Chapter-2

Experimental Techniques

CHAPTER 2

EXPERIMENTAL TECHNIQUES

2.1 Overview

This chapter deals with experimental methods and characterization techniques utilized in the thesis. This chapter explains sample preparation, fabrication methods, characterization techniques, and their working principles in detail.

This chapter consists of three sections:

(1) Different synthesis and materials fabrication techniques are involved in sample preparation.

(2) Characterization techniques used for crystal structure analysis, thermal analysis and electrical analysis.

(3) Data analysis tools such as X-ray Rietveld refinement, microstructural study and impedance spectroscopy.

2.2 Synthesis Technique

For the synthesis of all the systems, mainly two different synthesis routes were employed here. The schematic representation of the two routes is explained below.

2.2.1 Solid-state reaction synthesis route

The solid-state reaction route is the most commonly used method to synthesize perovskite ceramic materials. First constituent oxides and/or carbonates are weighed according to their stoichiometric ratio in the chemical reaction equation used. After mixing very well, long hours of wet grinding are done in a high-quality mortar pestle to get a homogeneous powder. Acetone can be used as a medium during grinding. This homogeneously mixed powder is calcined in an alumina crucible at a higher temperature. During the calcination process, thermal decomposition, phase transition or removal of a volatile fraction happens. This process usually takes place at temperatures below the melting point of the product materials.

In this heat treatment, the desired phase formation is due to various factors, such as solid-state diffusion of atoms, calcination temperature and holding time. The detailing of this synthesis route is explained by the schematic block diagram below-

