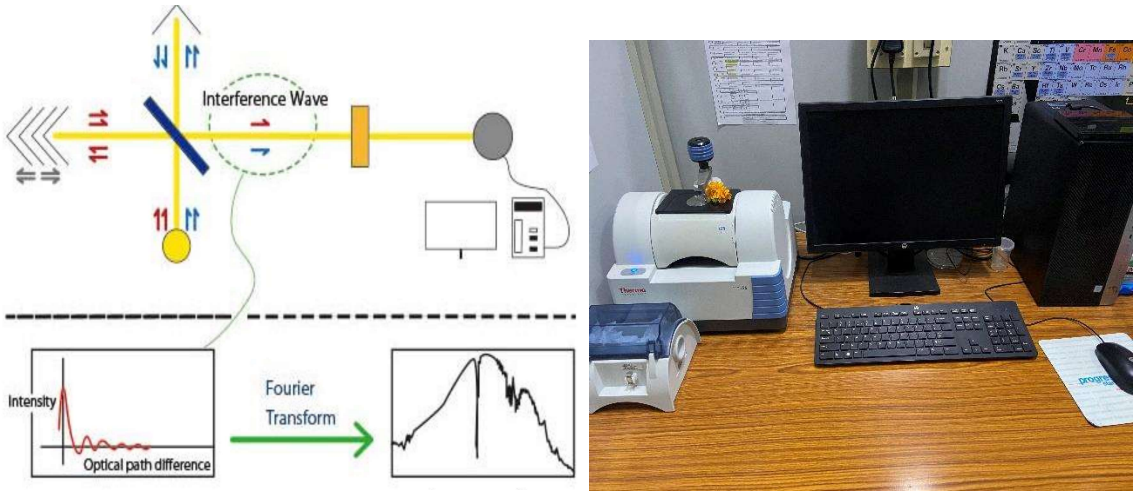

Figure 2.8: Schematic diagram of Working Principle of FTIR[115] (b) Experimental set-up of FTIR at Central instrumentation facility CIF IIT(BHU)

In FTIR, there are four major techniques available for sampling. These are Transmission (TR), Specular Reflection (SR), Diffuse Reflectance (DR), and Attenuated Total Reflection (ATR). In transmission technique, IR is completely passes through the sample. Therefore, several parameters such as thickness, homogeneity or particle size need to be considered for measurement. This method is most suitable for pressed pellets or thin film. SR method comes in frame when sample is bulk with glossy surface. The measurement of glasses or crystal faces can be performed through this method. Diffusion reflectance is applied on those sample which are adhering to a surface such as powder sample. ATR is the simplest method, which enables sample to be examined directly in the solid or liquid state with minimal to no sample

preparation. In this method, all is required to bring the sample into the contact with the ATR crystal[116]. In this thesis, FTIR is performed using Nicolet iS5 in ATR mode.

2.4.5 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) is a valuable method for the morphological analysis of the sample. It is based on the electron microscope, which produce images using the electron instead of visible light. SEM is the most widely used microscopic technique because it requires minimum sample preparation and is concise to operate. Mafred von Ardenne designed the first scanning electron microscope in 1937[117]. Spatial resolution of SEM may vary from 50 nm to 100 nm and its magnification can be anywhere between 20X and around 30,000X. However, some SEMs can achieve resolutions better than 1 nanometer. The essential component of SEM includes source of electron (gun), lenses, electron detector and sample chamber.

Working Principle: SEM uses a focused beam of high-energy electrons to generate a variety of signals on the surface of the solid specimens. Steady stream of electrons is produced at the source. A beam of electrons is fired at the item being examined using an electron gun. Basically, two types of electron gun are used in SEM. The most popular type is thermionic gun, which produces electrons by applying thermal energy to tungsten filament. Another is Field emission guns, which generates a strong electrical field that drags electrons away from the atoms they are attached to. After that, the electrons are accelerated to a voltage of 1-40 kV. The lenses then concentrate and regulate the electron stream, ensuring that the electrons land exactly where they should. The samples are mounted and put in an evacuated chamber. Accelerated electrons in a SEM carry high kinetic energy which is released as a variety of signals via interactions between the electrons and the solid sample as the incident electrons decelerate in the solid sample. These signals include secondary electrons (SE), backscattered

