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 is (a) Praseodymium Barium cobaltite oxide ($PrBaCo_2O_{6-\delta}$) (b) Pr excess $PrBaCo_2O_{6-\delta}$ i.e, $Pr_{1+x}Ba_{1-x}Co_2O_{6-\delta}$ (x = 0, 0.2, 0.4, 0.6, 0.8, 1.0) (c) Pr deficient $PrBaCo_2O_{6-\delta}$ i.e, $Pr_{1-x}Ba_{1+x}Co_2O_{6-\delta}$ (x = 0, 0.05, 0.10, 0.15, 0.20) and (d) $PrBaCo_2O_{6-\delta}$ and $Pr_{1.6}Ba_{0.4}Co_2O_{6-\delta}$ thin films. The parent composition was synthesized by solid-state ceramic route and the auto-combustion method. Whereases, the compositions listed in b and c were prepared by the solid-state route. The thin film of $PrBaCo_2O_{6-\delta}$ and $Pr_{1.6}Ba_{0.4}Co_2O_{6-\delta}$ was prepared by pulse laser deposition technique. 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. The specifications of these materials are listed in Table 2.1.

S. No	Raw Materials	Chemical Formula	Purity	Manufacturer
1.	Praseodymium (III, IV) oxide	Pr_6O_{11}	99.5%	Sigma Aldrich
2.	Cobalt (II, III) oxide	Co_3O_4	99.7%	Sigma Aldrich
3.	Barium carbonate	$BaCO_3$	99%	Sigma Aldrich
4.	Cobalt (II) nitrate	$Co(NO_3)_2$	99.99%	Sigma Aldrich
5.	Barium nitrate	$Ba(NO_3)_2$	99.7%	Sigma Aldrich

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 fabricated 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 film, Pulse laser deposition technique (PLD) was 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 that results in the formation of a new solid with well-defined structure from solid starting materials. Several metal oxides or salt do not react together at room temperature. 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 are shape and surface area of reactants, reaction conditions, structural properties of the reactants, their reactivity, diffusion rate and the thermodynamic properties associated with the nucleation or reaction[95], [96]. There are several benifits 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

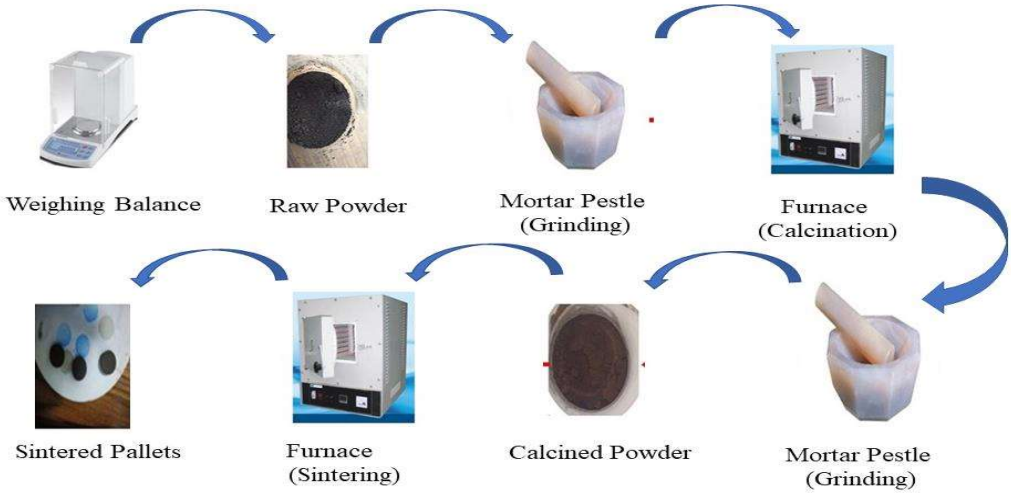

Figure 2.1: Schematic diagram of solid-state route (SSR) method

2.3.2 Auto-combustion synthesis (ACR)

Auto-combustion synthesis method is a simple and straightforward technique for the preparation of advanced ceramics, nanomaterials and catalyst. In auto-combustion method, metal nitrates are used as source of metal and oxidant and citric acid is fuel. This method is also known as Citrate-nitrate auto-combustion method (CNA). In this synthesis techniques, Nitrate solution are mixed well with each other are transformed into the solution. For ceramic materials, the amount of citric acid added to this solution should be 0.4 times of the total nitrate solution. (C/N=0.4). The solution needs to be transparent for the proper combustion. Transparency of the solution can be maintained 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 followed by the combustion, finally converted into a black ash powder. Structural stability such as grain growth and densification as well as other physical properties can be attained through the final sintering process. This method has a high similarity with the very well-known Pechini process. However, ACR is differ from Pechini process as nitrates 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 several gains 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.