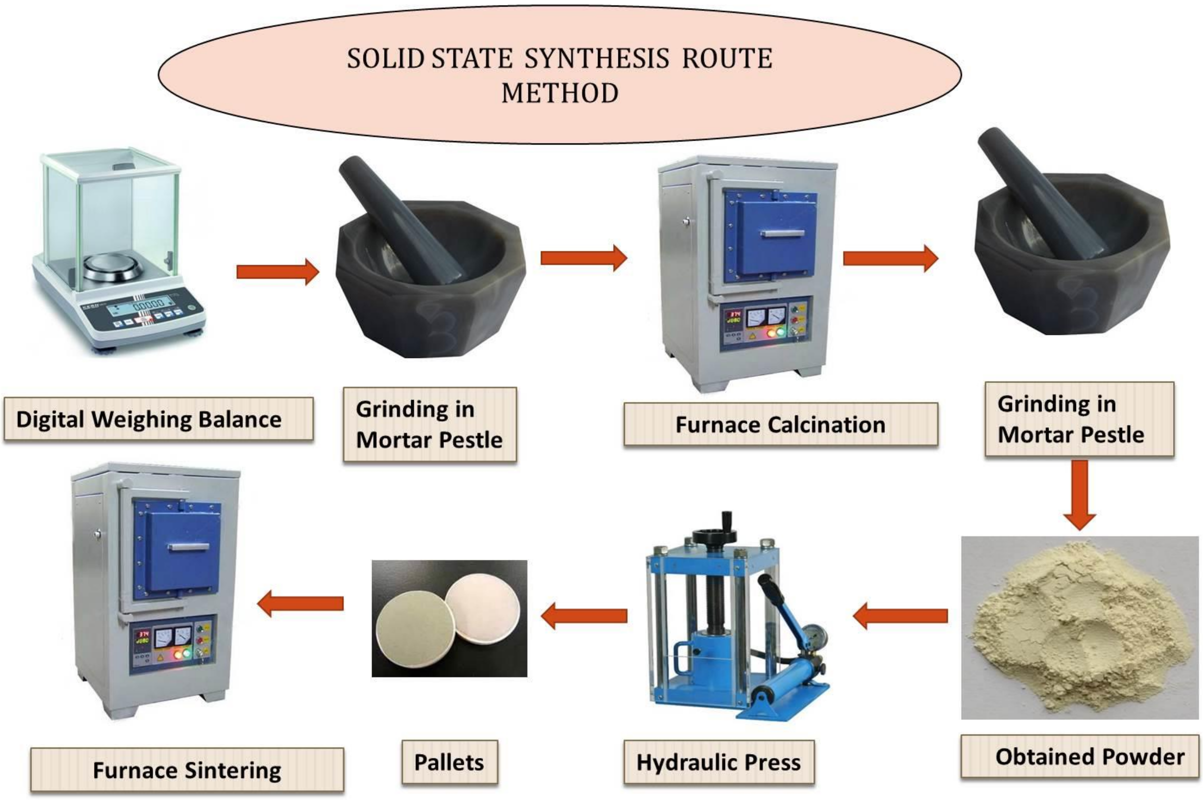

Figure 2.1 Solid State Synthesis Route

2.2.2 Sol-Gel Auto Combustion synthesis

This technique is a combination of chemical sol-gel and subsequent combustion process. A solution in nitric acid with a stoichiometric amount of precursors and organic fuel forms gel through the sol-gel process. Later, this gel gets ignited to combust, yielding a fluffy product with a larger surface area. In this synthesis, we used glycine as a complexing agent that acts as fuel and accelerates combustion. A detailed block diagram (Figure 2.2) shows the steps involved in the synthesis.

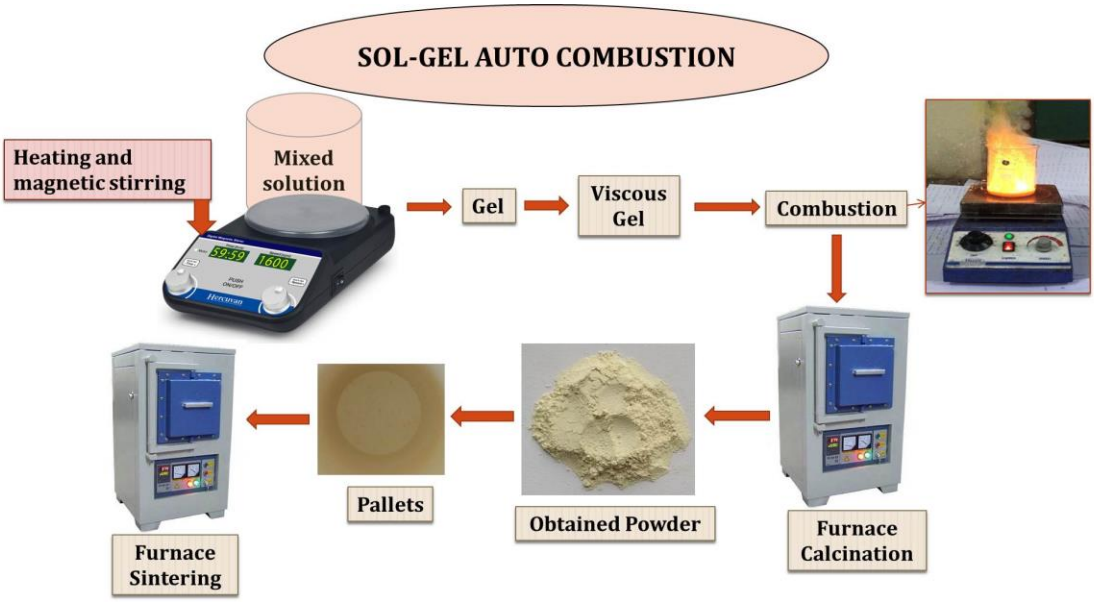

Figure 2.2 Sol-Gel Auto Combustion

2.2.3 Pelletization

For conductivity measurement, the powder was made into pellets of required size and diameter by pressing it with a 7−8 ton weight on a hydraulic press. These pellets were made with the help of press and die. Obtained pellets were fired at required temperature for densification. Steps involved are shown in Figure 2.3.