electrons (BSE), diffracted backscattered electrons (EBSD), visible light, photons and heat. Out of these signals, two signals are primary detected in SEM. These are backscattered and secondary electrons. Sample morphology and topography displayed best through the secondary electrons, whereas backscattered electrons are best for presenting compositional differences in multiphase samples[118]. When an electron beam interacts with a sample in a SEM, numerous things do happen. Different detectors are required to differentiate among secondary electrons, backscattered electrons, and distinct x-rays. The most precise images of an object's surface can be created using detectors that detect the secondary electron. The composition of a substance can be determined using various detectors, such backscattered electron detectors and X-ray detectors.

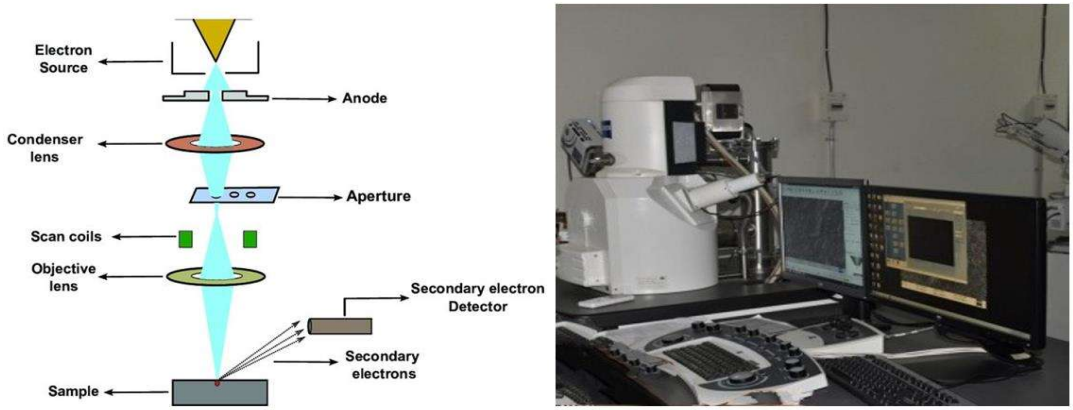

Figure 2.9: (a) Operating Principle of SEM (b) Experimental setup of SEM at central instrumentation facility CIF IIT(BHU)

SEMs (Scanning Electron Microscopes) are used for a wide range of commercial, research, and industrial applications. The SEM is used to create high-resolution images of object and to illustrate spatial variations in chemical compositions, such as creating elemental maps or performing spot chemical analyses using EDS. SEMs are widely employed in the

investigation of nanotubes and nanofibers, high temperature superconductors, mesoporous structures, and alloy strength in current materials science research. In reality, SEMs have facilitated nearly every industry in the field of material research, from electronics and chemistry to aerospace and chemistry. In this thesis, SEM is analyzed by EVO - Scanning Electron Microscope MA15 / 18 and EDS is investigated by 51N1000 – EDS System.

2.4.6 Atomic Force Microscopy (AFM)

Atomic force microscopy (AFM) is a high-resolution scanning probe microscopy (SPM), also known as scanning force microscopy (SFM). AFM was discovered by IBM research scientists in 1982. It has the resolution of the order of fractions of nanometers which is a thousand times better than the optical diffraction limit. The information is assembled by 'feeling' or 'touching' the surface of the sample by using the mechanical probe.

Working Principle: AFM has three important abilities such as force measurement, imaging, and manipulation. In force measurement mode, it measures the force between the sample and the probe as a function of their mutual separation. For imaging purpose, the reaction of forces that was imposed by the sample on the probe has been utilized to form the image of three-dimensional (3D) shapes or topography of sample surface at high resolution. Further, in manipulation measurement, the properties of the sample can be changed in a controlled manner by using the forces between the sample and the probe.