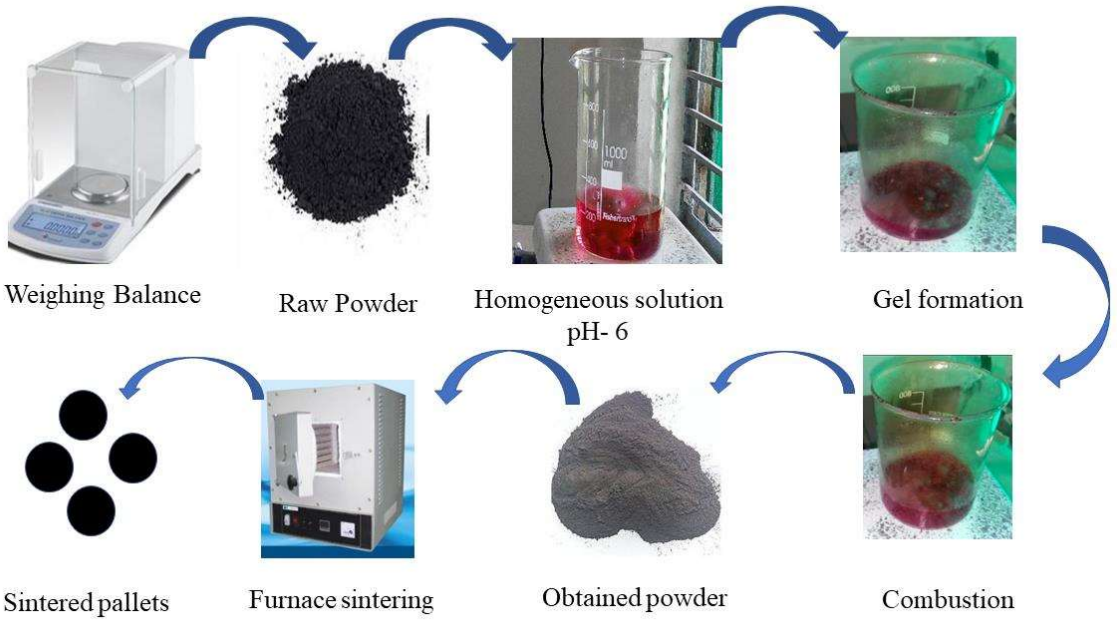

Figure 2.2: Schematic diagram of the auto-combustion synthesis method

2.3.3 Pulse Laser Deposition Technique (PLD)

Pulse laser deposition (PLD) is a very simple thin film deposition technique using high-power pulsed laser beam as an external energy source to strike a target of the material that is to be deposited. It comprises of a vacuum chamber housing a target holder and a substrate holder. Target holder are struck at an angle of 45° by the pulsed laser beam. The laser beam is aim at target material where the beam interacts with the surface and create a luminous plasma plume. The plume itself consist of atoms, ions, molecule and electron. Some of the extracted material is then deposited on the substrate forming a uniform film. The deposition process is carried out either in vacuum or at low gas pressure environment. During PLD, many experimental conditions can be changed, which have a great impact in the properties