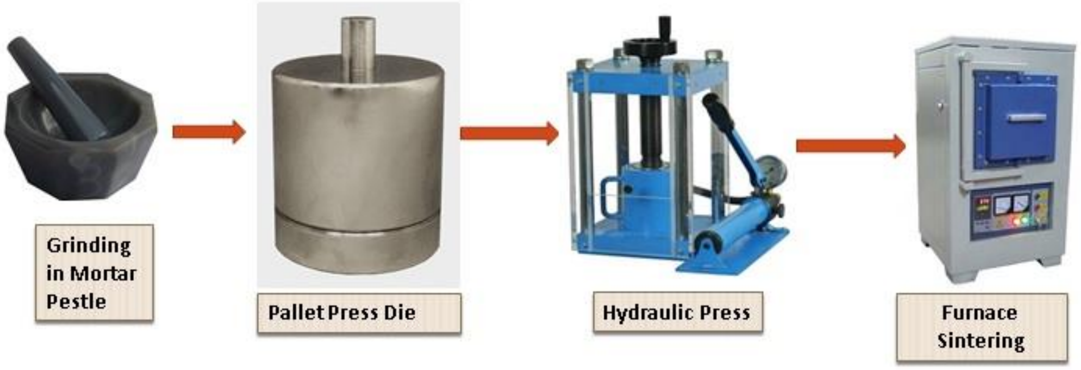

Figure 2.3 Palletization Steps

2.3 Material Characterization Techniques

The following section describes the characterization techniques used during this work. The basics of each method are briefly described in the next section. Here are the main techniques listed