Apart from the topography of the samples, other properties such as mechanical properties like adhesion strength or stiffness and electrical properties like surface potential or conductivity can also be measured by AFM. AFM comprises a cantilever having a sharp tip (probe) which is employed to scan the surface of the sample, displayed in Fig. 2.10 (a). A cantilever is built

of silicon or silicon nitride with a tip radius of curvature on the order of nanometer range. According to Hooke's law, when the tip is carried into the proximity of the surface of the specimen, the forces between the sample and the tip leads to the deflection of the cantilever. Depending on the situation, the AFM measures the forces such as mechanical contact forces, magnetic forces, capillary forces, chemical bonding, Van Der Waals forces, electrostatic forces and many more[119].

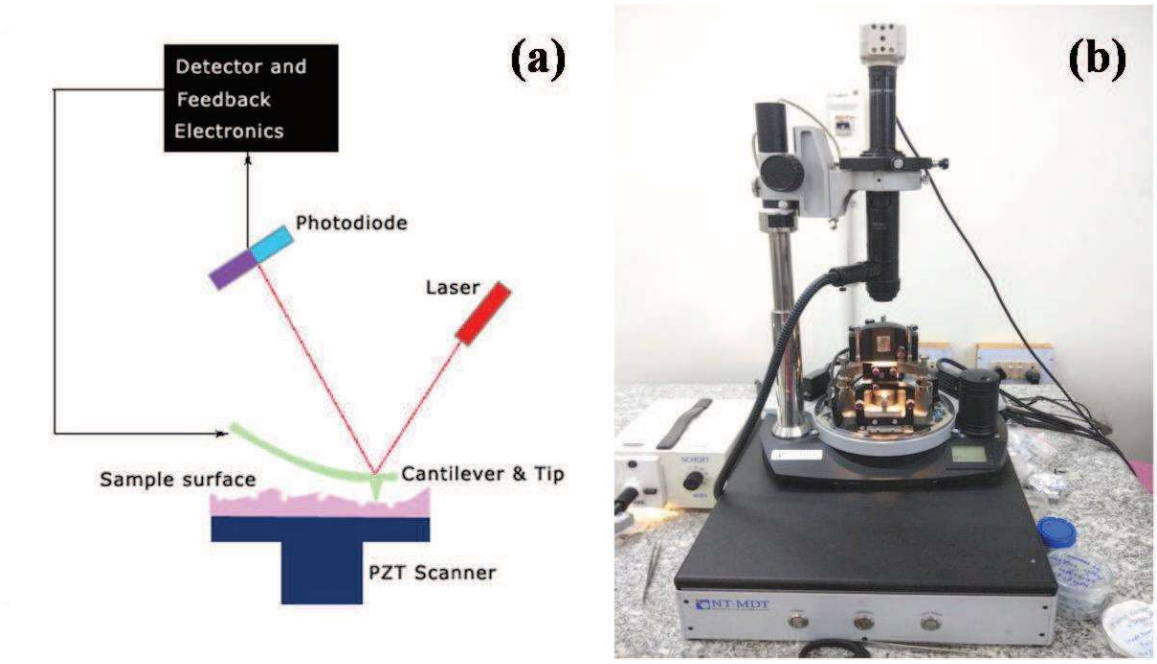

Figure 2.10: (a) Block diagram and (b) experimental set up of AFM.

The AFM has applications in the field of semiconductor science and technology, solid-state physics, polymer physics and chemistry, surface chemistry, molecular engineering, molecular biology, cell biology, and medicine. The topography of thin-film samples which have been synthesized in this work recorded by NT-MDT AFM instrument shown in Fig. 2.10.

2.4.7 X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is the most popular surface science technique for revealing information about the elemental composition, chemical state empirical formula and electronic state of the components within a material. XPS can analyze a sample up to depth of a 2 to 5 nm. Ultrahigh vacuum (UHV) is used for XPS, which has a pressure of about 10-9 millibar. Modern XPS was developed in the 1960s by Kai Siegbahn, who was awarded the Nobel Prize in Physics in 1981 for his work. It is based on the photoelectric effect, which Heinrich Hertz discovered in 1887. He gave it the name "Electron Spectroscopy for Chemical Analysis" to describe this newly developed technique (ESCA).