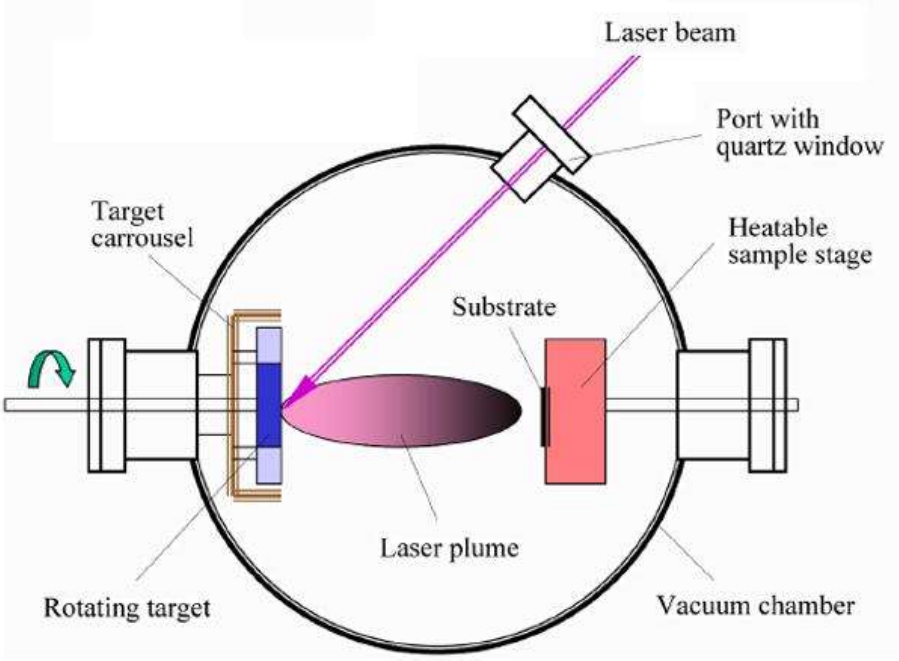

Figure 2.3: Schematic diagram of pulse laser deposition technique

of film. For multi-element materials, PLD is often easier to achieve the necessary film stoichiometry than other deposition processes. The main advantages of PLD are as follows[97]:

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)

Thermogravimetric Analysis is a technique that monitor the weight change of a material as a function of temperature or time when the sample specimen is exposed to a controlled temperature programme in a controlled environment. It is used to determine the thermal stability of a material. The concept of TGA was proposed by a physicist from Japan, Honda[98].

Working Principle: In TGA, a solid reactant when heated, it produces some product and the gas is emitted out. This change involves the loss in mass or weight. This mass loss is may be due to the gas which is obtained by the decomposition of reactants on heating or may be due to H_2O present with 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 gives the information on thermal stability, changes in sample compositions and kinetic parameters. Derivative of weight loss curve can deduce the point where weight loss is more apparent. TGA can also provide the information about the second order transition, vaporization, absorption, adsorption, oxidation and reduction[99].

A TGA comprised of a sample pan attached to a precision balance. During the experiment, that pan is heated or cooled in a furnace. Throughout the experiment, the mass of the sample is measured. The sample environment is controlled by a sample

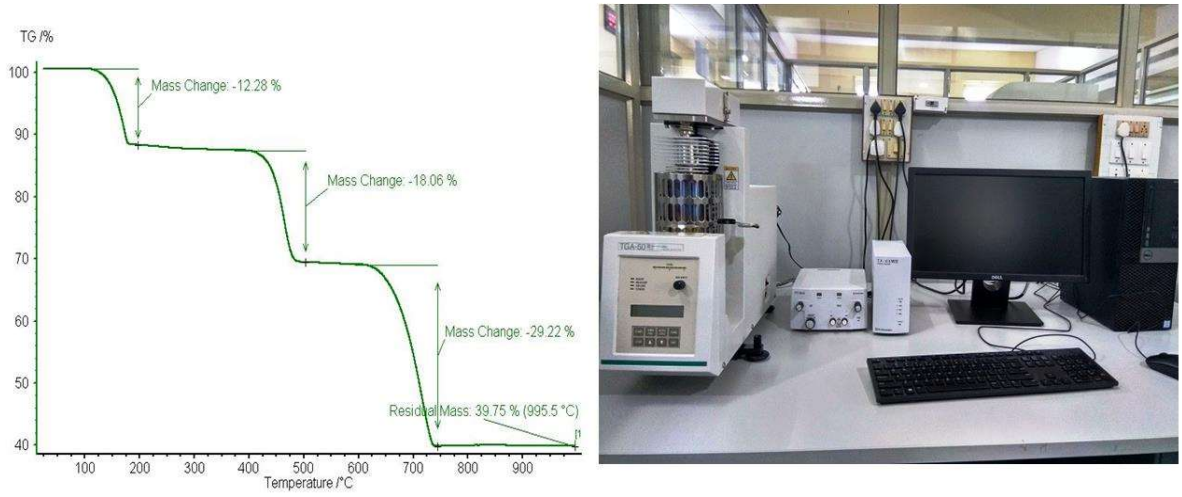

Figure 2.4: (a) A thermogram curve showing the change of mass of a substance at different temperatures (b) Experimental setup of TGA at Central instrument facility (CIF) IIT (BHU)

purge gas. This gas, which passes over the sample and departs through an exhaust, could be inert or reactive. 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, DSC measurement was recorded by SHIMADZU TGA-50.