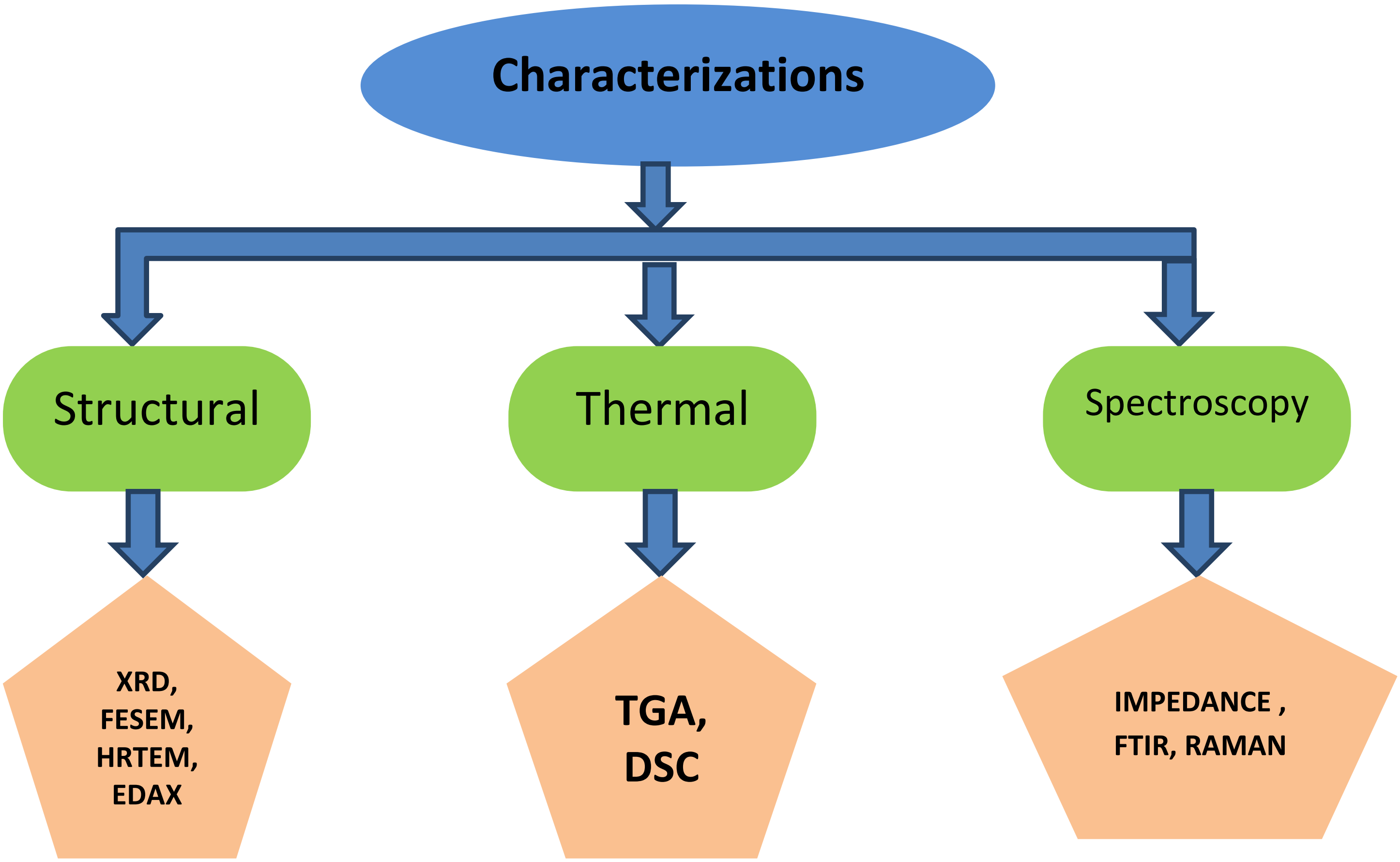

Figure 2.4 Characterization techniques used

2.3.1 Powder X-Ray Diffraction (XRD)

X-ray diffraction is an (XRD) powerful non-contact and non-destructive technique, making it ideal for structural studies. It identifies the crystalline phases present in the material. It can measures the structural properties like phase composition, grain size, preferred orientation, strain state, defect structure and epitaxy of these phases present in the compound.

The intensities obtained from the XRD can provide quantitative and accurate information on the atomic arrangements at interfaces. Materials having a different composition of elements can be successfully identified with XRD. Still, they are very sensitive to the elements having large atomic numbers because the diffracted intensities are enormous compared to those with lower atomic numbers. It predicts the quantitative phase analysis and qualitative structural and microstructural analysis.

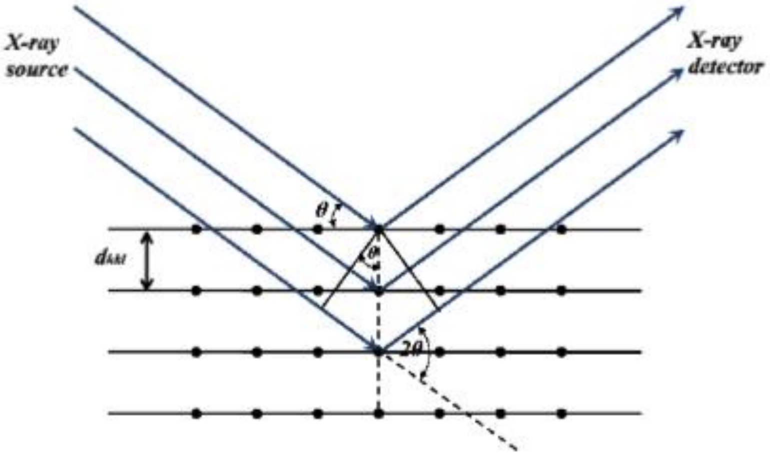

Figure 2.5: Demonstration for Bragg's Law

The diffraction satisfies the Bragg equation:

$$2d\ sin\theta = n\lambda$$ …. Eq (2.1)

Here d is the spacing between diffracting planes, is the incident angle, n is an integer, and λ is the beam's wavelength.[1-2]

The X–ray is generated in a Cu X–ray tube, filtered by monochromator to increase sensitivity, collimated to concentrate, and is directed towards the sample. The X–ray is diffracted by the atomic layers of the crystal, and the diffraction pattern is used for the analysis based on the Bragg's diffraction law (nλ=2d sinθ). The 2θ positions of the diffraction peaks provide a fingerprint of the phases present and the intensity and spread of the peaks are used to obtain the quantity of each phase. The different phases were interpreted by recording an X-Ray diffraction pattern at room temperature on an X-Ray diffractometer (Rigaku Miniflex II, Japan) has Cu Kα radiation having wavelength $\lambda = 1.5418$ Å at an applied voltage of 40 kV and current of 40 mA. In this work, the XRD pattern has been recorded in the range of 10°-90° with a step size of 0.02.

2.3.2 Phase Confirmation and Crystal Structure Studies by Powder X-Ray diffraction

X-ray diffraction (XRD) is a versatile, non-destructive technique that reveals detailed information about the crystallographic structure of natural and manufactured materials. X-ray radiations most commonly used are that emitted by copper, whose characteristic wavelength for the Cu-K_α radiation is λ=1.5418Å. When the incident beam strikes a powder sample, diffraction occurs in every possible orientation of 2θ. The diffracted beam may be detected using a hybrid pixel array detector. Routinely, 2θ range of 10 to 80 degrees is sufficient to cover the most valuable part of the powder pattern. The scanning speed of the counter is usually 2θ of 2° $\min^{-1}$; therefore, about 30 minutes are needed to obtain a trace. Based on the principle of X-ray diffraction, a wealth of structural, physical and chemical information about the material investigated can be obtained. A host of application techniques for various material classes are available, revealing the specific details of the sample studied.