Working Principle: When an x-ray is used to bombard a sample, some electrons get sufficiently excited to leave the atom. In XPS, sample is irradiated by the soft X-ray (lower then ~6 keV). The X-ray energy is totally transferred to the core level electron and emits the photoelectron. The energy of X-ray can be written as:

$$h\nu = B.E. + K.E. + \varphi_{spec} \qquad (2.2)$$

where, B.E. represents the Binding energy of the electron, K.E. represents the kinetic energy of emitted electron and φ_{spec} is work function of spectrometer.

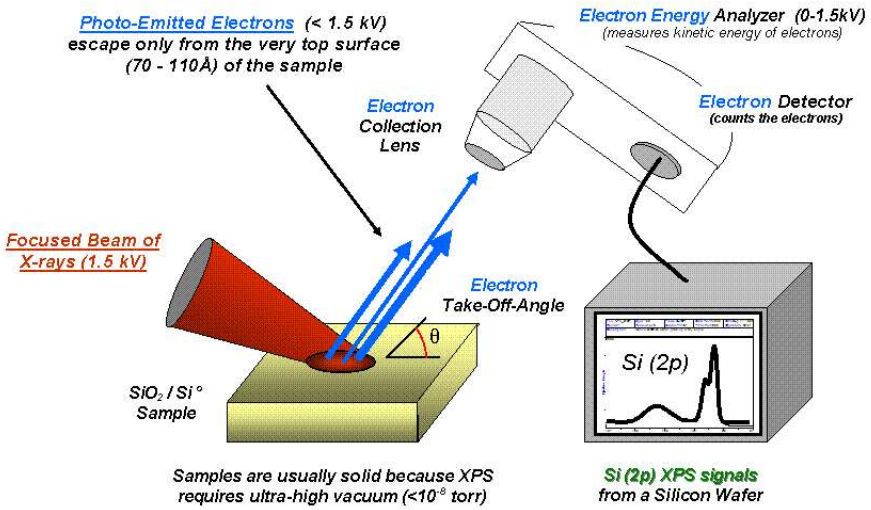

Figure 2.11: Basic component of monochromatic XPS system

In a normal XPS spectrum, some photo-ejected electrons scatter inelastically within the sample on their way to the surface, whereas others emit instantaneously and lose no energy in the process of escaping the surface and entering the surrounding vacuum. An electron analyzer collects these photo-ejected electrons in the vacuum and measures their kinetic energy and photoelectron spectrum can be recorded as spectrum between the intensity vs binding energy. An electron's binding energy is a material attribute that is unaltered by the x-ray source which ejected it. A "hole" and an excited ionized state are generated by the emission of photoelectron from the core level. These states are relaxed by filling the hole with an electron from the valence orbital. This relaxation process release energy in two processes, which are which are x-ray fluorescence and the emission of an Auger electron. X-ray fluorescence is undetectable in the electron spectrum. The only byproduct of the process that can be detected are the auger electrons, which are widely used in XPS for qualitative analysis. The binding energies of

specific orbitals in the atom from where it originated determine the Auger electron's kinetic energy, which makes it independent of the x-ray excitation energy[120].

Metal alloys, inorganic compounds, polymers, semiconductors, catalysts, ceramics, glasses, papers, woods, paints, inks, make-up, plant parts, bones, teeth, bio-materials, and many more materials are examined using the XPS technique[121]. In this thesis, the KRATOS (Amicus model) XPS apparatus was used to record the elemental analysis and chemical state of the synthesized samples.

2.4.8 Cyclic Voltammetry (CV)

CV (cyclic voltammetry) is an effective and popular electrochemical method for examining how molecular species undergo reduction and oxidation. The study of chemical processes like catalysis that are initiated by electron transport is also aided by CV. This approach is widely used in ORR, OER, and HER, and it may produce the reaction potential under a variety of conditions. For the first time in 1938, Randles gave a basic description of CV. Additionally, it can be used to gather both qualitative and quantitative information about electrochemical reactions, including their kinetics, reversibility, mechanisms, and other properties[122].