2.4.2 Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry (DSC) is the measurement of the change in the heat flow rate differential between a sample and a reference sample while they are both subjected to a controlled temperature programme. DSCs allow reaction heats and heats of transition, as well as heat flow rates and changes at specific temperatures, to be measured quickly on small sample masses over a wide temperature range, and with an accuracy that is usually sufficient for the purpose[100].

There are two basic types of DSC, which are, heat flux DSC and Power compensation DSC. In heat flux DSCs, 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[100].

Figure 2.5: 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 quickly determine precise heat changes, transitions, and reactions. Various Thermodynamic functions can be estimate from DSC curve by using the following equations:

$$C_V = \frac{dQ}{dT} \quad (2.1)$$

$$\Delta G = \Delta H - T\Delta S \quad (2.2)$$

$$\Delta S = \frac{C_V}{T} \quad (2.3)$$

$$K = e^{-\Delta G/RT} \quad (2.4)$$

where C_V is specific heat, Q is heat flow, T is temperature in Kelvin, S is entropy, G is Gibb's free energy, H is enthalpy, K is an equilibrium constant for reaction kinetics and R is the universal gas constant. 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). An X-ray tube, a sample holder, and an X-ray detector are the three fundamental components of an X-ray diffractometer.

Working Principle: This analytic technique is based on the diffraction of X-ray by matter. Copper is the most common target material for single-crystal diffraction and the analysis is done with an X-ray source of 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 placed into the center of an instrument and illuminated with a beam of X-rays. The X-ray tube and detector move in a synchronized motion. Since wavelength of X-rays is similar to the distance between atoms in a crystal, a special interference effect called 'diffraction' is used to measure the distance between the atoms. The most prevalent type of diffraction is to X-ray crystallography is known as Bragg's diffraction. The interaction of incident X-rays with the atoms' electrons scatters incident X-rays. This phenomenon is elastic scattering and electron is scatterer. These scatterers in a regular array produce a regular array of spherical waves. These waves cancel each other out in most directions due to destructive interference, but they contribute constructively in a few select directions, as indicated by Bragg's law[101]. The condition for the constructive diffraction according to Bragg's law is:

$$2d\ sin\theta = n\lambda \qquad (2.5)$$

Where, d denotes the distance between lattice plane and θ indicates the angle of diffracted wave. Constructive interference occurs when the geometry of the incident X-rays collide on

the sample satisfies the Bragg Equation, resulting in an intense peak. The signal coming from the sample is recorded and graphed, where peak is observed related to the atomic structure of sample[102].

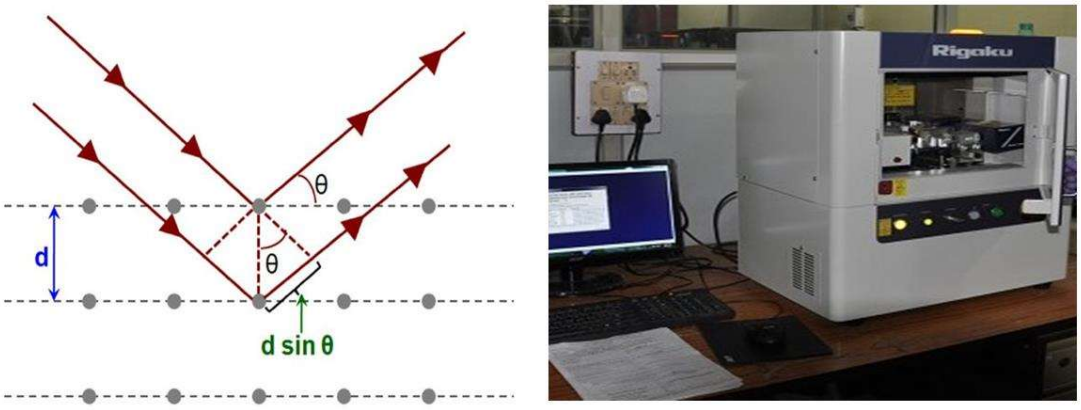

Figure 2.6: (a) Interpretation of Bragg's law in 2-dimensional crystal lattice (b) Experimental set-up of BT-XRD at Central instrumentation facility CIF IIT(BHU)