Whether the unknown sample is single phased or multi-phased, phase identification is the most crucial application of X-ray diffraction studies. This identification guides us in understanding the sources of mechanisms that are taking place behind this phase formation. This also gives an idea of the correlation of crystal structure with different properties, i.e. structure-property correlation (Neumann's principle).[2]

2.3.3: Field Emission Scanning Electron Microscope:

A field emission scanning electron microscope (FESEM) is a type of electron microscope that produces images of a sample by scanning it with a focused beam of electrons. A field emission cathode in the electron gun of SEM provides a narrower beam at low and high electron energy, resulting in improved spatial resolution and minimized sample charging and damage. The field gradient in a vacuum generates the electrons. Then the beam passed through electromagnetic lenses was focused onto the specimen, resulting in the generation of various types of electrons through this interaction. A detector discovers the secondary electrons, and an image of the sample surface is formed by comparing the beam's intensities of secondary & primary electrons. The electrons interact with atoms in the sample, producing various signals that can be detected and contain information about the sample's surface topography and composition. The electron beam is scanned in a raster scan pattern, and the beam's position is combined with the detected signal to produce an image.[3-4]

2.3.4: High-Resolution Transmission Electron Microscopy (HR-TEM)

In material science and engineering advancement, it is necessary to observe, analyse, and understand the phenomena occurring on a small size scale by transmission electron microscopy. The fine ground powder of the samples is mixed in ethanol and ultrasonicated for about 50 minutes. After proper mixing and homogenization, the sample was drop cast on a copper grid. The sample was dried in an oven at 100 °C overnight. Both diffraction and imaging mode sample was investigated. The transmission electron microscope (TEM) is a powerful and versatile instrument which permits the characterization of materials. It provides a variety of information obtained from different modes such as bright field (BF) & dark field (DF) imaging, selected area diffraction (SAD) and high-resolution lattice imaging. BF and DF imaging are used to characterize defects and domain structures. SAD with a combination of tilting of crystal in the microscope allows reconstructing the reciprocal space and, in the way, obtaining information about the crystal structure and identifying different phases. In a TEM, a high energy (~200 keV) electron beam is transmitted through the specimen. During transmission, electrons interact with the specimen, giving rise to signals containing information about the internal structure and chemistry of the specimen. Electron diffraction patterns and lattice images are two forms of data which give an insight into crystallographic information in TEM.

Interaction of electrons with the specimen after entering the sample, most electrons are elastically scattered by the nuclei of the atoms in the specimen. Some electrons are inelastically scattered by the nuclei of the atoms in the specimen. (Figure2.8). Compared to X-ray or neutron diffraction, the interaction of electrons with the specimen is vast, and multiple scattering events are expected. For thick specimens at lower resolutions, an incoherent particle model can describe the interaction of the electrons with the specimen. The electrons passing the specimen near the nuclei are somewhat accelerated, causing a slight, local reduction in wavelength, resulting in a small phase change of electrons. Information about the specimen structure is therefore transferred to the phase of the electrons. For the formation of high-resolution images, only the elastically scattered electron is of importance. The inelastically scattered electrons contribute mainly to the background of the image. The inelastic scattered electrons also produce Kikuchi lines in the electron diffraction pattern, which is helpful for the crystal's accurate crystallographic alignment in the specimen.[5]