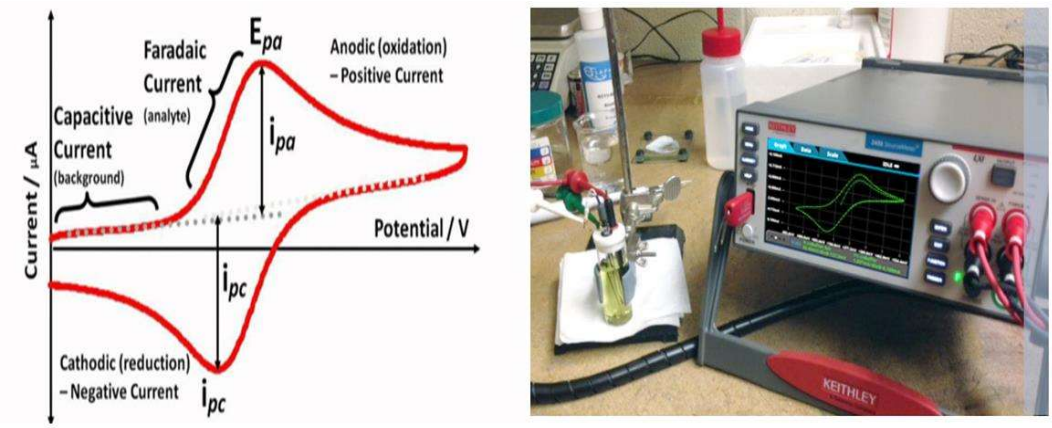

Figure 2.12: (a) cyclic voltammogram (b) Experimental set up of Cyclic voltammetry

Under varying circumstances, such as the presence of intermediate in oxidation-reduction reactions and the reversibility of a reaction, cyclic voltammetry can be used to explore qualitative information about electrochemical processes. CV may also be used to estimate the analyte's diffusion coefficient, system's electron stoichiometry, and the formal reduction potential, which can be used as a tool for identification. Additionally, a current vs. concentration calibration curve can be used to estimate the concentration of an unknown solution[123], [124].

Working Principle: The electrode potential ramps linearly vs time in cyclical phases in cyclic voltammetry (CV). The graph observed during this scan is known as voltammogram of cyclic voltammogram. The applied potential is along x-axis and observed current is recorded along y-axis. The experiment's scan rate (V/s) is the rate of voltage change over time throughout each of these phases. A three-electrode configuration or electrochemical cell with a working electrode, counter electrode, and reference electrode along with electrolytic solution is often used for the measurement. The potential is determined between the working electrode and the reference electrode, and the current is calculated between the working electrode and

the counter electrode. The electrodes are intended to receive ions from the electrolytic solution during the oxidation and reduction reactions[125]. There will be no current flowing at the starting potential, therefore there will be no peak on the voltammogram. As the potential rises and oxidise species are present, anodic current (i_a) rises and rises until it reaches a maximum value (i_{pa}), at which point all the species are oxidised. After that, i_a gradually decreases till it reaches the current background level. The potential has now been reversed, allowing the oxidised to be reduced again. As a result, i_c decreases to its maximum (i_{pc}), at which point all species have been reduced. i_c returns to the background level once more. It is possible to change the potential from negative to positive or vice versa. The anodic and cathodic peak regions of the voltammogram will shift depending on potential.

2.4.9 Density Measurement

The Archimedes principle was used to determine the density of synthesized samples. Using a circular die, the powder samples were pelletized using a hydraulic pressing machine. The pellets are first weighed in air and then fully submerged as a liquid medium in this procedure. Figure 2.13 shows an illustration of the density measuring kit (Sartorius, BSA2245-CW). Archimedes's principle is represented by

$$D = \frac{w_1}{w_2} \times \rho \qquad (2.3)$$

where D is the object's density, w_1 and w_2 are the sample's and displaced water's weights, respectively, and ρ is the water's density.