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 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. Due to its simple sample preparation and its easy handling, SEM is the most prevalent microscopic technique. Mafred von Ardenne designed

the first scanning electron microscope in 1937[103]. Spatial resolution of SEM may vary from 50 nm to 100 nm with magnification ranging from 20X to approximately 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 generates a range of signals on the surface of solid specimens using a concentrated beam of high-energy electrons. 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. One is thermionic gun, which is most common type, apply thermal energy to the tungsten filament to produce electrons. Another is Field emission guns, generates a powerful electrical field that pulls electrons away from the atoms with which they are linked. 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. In a SEM, accelerated electrons carry a lot of kinetic energy, which is dissipated as a variety of signals caused by electron-sample interactions 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 primilary detected in SEM. These are secondary electrons and backscattered electrons. Secondary electrons are best for displaying sample morphology and topography, whereas backscattered electrons are best for presenting compositional differences in multiphase samples[104]. Multiple events occur when an electron beam interacts with a sample in a SEM. To differentiate secondary electrons,

backscattered electrons, or distinctive x-rays, various detectors are required. Detector that detects the secondary electron are capable of producing the most detailed images of an object's surface. Other detectors, such as backscattered electron detectors and X-ray detectors, can provide data on a substance's composition.

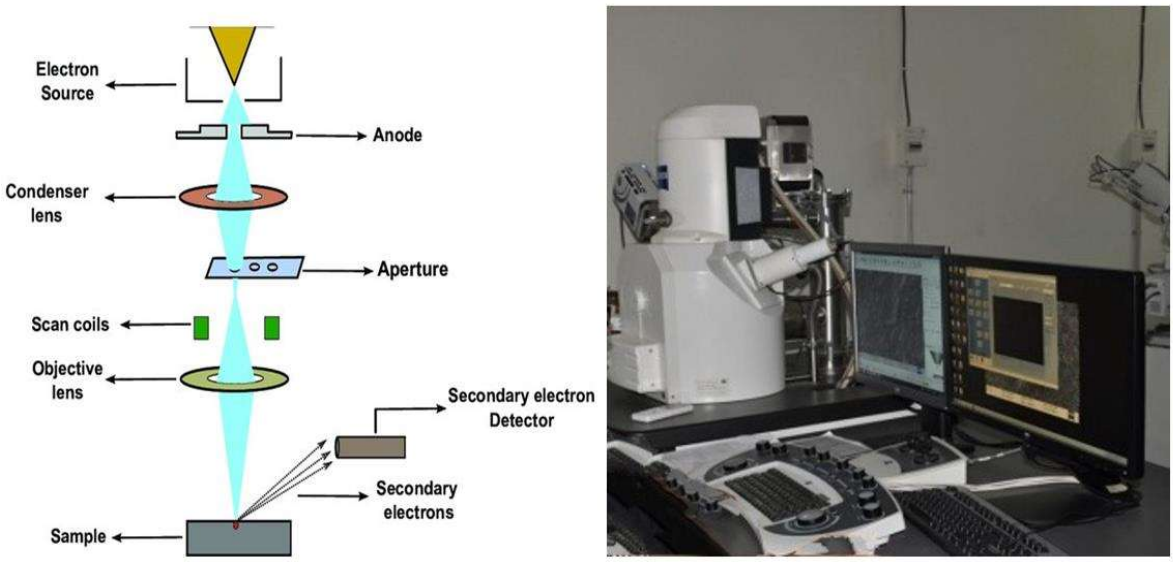

Figure 2.7: (a) Operating Principle of SEM (b) Experimental setup of SEM at central instrumentation facility CIF IIT(BHU)

SEMs (Scanning Electron Microscopes) are employed in a variety of industrial, commercial, and research applications. The SEM is used to create high-resolution images of object and to illustrate spatial changes in chemical compositions, such as creating elemental maps or performing spot chemical analyses using EDS. SEMs are used extensively in current materials science research and analysis of nanotubes and nanofibers, high temperature superconductors, mesoporous structures, and alloy strength. In fact, SEMs have enabled almost every material science business, from aerospace and chemistry to electronics and

energy utilization. In this thesis, SEM is analyzed by EVO - Scanning Electron Microscope MA15 / 18 and EDS is investigated by 51N1000 – EDS System.

2.4.5 Transmission Electron Microscopy (TEM)

The technique of transmission electron microscopy (TEM) is used to examine the characteristics of very small specimens. TEM visualizes specimens using an accelerated beam of electrons to generate a highly magnified image that allows a scientist to examine aspects such as structure and morphology. TEM was invented by German scientists Max Knoll and Ernst Ruska in 1931, and it has since grown into a widely utilized tool for studying micro and nanoparticles in science and engineering across the world. SEM generates images by detecting reflected or knocked-off electrons, whereas TEM generates images by using transmitted electrons (electrons travelling through the material). As a result, TEM gives information on the sample's inner structure, such as crystal structure, morphology, and stress state, whereas SEM provides information on the sample's surface and composition[105].