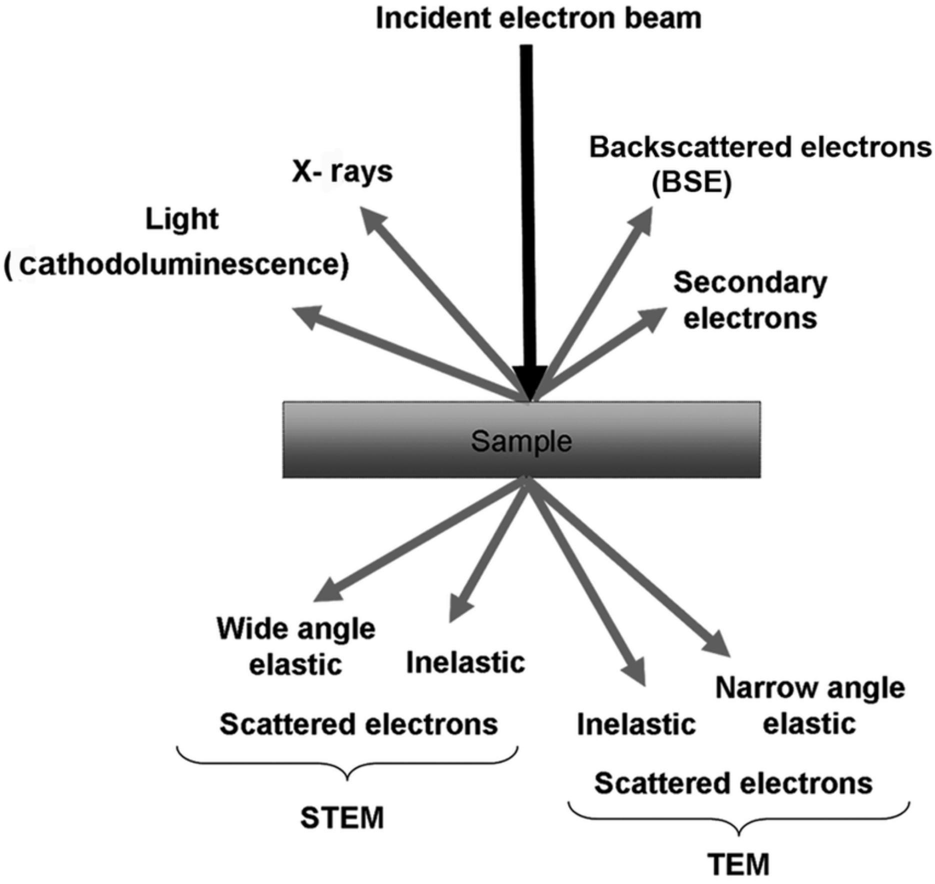

Figure 2.8 Interaction of electrons with sample [5]

2.3.5: Energy Dispersive X-Ray Spectroscopy (EDAX)

The Energy Dispersive X-Ray analysis is a non-destructive X-ray analysis to identify the elemental composition of materials. This is generally attached with structural analysis techniques such as SEM and TEM, where a high energy electron beam & the ejected electrons from the inner shell of an atomic orbital is used to identify the specimen of interest. The resulting inner shell vacancy is filled by electrons available in the shell close to the vacant shell; these transitions are emitted as X-rays. Thus the information corresponding to the elements of the samples can be analysed based on the energy of emitted X-Rays. Sometimes X-Ray mapping may not show the distribution of elements that are not of interest because characteristics X-Rays of elements of interest are close to those not desired. It happens when the energy difference between the desired and undesired elements is equal to the spectrometer energy resolution. This method quantitatively evaluates the points on the sample while scanning the electron beam; that is why it is also called quantitative mapping of the sample. In this thesis work, we have used EDAX with HRSEM and HRTEM to study the electron mapping of the composition.[6]

2.3.6: Thermogravimetric analysis (TGA):

The TGA analysis is a technique used to determine the thermal stability of the materials. In this method, the mass of the sample is recorded as a function of temperature, which is used to take information about the change in mass (absorption or desorption), phase transition, and thermal decomposition. If the mass of the sample remains constant in a given temperature range, then the sample is said to be thermally stable in that range. TGA also helps determine the calcination temperature of the sample as it provides the upper limit of temperature beyond which degradation of the sample starts.

2.3.7: Differential Scanning Calorimetry(DSC) :

Differential scanning calorimetry (DSC) is a thermo analytical technique to analyse any thermal behaviour change during the phase transition within the system. In this technique, heating or cooling of a test sample and an inert reference sample is done under identical conditions. The difference in the amount of heat required to increase the temperature of test sample and reference sample to maintain them both at the same temperature is recorded. In this technique, the material under consideration is placed in fine powder in a tiny capsule that is often of alumina or other suitable refractory material. Along with this test sample, a second capsule containing an inert powder such as α-Al_2O_3, which does not exhibit endothermic or exothermic effects, is placed. Thermocouples are embedded in the test substance and the α-Al_2O_3 powder and are connected. Therefore, their electromotive forces are opposed; the net electromotive forces represent the temperature difference between the sample powder and the inert α-Al_2O_3. The two capsules are heated at a constant rate, and the temperature difference is plotted either against time or against the temperature at some fixed points within the apparatus. Any physical or chemical change occurring to the test sample, which involves the evolution of heat, will cause its temperature to rise temporarily above the reference sample leading to an exothermic peak.