Figure 2.13: Density measurement kit by Sartorius, BSA2245-CW

2.5 Methods and Analysis

2.5.1 Rietveld Refinement Technique

The structural information of the synthesized compositions in this work is an important tool for better understanding their attributes. X-ray diffraction is the most effective and widely used approach among the many analytical instruments. R. M. Rietveld developed a structural profile refinement approach for Neutron and X-ray powder diffraction data. The Rietveld refinement approach creates an effective separation of these overlapping data, allowing for an accurate structural evaluation[126]. Different properties of these reflections, such as height, breadth, and location, can be used to characterize various features of the material structure. Least-square refinement was used in this approach to find the best match between the theoretical and measured profiles.

The sample size, shape, beam parameters, and experimental setup each have an impact on the way the powder diffraction reflection appears. For monochromatic neutron sources, the convolution of multiple effects has occurred, generating a Gaussian form. The contribution of specific reflections to the profile y_i at position $2\theta_i$ when distribution is taken into account is:

$$y_i = I_k \exp\left[\frac{-4\ln(2)}{H_k^2}(2\theta_i - 2\theta_k)^2\right] \qquad (2.4)$$

H_k is the full width at half peak height, also known as full-width half-maximum (FWHM), 2k is the centre of reflex, and I_k is the computed intensity of reflex (obtained from the Lorentz factor, the structure factor, and the multiplicity of the reflection). The reflections might become asymmetrical because of the vertical divergence of the beam at very low diffraction angles. Rietveld used a semi-empirical correction factor to adjust this imbalance,

$$A_S = 1 - \left[\frac{SP\,(2\theta_i - 2\theta_k)^2}{\tan\theta_k}\right] \qquad (2.5)$$

The width of the diffraction peaks widens as the Bragg angle increases. Previously, this angular dependency was described by

$$H_k^2 = U\,tan^2\theta_k + V\,tan\theta_k + W \qquad (2.6)$$

During the fitting process, the half-width parameters, U, V, and W, can be throughout refined. The operation of the Rietveld refinement works by minimizing a function M. This function calculates the difference between observed data $y^{(obs)}$ and a computed profile $y^{(calc)}$. The equation was defined by Rietveld as:

$$M = \sum_i W_i \left\{y_i^{obs} - \frac{1}{C}\,y_i^{calc}\right\}^2 \qquad (2.7)$$

where, c denotes the overall scale factor and W_i denotes the statistical weight such that $y^{calc} = cy^{obs}$. The Rietveld refinement in this thesis was done with the 'Fullprof Suite' program.

The main features and advantages of FullProf software are:

1. The data obtained through X-ray diffraction and neutron diffraction can be used for refinement through this software.
2. The backgrounds are defined by a variety of functions like constant function, higher-order polynomial through Fourier filtering.
3. The peak shape is modelled in variety of functions for each phase. These peak shapes are Lorentzian, modified Lorentzian, Gaussian, pseudo-Voigt, Thompson-Cox Hashing (TCH), pseudo-Voigt, split pseudo-Voigt, Pearson-VII, numerical and the convolution of a double exponential with a TCH pseudo-Voigt.
4. The Rietveld refinement can be performed for multiple phases (up to 16 phases).
5. Two types of functions are available for the modelling of preferred orientation of peak.
6. Absorption corrections for different geometries and micro-absorption correction for the Bragg Brentano set-up are available.
7. It offers the choice of automatic symmetry and/or hkl operator generation.
8. Magnetic structure refinement can also be performed.
9. For an incommensurate structure, it can automatically generate reflections up to 24 propagation vectors.
10. Dependence of the position shifts of Bragg reflections for special kinds of defects.

2.5.2 Software for Analyzing the Obtained Data

The studied materials' structural, catalytic, and electrical properties were investigated using the OriginPro 8.5 software, and the SEM micrographs was processed using Image-J software.