Figure 2.8: Experimental set up of the TEM technique at CIF-IIT (BHU), inset shows the sample holder

Working Principle: The TEM operates on the same principles as a light microscope, but instead of light, it employs electrons. TEM, on the other hand, has the benefit of higher resolution. An electron gun, an image creating system, and an image recording system are the three main components of a TEM. Electrons are emitted by an electron gun at the top of a TEM and pass through the vacuum tube of the microscope. Rather than using a glass lens to focus the light (as light microscopes do), the TEM employs an electromagnetic lens to focus the electrons into a very fine beam. The electrons either scatter or hit a fluorescent screen at the bottom of the microscope as the beam passes through the thin specimen. On the screen, there is an image of the specimen with its various components in different shaded based on its density. This image can then be analyzed or captured immediately within the TEM.

A Transmission Electron Microscope is an effective instrument that offers a range of advantages, including: TEMs give information on element and compound structure, surface properties, shape, size, and structure, and images are high-quality and detailed.

2.4.6 X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is the most commonly used 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. XPS is carried out in ultrahigh vacuum (UHV), at a pressure of roughly 10-9 millibar. XPS is based on the photoelectric effect, which was discovered by Heinrich Hertz in 1887, however modern-day XPS was invented in the 1960s

by Kai Siegbahn, who earned the Nobel Prize in Physics in 1981 for his work. He named this newly developed technique as Electron Spectroscopy for Chemical Analysis (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 ~6keV). The X-ray energy is totally transferred to the core level electron and emitted photoelectron. The energy of X-ray can be written as:

$$h\nu = B.E. + K.E. + \varphi_{spec} \qquad (2.6)$$

where, B.E. is Binding energy of the electron, K.E. is the kinetic energy of emitted electron

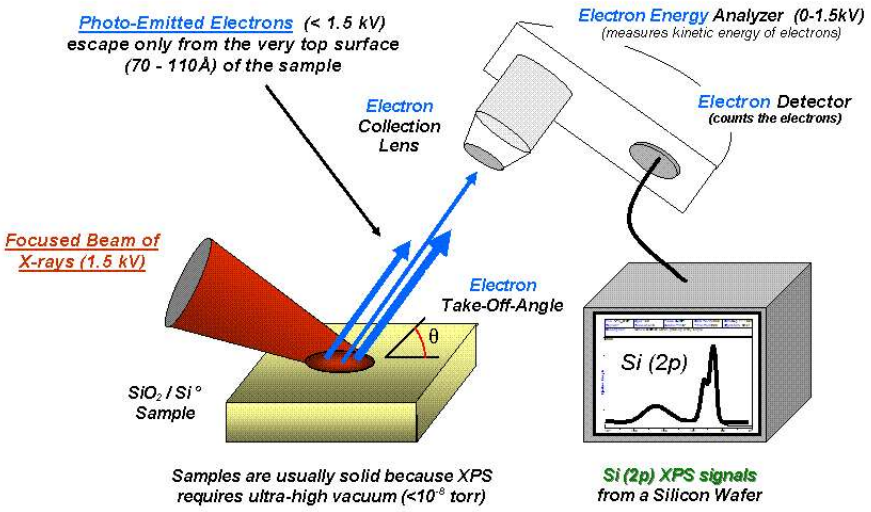

Figure 2.9: Basic component of monochromatic XPS system

and φ_{spec} is work function of spectrometer. In a typical 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 into 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. The emission of photoelectron from core level results in a 'hole' and excited ionized state, which is relax by the filling of 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. In the electron spectrum, there is no detection of X-ray fluorescence. Only the auger electrons produced by the process can be detected, and these are frequently employed in XPS for qualitative analysis. The Auger electron's kinetic energy is governed by the binding energies of specific orbitals in the atom from which it originated; therefore, the Auger electron's kinetic energy is independent of the x-ray excitation energy[106].

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[107]. In this thesis, the KRATOS (Amicus model) XPS apparatus was used to record the elemental analysis and chemical state of the synthesized samples.

2.4.7 Scanning Tunneling Microscopy (STM)

Scanning Tunneling Microscopy, or STM, is an imaging method that uses light or electron beams to create ultra-high-resolution pictures at the atomic scale. While working at IBM Zurich Research Laboratories in Switzerland, Ed Binnig and Heinrich Rohrer invented

the first operational STM. Binnig and Rohrer received the Nobel Prize in Physics in 1986 for their work on this instrument[108].