Conversely, a process accompanied by the absorption of heat will cause the temperature of the test sample to lag behind that of the reference sample, leading to an endothermic peak. The area under any given peak can be used as a quantitative measure of the amount of heat evolved or absorbed by the physical or chemical changes. The Combined study of TGA/DSC also gives an idea about the reaction pathway for the prepared mixture of raw materials and various transition points such as melting point, glass transition temperature, crystalline temperature etc. In this thesis work, TGA & DSC has been carried on multiple samples in the temperature range of 30°C to 900°C in a nitrogen gas atmosphere.

2.3.8: Raman Spectroscopy

Raman Spectroscopy is a spectroscopic technique used to observe vibrational, rotational and other low-frequency modes in a system. Raman spectroscopy is commonly used in material chemistry to provide structural fingerprints by which molecules can be identified. Raman spectrum was recorded with a multi wavelength high resolution micro Raman spectrometer. It relies on inelastic scattering, or Raman scattering of monochromatic light, usually from a laser in the visible, near infrared, or near ultraviolet range. The laser light interacts with molecular vibrations, phonons or other excitations in the system, resulting in the energy of the laser photons being shifted up or down. The shift in energy gives information about the vibrational modes of the system. Raman spectroscopy of powdered sample was carried out by using STR-

300 micro-Raman spectrometer with a laser excitation wavelength of 532 nm and step size of 1.9 cm^{-1}.

2.3.9 FTIR Spectroscopy

Infrared Spectroscopy is an important technique for the analysis of materials which provides the fingerprint of the samples. The absorption of FTIR peaks corresponding to the frequencies of vibrations between the bonds of the atoms which is responsible for building up the materials. Since each material possesses a unique combination of atoms so no two compounds produce the exactly same infrared spectrum. This thesis work uses Thermo Scientific Nicolet iS5 FTIR spectrometer and data was recorded within 400-4000 cm^{-1}. In FTIR, beam of light of different frequencies interacts with sample which excites and vibrates the covalent bond containing dipole moments, and the detector detects the intensity of light after the interaction. To determine the amount of light absorbed at each wavelength, the interferogram is subjected to Fourier transform. The data set can be collected in reflected, absorbed, or transmitted mode. The energy consumed by the bonds are determined by the types of bonds present, thus characteristic spectrum were obtained.

2.3.10 Electrochemical Impedance Spectroscopy (EIS):

Electrochemical Impedance spectroscopy is a non-destructive technique & involves measurements and analysis of materials in which ionic conduction predominates. This technique is used in material research and development because it involves relatively simple electrical measurements, which can be readily automated. The results may often be correlated with many complex material properties. AC impedance used for SOFC material testing mainly provides information about oxide-ion conduction. It involves passing an AC voltage across a sample and measuring the resulting current response. Most of the materials have some degree of resistance and some capacitance.[7] They can be modelled as a series with resistance and capacitance. The current in the case of pure capacitive resistance can be shown as in Equation (2.2)

$$i = \frac{E}{X_c} sin\left(\omega t + \frac{\pi}{2}\right) \qquad \text{Eq (2.2)}$$

Where $X_c = 1/\omega_C$

$E = E_R + E_C$

Current for pure resistor can be shown as in Equation (2.3)

$$i = \frac{E}{R}\sin(\omega t) \qquad \text{Eq (2.3)}$$

This data obtained through EIS is expressed in a Nyquist plot, where the imaginary part of the impedance (Z") is plotted against the real part of the impedance (Z') as a function of frequency (ω).[8] An example Nyquist plot can be seen in Figure 2.13.

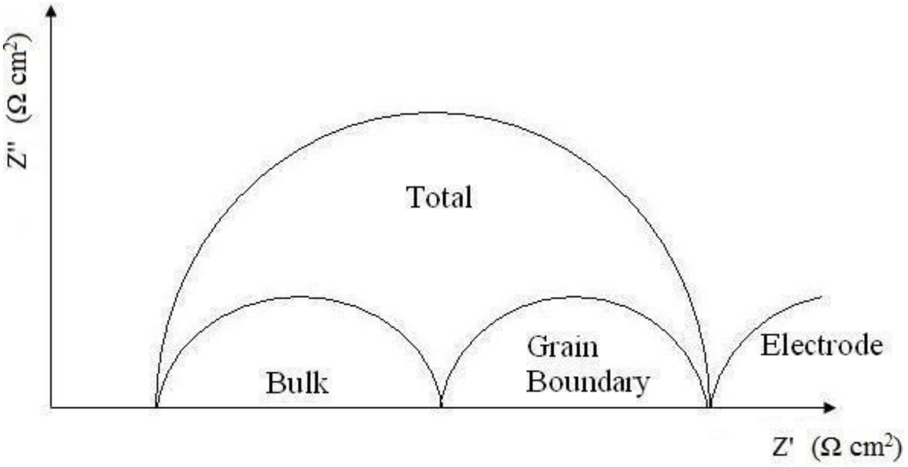

Figure 2.13 Nyquist Plot for ionic solids (Z'' = imaginary impedance, Z' = real impedance) [8]

Numerous physical phenomena cause capacitance values of varying amounts, which can be easily identified on a Nyquist plot. For example, ionic resistance in the bulk of the material would have a capacitance value in the region of 10^{-12} F, whereas that of the grain boundaries within the material would have a capacitance value of 10^{-11} - 10^{-8} F. The bulk and grain boundary resistances can manifest themselves as separate curves on the Nyquist plot; however, it is not uncommon for the curves to be partially or fully merged, especially when the resistance is significantly greater than that of the other. If impedance spectra are collected over a range of temperatures, it is possible to calculate the activation energy as per Equation 2.4.

$$\sigma T = Ae^{\frac{-E_a}{RT}} \qquad \text{Eq (2.4)}$$

where σ = conductivity, T = temperature, A = sample surface area, E_a = activation energy and R = resistance

The Plot has been drawn between $Log_{10}(\sigma T)$ / S cm^{-1} K vs T^{-1} / K^{-1} to determine the activation energy, which is represented by the slope of the resultant line.[7-8]

2.3.11 Conductivity Measurement Using EIS

Our setup for measuring the conductivity shown in Figure 2.14. It consist of sample holder which was set inside split furnace The sintered pellets were coated with silver paste and cured at 500 °C for 30 min. The conductivity measurements were performed using an Autolab potentiostat as a function of frequency from 1 MHz to 1 Hz at different temperatures. All measurements were taken during the cooling cycle.

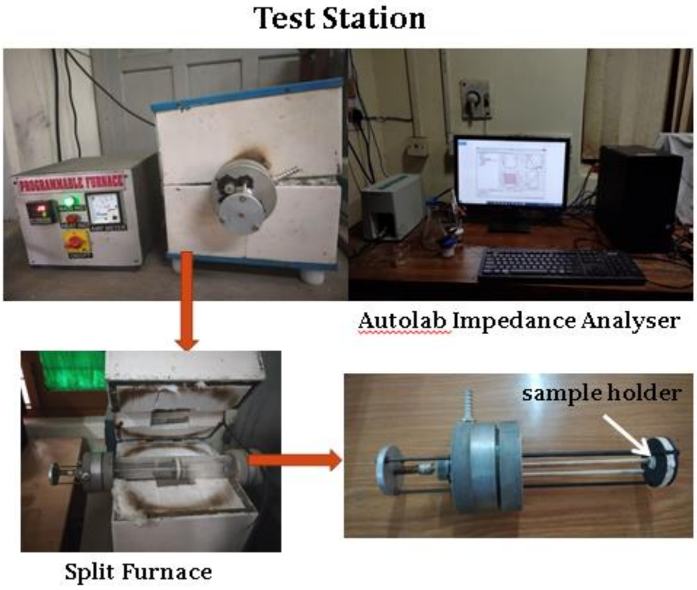

Figure 2.14 Conductivity Test station