Working Principle: The working principle of STM is based on the quantum mechanical phenomena of tunnelling, in which electrons' wavelike properties allow them to "tunnel" below the surface of a material into regions of space where they are banned by classical physics. As the distance from the surface grows, the likelihood of detecting such tunnelling electrons diminishes exponentially. This extraordinary sensitivity to distance is exploited by the STM[109]. A tungsten needle with a sharp tip is positioned a few angstroms from the sample surface in STM. Between the probe tip and the surface, a small voltage is applied, allowing electrons to tunnel over the gap. The probe captures fluctuations in the tunnelling current as it scans the surface, and this information may be used to generate a topographical image of the surface.

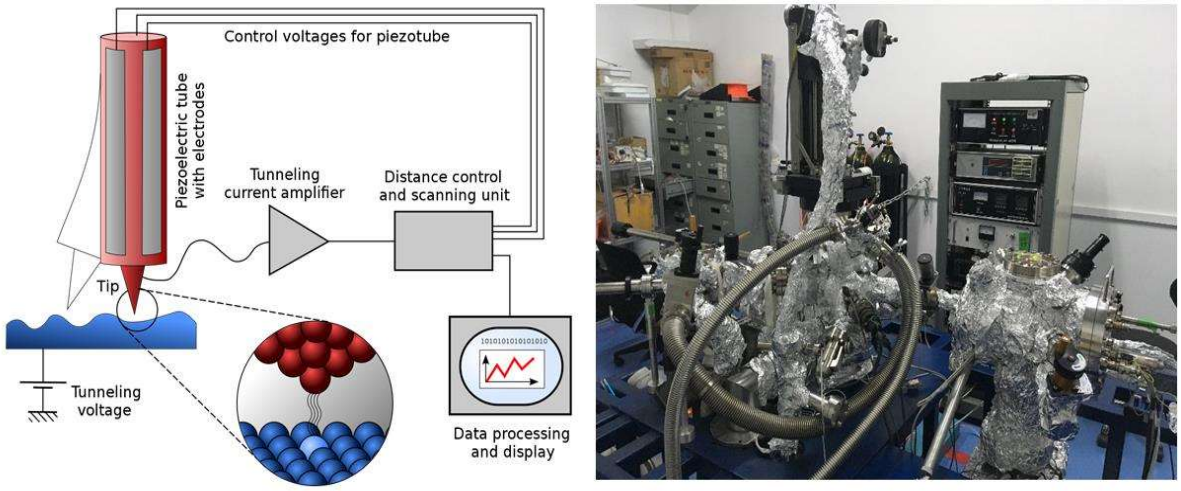

Figure 2.10: (a)Schematic view of STM [Ref. Wikipedia] (b) Experimental set up of STM

STMs are particularly valuable for investigating friction, surface roughness, defects, and

surface reactions in materials such as catalysts because of the extraordinary detail they can perceive about a material's surface. STMs are also crucial in semiconductor and microelectronics research. They may also be used for lithography, which involves tunnelling individual electrons onto a layer of photoresist. This gives previously proven technologies like electron beam lithography additional control. STM has been employed in the deposition of metal atoms such as gold and tungsten, which are used in the creation of nanodevices, and is not restricted to electrons[110].

2.4.8 Cyclic Voltammetry (CV)

CV (cyclic voltammetry) is a powerful and widely used electrochemical method for studying the reduction and oxidation processes of molecular species. CV is also useful for studying chemical processes that are triggered by electron transfer, such as catalysis. 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. It may also be used to collect qualitative and quantitative data on electrochemical reactions, such as electrochemical kinetics, reaction reversibility, reaction mechanisms, electrocatalytic processes, and other features[111].

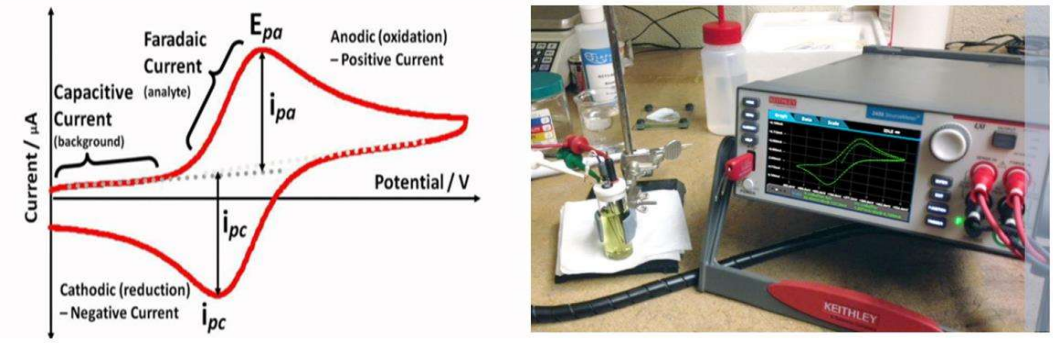

Figure 2.11: (a) cyclic voltammogram (b) Experimental set up of Cyclic voltammetry

Cyclic Voltammetry may be used to investigate qualitative information about electrochemical processes under a variety of conditions, such as the existence of intermediates in oxidation-reduction reactions and a reaction's reversibility. CV may also be used to estimate a system's electron stoichiometry, an analyte's diffusion coefficient, and the formal reduction potential, which can be used as a tool for identification. Furthermore, concentration of an unknown solution may be calculated by producing a current vs. concentration calibration curve[112], [113].

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. Between the working electrode and the reference electrode, the potential is measured, while the current is measured between the working electrode and the counter electrode. The electrolytic solution's purpose is to provide ions to the electrodes during the oxidation and reduction reactions[114]. 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 2.19 shows an illustration of the density measuring kit (Sartorius, BSA2245-CW). Archimedes's principle is represented by

$$D = \frac{w_1}{w_2} \times \rho \qquad (2.7)$$

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 2.12: 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[115]. 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 experimental setup, beam parameters, sample size, and shape all influence the shape of the powder diffraction reflection. The convolution of various effects has been initiated for monochromatic neutron sources, resulting in a Gaussian form. If this distribution is taken into account, a particular reflection's contribution to the profile y_i at position $2\theta_i$ is:

$$y_i = I_k \exp\left[\frac{-4\ln(2)}{H_k^2}(2\theta_i - 2\theta_k)^2\right] \qquad (2.8)$$

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). Due to the vertical divergence of the beam at very low diffraction angles, the reflections may develop an

asymmetry. To adjust for this imbalance, Rietveld used a semi-empirical correction factor,

$$A_s = 1 - \left[\frac{sP\,(2\theta_i - 2\theta_k)^2}{\tan\theta_k}\right] \qquad (2.9)$$

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

$$H_k^2 = U\tan^2\theta_k + V\tan\theta_k + W \qquad (2.10)$$

The half-width parameters, U, V, and W, can be refined throughout the fit. The Rietveld Method works by minimizing a function M that measures the difference between observed data $y^{(obs)}$ and a computed profile $y^{(calc)}$. The equation was defined by Rietveld as:

$$M = \sum_i W_i \left\{ y_i^{obs} - \frac{1}{c} y_i^{calc} \right\}^2 \qquad (2.11)$$

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.

2.5.2 Software for Analyzing the Obtained Data

The OriginPro 8.5 program was used to analyze the structural, catalytic and electrical properties of the studied materials, and the Image-J software was used to process the SEM micrographs.

2.6 Theoretical Studies

On $PrBaCo_2O_{6-\delta}$, first-principles hybrid functional calculations have been performed. The specifics of the calculations are provided below.

2.6.1 Computational Details

The computations were carried out with the help of the Vienna ab initio simulation programme (VASP)[116],[117] and the projector augmented-wave approach[118]. To comprehend and evaluate the experimental data, three alternative functionals are used: the Perdew, Burke, and Ernzerhof (PBE) generalized-gradient approximation (GGA) functional[119], and the PBE0 hybrid functional[120]. With a tolerance value of 0.01 eV/Å, the GGA functional is generally employed for ionic relaxation, in which their positions are relaxed to minimize the Hellmann-Feynman force on each atom. The hybrid functional PBE0 offers the most exact representation of the electrical characteristics of bulk $PrBaCo_2O_{6-\delta}$ among these functionals. As a result, all surface computations are done using the PBE0 hybrid functional[121] in order to provide a reliable description of the surface properties. In all of the bulk computations, a 4 ×4 ×4 k mesh is employed for Brillouin-zone integration.

The phonon frequencies at the site of the Brillouin zone are calculated using density functional perturbation theory (DFPT)[122], and the stability of the surface structures corresponding to the lowest thicknesses is studied. The system's stability is ensured by the absence of any imaginary frequency mode for both surface structures.